Joint Research Project

Sustainable Management of the Newly Created Ecosystem at the Three Gorges Dam (YANGTZE-PROJECT)

Research Group HYDRO

Pollutants / Water / Sediment – Impacts of Transformation and Transportation Processes on the Yangtze Water Quality

Final Report

COMPILED BY

Rolf-Dieter Wilken, Prof. em. Dr.

together with all Scientists of the Project

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Contents

I Executive Summary

1 FKZ_02WT1129: WATERQUALITY, WATER USE (IWW)

- ***Water Sampling***

The water sampling campaigns in the area of the TGR showed that 48 substances out of 213 analyzed organic substances have been found, however, often with low frequency (< 11%).

- ***Concentrations compared to Western Countries***

Concentrations are, in general, in the same range or even lower compared to surface waters in western industrialized countries.

- ***Contaminant Loads***

Contaminant loads, however, can still be high due to a high discharge, as shown by Müller et al (Müller et al. 2008; Müller et al. 2012).

- ***Compound Patterns***

In the different water sources typical compound patterns have been found, such as

(i) pesticides in surface water reflecting the surface runoff from agricultural areas,

(ii) disinfection by-products (trihalomethanes) in tap water due to an intense chlorination/disinfection in drinking water treatment, and

(iii) pharmaceuticals in waste water treatment plant effluents, which are not eliminated in the waste water treatment due to their high persistency.

- ***Tap Water Pesticides***

The two pesticides clopyralid and picloram, further, were detected in tap water in comparable concentrations as in adjacent surface water indicating a scarce elimination of these compounds in drinking water treatment.

- ***Chinese Standards***

Due to the results of this study, the supply of drinking water from TGR surface water is legal with respect to the Chinese Environmental Quality Standards for Surface Water (GB 3838-2002) (SAEP 2002). The compounds relevant for drinking water production (this means either they exceed Chinese or European limit values in drinking water or they are of ecotoxicological risk) were investigated to be mainly

(i) the herbicides clopyralid, picloram, and atrazine,

(ii) the antibiotic sulfamethoxazole in Wushan bay, and

(iii) chloroform in Wushan tap water.

- ***Oxidation and Ozonation***

The tested drinking water treatment steps, oxidation due to ozonation and powdered activated carbon adsorption, are both feasible for an application in the TGR area since the observed pollutants are removed satisfactorily and the formation of toxic by-products is within the legal limits.

2 FKZ_02WT1130: MICROBIOLOGICAL DEGRADATION, TRANSMIC (TZW)

- ***Detection of dechlorinating bacteria in Yangtze River samples:***

  The dechlorinating microorganisms Dehalococcoides spp., Dehalobacter spp., Desulfomonile spp., Desulfuromonas spp. and Desulfitobacterium spp. were detected by PCR analysis in water or sediment samples taken within the TGR. In 85 % of the samples at least one of dechlorinating microorganisms was detected

- ***Tetrachloroethene degradation in Yangtze River sediments:***

In all batch tests incubated with sediments from the TGR catchment area, anaerobic biological dechlorination of Tetrachloroethene was demonstrated. Dehalococcoides spp. Dehalobacter spp., Desulfomonile spp., and Desulfitobacterium spp. were detected, with increasing numbers, in most of the batch dechlorination tests. However, differences in the biochemical pathways and end-products of reductive dechlorination were observed, most probably due to different halorespiring bacteria community compositions.

- ***Degradation of Hexachlorocyclohexanes, Pentachlorophenol, Polychlorinated Biphenyl 180 and Hexachlorobenzene:***

The indigenous microbial community was capable to dechlorinate all four Hexachlorocyclohexanes, Pentachlorophenol, Polychlorinate Biphenyl 180 and Hexachlorobenzene to lower chlorinated products. These pollutants and their dechlorination products are relevant environmental pollutants in the Yangtze River.

- ***Activity after oxygen exposure:***

For the three dechlorinating bacteria Desulfitobacterium spp., Desulfomonile spp. and Desulfuromonas spp. in none of the experiments influence of the oxygen contact on the inactive microorganisms was detected. After oxygen exposure, increasing numbers of Dehalococcoides spp. were detected during the anaerobic dechlorination of cDCE to ethene. The results indicate that reductive dechlorination is possible in anaerobic areas even after temporary transfer of the bacteria into aerobic zones.

- ***Demonstration of gene expression (mRNA detection):***

The extraction of high quality mRNA was demonstrated. The new molecular method enables a direct monitoring of microbial activity by mRNA detection. Therefore, the relevance of different bacteria and reductive dehalogenase genes can be studied. Furthermore, a monitoring of microbial activity in the field might be possible in the future.

- ***Indigenous Microorganisms contribute substantially to Pollutant Elimination:***

The potential of indigenous microorganisms within the Yangtze River for reduction of chlorinated pollutants was demonstrated. The results indicate that these processes are active in the field and contribute substantially to pollutant elimination in the Yangtze River and the TGR.

3 FKZ_02WT1131: MONITORING AND MODELLING, MINIBAT (KIT)

- ***Enhancement and commissioning of the MINIBAT:***

A new underwater multi-sensor probe MINIBAT was developed and adapted to the conditions in the Three Gorges Reservoir. It was successfully applied for in situ and online monitoring from boats during eight fieldtrips. The MINIBAT carries sensors for pressure, temperature, pH, turbidity, electrical conductivity, H_2S, O_2, *coloured dissolved organic matter, photosynthetic active radiation and chlorophyll a.*

- ***Water sampling system integrated into the MINIBAT:***

For the first time, a remote-controlled water sampling system was designed and implemented successfully into the MINIBAT. Now, five 50 mL water samples can be taken selectively according to the specific ambient water quality conditions.

- ***Impact factors of algal bloom formation:***

The stratification and nutrition conditions during algal bloom formation were analysed with extraordinary resolution. Particularly, the impacts of nutrient sources such as sewage plant discharges could be identified.

- ***Identification of water mass interaction processes:***

The water quality conditions in tributary backwaters of the TGR are largely dependent on interactions with the Yangtze River main stream. These are to a large extent driven by water level fluctuations and considerably amplified by density current circulation cells.

- ***Urban impacts on water quality conditions in the TGR:***

Significant pollutant plumes including heavy metals, nutrients, and CDOM were identified to originate from cities at the TGR. These plumes were most pronounced during high water level conditions in winter.

- ***Spatio-temporal geostatistical model for water quality data:***

The MINIBAT data were used to develop a GIS based spatio-temporal geostatistical model for water quality conditions along a TGR tributary backwater. This model revealed pollutant transport processes and dynamics affecting the water quality distribution in the TGR.

- ***Establishment of the numerical hydrodynamic model TELEMAC2D:***

Pollutant transport and distribution processes for several sections of the TGR were modelled successfully. The results were integrated with the collected monitoring data to elucidate underlying hydrodynamic processes and their impacts on water quality.

- ***Implications for water quality management in the TGR:***

It was demonstrated that the adapted methods can be used to identify water pollution problems and to propose infrastructural improvements such as modified sewage plant discharges. Exemplarily, an alternative sewage plant discharge location was simulated for Wushan city. The modified discharge location could considerably reduce the nutrient input into the Wushan Lake and the Daning River backwater, which are both highly susceptible to algal blooms.

4 FKZ_02WT1132: BIOMONITORING VIRTUAL ORGANISMS, BIOVIRTOUS (TUM)

- ***Losses of pollution:***

TGR exhibits substantial losses of pollution (up to 80 % from Chongqing to the dam) after being contaminated at Chongqing. These losses can be attributed to ecological services based on degradative processes and volatilization of chemicals from the water phase.

- ***Pollution tributaries:***

The contribution to the pollution of the reservoir for the most important tributaries during low water regime could be evaluated as a basis of environmental management.

- ***Total mass transport:***

Homogeneity investigations of the pollution in the cross-sectiona area in front of the dam allowed the verification of total mass transport calculations of pollutants.

- ***Homogeneity Investigation:***

The homogeneity investigation in front of the dam was extended to some polar contaminants among pharmaceuticals and pesticides. Atrazine was found in similar *ranges of about 4500 pg/L followed by Carbamazepine (~ 100 pg/L) and Simazine (~25 pg/L) at 11, 31, and 50 meter water depth.*

- ***Sediment Cores:***

The investigation of sediment cores from the reservoir and selected tributaries witness their homogeneity and young age. Their low contamination status with respect to pollutants (Dioxins, Polycyclic Aromatic Hydrocarbons) and their young age with respect to sedimentation pinpoint to their recent formation which is mainly based on low contaminated eroded material.

- ***Persistent Bioaccumulative Toxins (PBT):***

All in all the BIOVIRTUOUS generated first data about the status of persistent bioaccumulative toxins (PBT) and estrogenicity of the whole reservoir as a basis for further follow-up investigations and risk assessments.

- ***Potential Contamination Status:***

Virtual organisms (VO) were very effective to estimate the potential contamination status due to their high reproducibility and allowed seasonal cost-effective investigation of PBT in TGR in a short time along the whole stretch of the huge reservoir.

5 FKZ_02WT1141: ORG MICROPOLLUTANTS, MICROTOX (RWTH Aachen)

- ***Calibrated Ecosystem Model:***

led to plausible results and proved useful to understand the basic principles of nutrient and population dynamics of a tributary system strongly influenced by the TGR water level fluctuations.

- ***Relevance of Propanil:***

This model substance was highly relevant as lastly being intensively used in the region. It turned out to be problematic regarding a lack of knowledge on degradation in soils and sediments.

- ***Polycyclic aromatic hydrocarbons:***

Were identified as most relevant pollutants at TGR.

- ***Identification of effects of sediments (in vitro and in vivo) and as indicated by biomarkers in aquatic organisms:***

Sediment samples from upstream tributary sites revealed in most cases a higher activity than from downstream tributary sites. The mostly moderate toxicity reached potential threat levels for fish at Chongqing and the Hanfeng Lake.

  - ***Characterisation of the environmental risks:***

Propanil as widely used herbicide in rice cultures forms critical metabolites: besides the well-known DCA the follow-up product TCAB is present in the sediments for which only limited data on fate and ecotoxicity are available. In general, only moderate to low toxicity levels have been concluded, most likely due to strong dilution caused by high mass transport of water and sediment in the Yangtze River.

  - ***Impact of TGD on the environment in the region:***

As shown by the modelling exercises, the stagnating conditions at the TGR turned out to affect the nutrient dynamics clearly. But it showed slight impact on the aquatic communities only, thus the risk of algal blooms at the Daning River was considered low.

  - Integrative monitoring strategy:

We propose a combination of an extended TRIAD approach complemented by ecosystem modelling exercises to better understand the mechanisms of transport and metabolism in an upscaled sense to identify a couple of priority pollutants of genuine relevance.

- ***Outlook to future applications and utilization of the findings of the MICROTOX project:***

  To understand the complex environment of the Three Gorges Reservoir a long standing and sustainable cooperation and joint forces supported by bi- and multilateral, international research programs are needed.

6 BEHAVIOUR OF ORGANIC MOLECULES (JÜLICH RESEARCH CENTRE, ZEA)

- ***Behaviour of organic molecules***

  A procedure for the evaluation of the behaviour of organic molecules in water has been developed to mimic the fate of these chemicals under oxidative or reductive conditions and their potential chemical reactions with soil organic matter and applied to typical water pollutants.

7 RESEARCH CAMPAIGNS AND EXCHANGE OF SCIENTISTS (JÜLICH RESEARCH CENTRE)

- ***The extensive bilateral discussion***

  of research campaigns and results linked with the comprehensive exchange of scientists has led to a very successful outcome in the project network.

II General Introduction

1 The research area

The 6,300 km long Yangtze, which rises on the Qinghai-Tibet Plateau, China's longest river, is after the Nile and the Amazon the third longest river in the world. The river passes ten Chinese provinces, with about 400 million inhabitants, including the city of Shanghai. In Shanghai, the Yangtze flows into the East China Sea. The upper reaches of the Yangtze to Yichang City is 4,300 km long (with a catchment area of about 100 * 10^4 km²), the middle course of the river until Hukuo (outflow of the Poyang Lake) about 950 km (catchment area extends approximately 63 * 10^4 km²). The lower reaches of the Yangtze River to its mouth is about 930 km long (catchment area of some 12 * 10^4 km²). With a catchment area of 1.8 million km² the Yangtze covers 19% of the land area of China and this captures 37% of the total runoff of the country. Its great hydropower potential and use as a major east / west transport line gives it an essential role in the development and industrial growth of China.

The Yangtze also plays an essential role in developing strategic plans of the Chinese central government. This provides, among other things, the transfer of the generated hydropower in western areas of and coal power in eastern China as well as measures to address the water shortage in the north by recourse to the water resources in the catchment areas of major rivers.

Over the past 100 years the annual runoff rates of the Upper Yangtze at Yichang varied between 3,000 $m^3 s^{-1}$ in January and 60,000 $m^3 s^{-1}$ in the rainy summer months. In the months of June to September, with the greatest amounts of precipitation, also an extensive suspended sediment transport is associated. The periods of low (and high) water management in recent decades, more and more extreme with the consequence that in the late 1970s, the penetration of saline water from the East China Sea in conjunction with very low water levels of the Yangtze, impaired the water supply of the city of Shanghai for several months.

The completion of the entire project, including the commissioning of the hydropower plants and the two lock systems took place in 2009. The length of the dammed river section (reservoir) at a mean width of about 1,100 m is more than 600 km.

Some other figures illustrate the technical dimensions and the magnitude of this structure (www.yangtze-project.de):

- Tailback of the lock > 620 km,
- Mean storage width about 1.6 km,
- Storage volume about 39.1 billion m³,
- High water storage volume 22.1 billion m³,
- Height of the dam 185 m above sea level,

- Smaller floods of the Yangtze 40,000 $m^3 s^{-1}$,
- Low water discharge (November to May) 3,000 $m^3 s^{-1}$,
- Mean annual water freight 451 billion m^3,
- Mean bedload 526 million tonnes a^{-1},
- Mean concentration of suspended solids 1.2 kg m^{-3} and
- Catchment area of 1.8 million km^2, with 400 million inhabitants.

The construction of this large dam is a strategic part of the approach to the development of the entire Yangtze basin. With tremendous technical projects, the Chinese leadership has the following objectives:

- Avoiding floods or reducing peak discharge downstream of Three Gorges Dam,
- Navigability of the Yangtze and its main tributaries and thus infrastructural expansion and connectivity,
- Water security and simplified transfer of water to the north Chinas (North-South water transfer project)
- Hydroelectric development.

In 2009, the water level of 175 m above sea level was reached at the dam. However, the main objectives of the project for energy, water security, canalization and flood control require in their implementation of a seasonal lowering of the water level by 30 meters at the dam and re-damming of the Yangtze to the maximum dam height (Figure 2).

Figure II-1 Yangtze in Chongqing, Yangtze upstream dam, Yangtze dam (Photos: RD Wilken)

Until the beginning of the rainy season, from late May to early June, the water level is drawn down to 145 meters above sea level to gain during heavy rainfall the following months a sufficient compensation volume available. After passing the maximum amounts of water again in October, the water level should rise to a maximum of 175 meters above sea level. After that the peak energy generation starts. In the months of January to May, the water level is gradually down to 145 meters above sea level, so as to compensate the lack of rainfall during the dry winter and to stabilize the flow of water below the dam. This should in the months of June to September, when with the greatest amount of precipitation is also accompanied by a stronger solids transport, counteracted the suspensions deposition in the reservoir and at the same time the existing deposits are washed away partly. With the start of early summer, the water level has reached the required low level in order to accommodate the large amounts of precipitation during the following months back again.

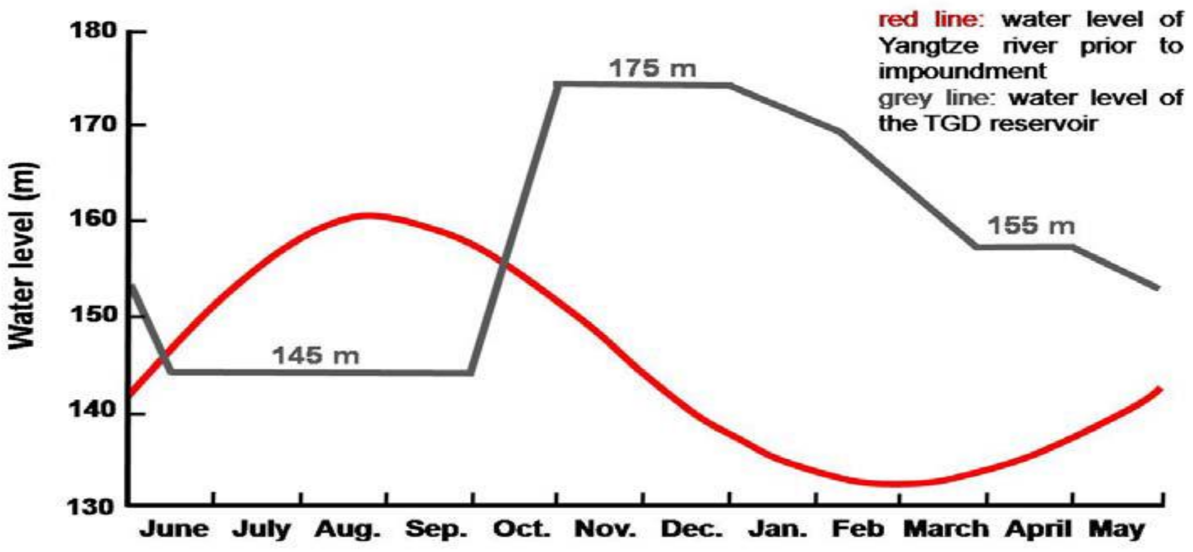


Figure II-2 Seasonal progression of the natural, unregulated runoff of the Yangtze River before impoundment (red line, water level does not scale) and the course of the regulated discharge of the Yangtze River after the impoundment by the Three Gorges Dam to prevent flooding (*Water Level does not scale!*).

The Yangtze was known for its flood catastrophes, which cost the lives of three million people in the last 100 years. That was one reason that China decided to regulate the flow of the Yangtze by dams. The largest and most famous of these dams is the Three Gorges Dam near Yichang City. The dam, built in a relatively short section with solid bedrock (only about 31 km) of the over 4,000 km long Yangtze river bed, has - next to flood control – severe impacts on the ecology, what is the main reason for research activities of the German research project network **YANGTZE-PROJECT** and here its sub-network Yangtze-HYDRO.

No other major project in the People's Republic of China was as controversially discussed as this dam in the last years. Proponents justify its necessity mainly with the improvement of flood protection. The protection of human life was also an important argument for the construction followed by the flooding damage impact. Additional reasons for the construction were winning energy by a hydroelectric power plant and the improvement of navigation. Opponents feared disadvantages because of the ecological consequences, the geological potential hazards and the sociocultural consequences of the project.

Thus, the construction of the largest dam in China, the Three Gorges Dam, since the beginning of the planning phase until today was highly controversial. The long-term ecological impacts of dam construction and the associated damming of the Yangtze River and its main tributaries are difficult to predict in their dimension and dynamism until now. The former untamed river was changed to a 600 km long lake with a behaviour that differs significantly from a stream. In the resulting lake other interactions prevail between contaminants and the water, suspended matter and sediment phase than in the river. It is noted an eutrophication by entry of nutrients that lead in the dam area to troublesome algae blooms and water hyacinth growth. The nutrients and pesticides from agriculture are difficult to reduce because the agricultural land is divided into a lot of small plots with many users and is used intensively.

Figure II-3 Course of the Yangtze in China. Source: Wikimedia Commons

With these changes, the projects employ the Yangtze-HYDRO group. The already in 2008 launched Yangtze GEO-Research Group focuses on the topics: Land Use Change - Erosion - Landslides - Material inputs, in which the part-project "land use change" in the Yangtze catchment both projects have a common interface.

2 *The project and its priorities*

In addition to the focused search for substances, their concentrations, and behaviour, the mechanism of action of pollutants, is increasingly studied in today's environment research. The group of researchers from universities and research institutions in the Yangtze-HYDRO project has come together to share their current knowledge with the Chinese groups on the Yangtze River. On the German side the universities of Aachen, Karlsruhe, Stuttgart and Munich (TU) are involved. As research institutions are IWW Water Research at Muelheim (Ruhr) and Biebesheim, and the Water Technology Center (TZW) in Karlsruhe project partners. In addition, there is a very close collaboration with Research Centre Jülich (FZJ), which maintains contacts with the Chinese groups for a very long time and intense cooperation.

Priorities of the Yangtze hydro project are the chemical trace analysis and contaminant behaviour (IWW, TZW, RWTH Aachen, Jülich) and novel sampling devices which are BIOVIRTUOS used in the project with "virtual organisms" where pollutants are concentrated in adsorber tubes (TUM). As a novel sampling system applies the MiniBAT that can take under water behind a boat, controlled samples (KIT); included in the sub-project is a modelling group from University of Stuttgart.

After the start of the project funding in summer 2010 a first consultation of research activities with Chinese partners was held at the facilities in Beijing (State Council Three

Gorges Project Construction Committee, Chinese Research Academy of Environmental Sciences), Chongqing (University), Wuhan (Changjiang Water Resources Protection Institute and the Institute of Hydro Ecology) and Shanghai (Tongji University, attended together with representatives of the Universities of Nanjing and Zhejiang) and have been agreed.

The narrow research contact is maintained through regular meetings in China and Germany, which meet groups from the two countries or the entire research network.

2.1 Cooperation with the YANGTZE GEO Project

Before the Yangtze HYDRO project could start, the Yangtze GEO project started already on April 1st 2008. Since that time, there was an intense exchange between the two groups, particularly in the project meetings at Jülich. In the first workshop on August 1st 2010 the just approved HYDRO-project the groups of the GEO project were present to foster an intense exchange in Karlsruhe, as well as at the following workshop in Aachen. The experience allowed the newly approved HYDRO project an easier start of the project. This exchange was intensified and refreshed in the project events of both projects. In particular, the project got starting advice by the head of the Yangtze GEO project, Prof. Dr. Thomas Scholten, which is gratefully acknowledged.

Another aspect of cooperation refers to the creation of a common database. All spatial data sets (climate, topography, geology, soil, hydrology) from YANGTZE GEO were already at the beginning of the work in YANGTZE HYDRO available.

2.1.1 Project meetings and workshops

- **‚Yangtzientists‘ PhD Meetings**

– Interconnection within Yangtze Hydro & Geo Network between PhD candidates
2012 January 26-27 - TZW Karlsruhe (Hydro)
2012 September 5-6 -IWW Biebesheim (Hydro)
2013 June 13-14 - University Kiel (Hydro & Geo)
2013 October 21-22 - RWTH Aachen (Hydro & Geo)

- **Yangtze Hydro Network Meetings**

- Interconnection within Yangtze Hydro Network
2010 September 100 - IWW Mülheim a.d. Ruhr
2010 November 30 - KIT Karlsruhe
2011 March 10 - TZW Karlsruhe
2011 May 9-10 - University Gießen
2011 August 02 - IWW Mülheim a.d. Ruhr (WATERUSE & MICROTOX)
2013 November 12 - RWTH Aachen

- **Sino-German Workshops**

– Interconnection between German and Chinese scientific institutions
2011 March 27 – April 2 – Tongji University, Shanghai, China ‘Workshop on Interactions in the Water System – in the Frame of the Sino German Yangtze Project’

2011 November 28-29 – RWTH Aachen University, Aachen, Germany ‘Processes in the Yangtze River System-Experiences and Perspectives’
2012 September 21-23 – Tongji University, Shanghai, China ‘Processes in the Yangtze River System - 10th Anniversary of Sino-German Cooperation’

2.2 Development of Yangtze Hydro

The cooperation with the Yangtze Geo project has been described already.

The first written ideas of the project, with its final annual report now in 2014, dates from the year 2005.

It is particularly Prof. Dr. Günter Subklew and Forschungszentrum Jülich, whom we have to thank that the proposals eventually led in 2010 to the approved grant applications.

However, the long temporal gap led to a promotion of the Chinese partner: the Ministry of Sience and Technology (MOST) has already being phased out; the parallelism of work and financial support unfortunately existed only in the short term. The Chinese partners had consistently no longer the resources available, which would have been necessary for a balanced cooperation, such as joint field trials. It must be especially commended the power of cooperation and support by the previously well-maintained contacts from the Chinese side.

The cooperation with the Institute of the Helmholtz Association and the working groups are now showing here exemplary results; it must be stressed that this project without the stamina and the good contacts of Prof. Dr. Günter Subklew would not have been established.

III WATERUSE - Suitability of Surface Water from the TGR for Public Drinking Water Supply

FKZ: 02WT1129

IWW Water Centre

Anja Wolf

Axel Bergmann

Figure II-4: Air and Water Pollution Chongqing Photo: Bergmann, IWW

Figure III-1: Water Discharge Channel, unused Photo: Bergmann, IWW

Figure III-2: Waste Water Treatment Photo: Bergmann, IWW

1 Introduction & Problem

1.1 Our Study Area

The Yangtze River and its catchment are home to 420 million people (CIESIN 2000), 500 terrestrial vertebrates, 3418 insects, and 350 fish (Wu et al. 2004) of which 112 are endemic (Park et al. 2003). They also account for 6388 terrestrial and 1085 aquatic plant species (Wu et al. 2004). About one third of the national gross output for agriculture and industry is produced in the Yangtze River catchment (Zhang et al. 1999; Xing and Zhu 2002; WWF 2007). This includes more than 70% of the national fishery and 40% of crop productions and is commonly divided in three major parts, referred to as the upper, middle, and lower reaches (Figure III-4).

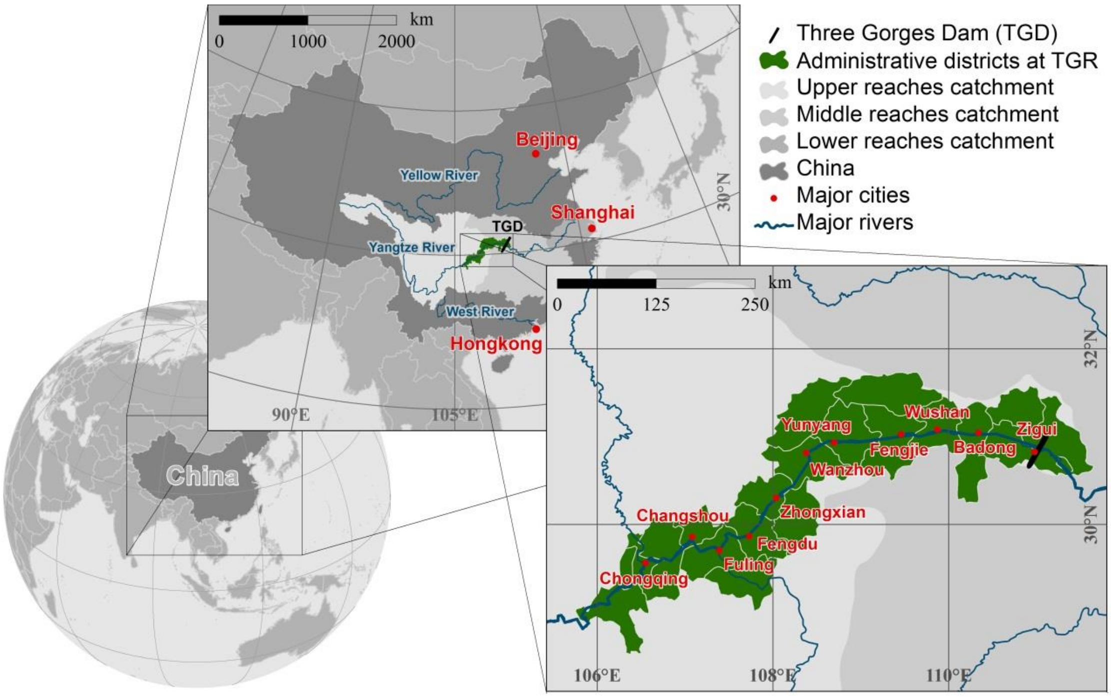


Figure III-3: Overview of the Yangtze River, Yangtze River catchment, and location of the study area at the Three Gorges.

As the Yangtze Three Gorges are located in the upper reaches at the borderline to the middle reaches the upper reaches have great influence on its water quality and ecosystem. The upper reaches cover an area of about 980000 km2 and are mainly formed by remote natural areas of the Himalayas with steep slopes and population density of 160 people km-2 (CIESIN 2000) (Figure III-4). The typical geology is clastic rocks and limestones overlying Mesozoic granitoids and Triassic low-grade metamorphic rocks (Chen et al. 2002; Li et al. 2011).

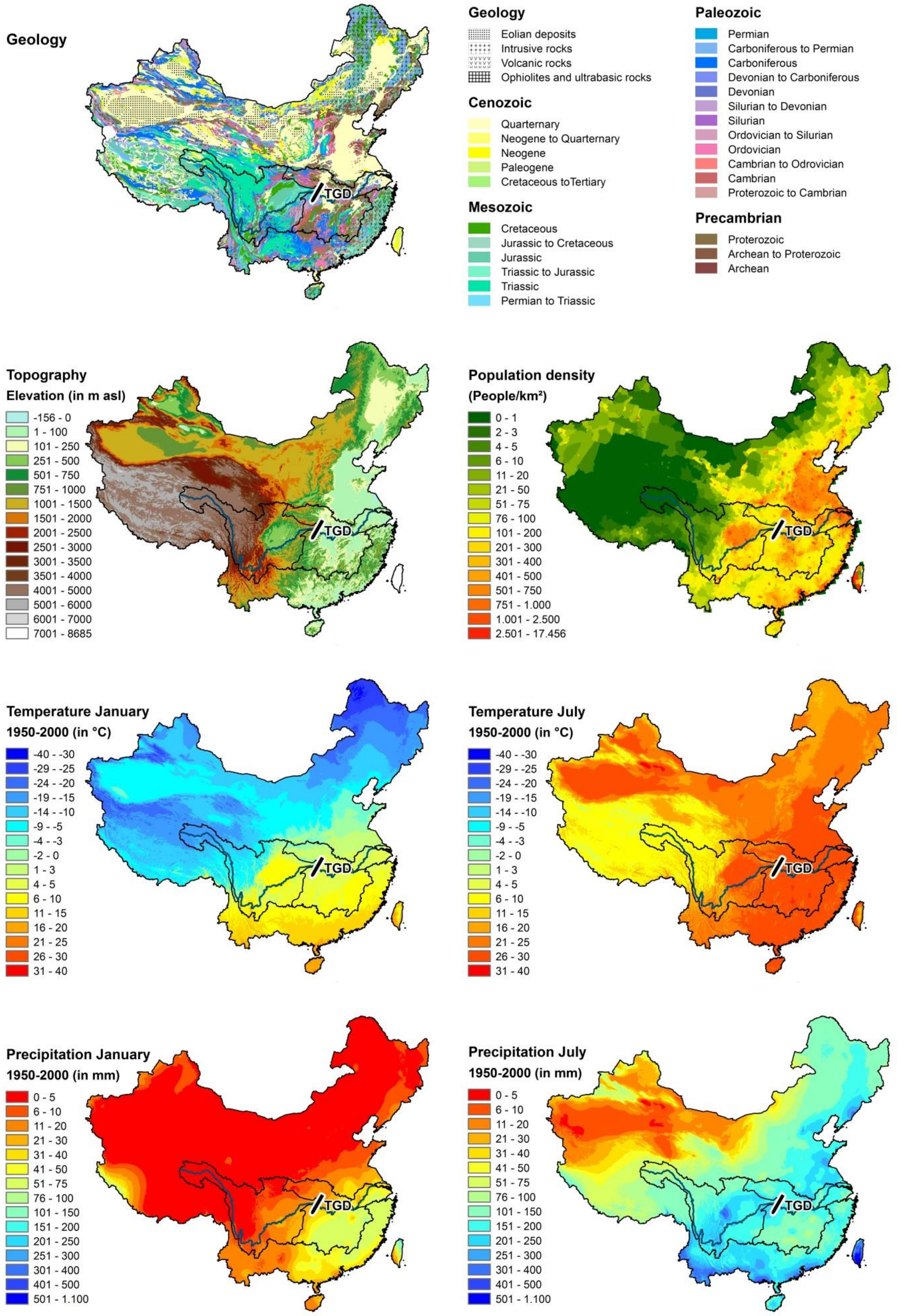


Figure III-4: Overview of topography, population density, geology, and climate in China and the Yangtze River catchment. Data base sources: Topographical map (NASA 2000), population map (CIESIN 2000), geological map (USGS 1997), climate data (WorldClim 1950-2000).

Evaporitic rocks and Jurassic red sandstones are also widely distributed throughout the basin (Figure III-4). The climate varies from cool mountain to subtropical conditions with precipitation totals of 300 and 1400 mm a-1 and mean annual temperatures of about 4 and 18 °C, respectively (WorldClim 1950-2000; NOAA 2011-2013) (Figure III-4). Summer precipitation accounts for around 45% of the annual precipitation, often generating high discharges and following floods. This is connected to summer monsoon activities that deliver a huge amount of atmospheric moisture from the East and South China Sea (Jiang et al. 2007). The winters, in contrast, are dry with low precipitation. Agglomeration centers and industries are rare in comparison to the huge cities and industrial areas in the middle and lower reaches of the Yangtze River and limited to the Sichuan basin and Chongqing (Figure III-4).

1.2 The Three Gorges Dam and Reservoir

In October 2008 the 185 m high Three Gorges Dam (TGD) was finished, impounding the Yangtze River for the world’s largest comprehensive project for hydroelectric power generation, housing two power stations with 26 turbine generators. Its installed capacity of 18.2 GW approximately equals that of 15 nuclear power stations. The construction period of the 2335 m long structure lasted 15 years and consumed 26 billion US $ (Figure III-5). The impounded Three Gorges Reservoir (TGR) reached its full capacity of 39.3 km^3 in 2011 at a maximum target water level of 175 m. It is 660 km long and about 1.1 km wide, twice as wide as the river was before dam construction.

The installation of the hydroelectric power station of the TGD and other hydropower plants in the Yangtze River catchment was decided as a consequence of the Chinese economic development since the 1970´s because the electricity supply has lagged far behind the exponent-tially expanding demand (Jackson and Sleigh 1998). Being by far the largest of these projects the TGD has increased China´s total electricity supply by 10% (Jackson and Sleigh 1998). Besides energy production, the TGD project provides additional benefits such as (i) the prevention and control of frequent floods with a reduced flood probability of once in 50 to 100 years by a reservoir system with keystone TGR (YWRPB 1999; Zhang et al. 1999), (ii) water supply assurance for people living in its catchment area and for the South-North Water Transfer Projects (SNWTP) (Bergkoff 2003), and (iii) enhanced navigability and expansion of Chongqing harbor, supporting the development of the western part of the country.

The TGD project, however, was controversial from the very beginning and resulted in a huge amount of attention from journalists and scientists worldwide. The impounded reservoir inundated an area of 34200 ha in 20 districts including 24600 ha of farmland and orchards, about 5500 ha of forest, 3500 ha of residential districts, and 824 km of roadway (Zhu and Zhao 1996; Asarin and Lapin 2001). Two large cities, 11 district centers, 116 villages, and numerous ancient cultural relics had to be displaced (Asarin and Lapin 2001) such as at least 1.2 million local people (Heggelund 2006). Additionally, there is an ongoing controversy about the environmental impacts of the dam since large amounts of organic and inorganic pollutants were released into the reservoir (Wang et al. 2009; Ma et al. 2010). Further, lots of scientific discussions have focused on changes in the hydraulic regime and ecology up- and downstream of the TGD (Chai et al. 2009; Xu and Milliman 2009; Xu et al. 2011). Hence, the TGR is still in the center of public awareness and data are therefore highly sensitive and often not shared.

Figure III-5: **The Three Gorges Dam (TGD) on June 15, 2012. Photo: A. Wolf**

Several studies report water quality data from the Yangtze River, mostly focusing on inorganic parameters (Yang et al. 2004; Müller et al. 2008; Shen and Liu 2009; Ran et al. 2010; Müller et al. 2012). Data on organic compounds in Yangtze River surface water are comparatively rare. In a recent review, Bao et al. (2012) report concentrations of persistent organic pollutants at the high end of the global range of various drinking and coastal waters in China, with few data and lower concentrations in the western part that includes the TGR. Most studies on organic compounds address the middle and lower reaches of the Yangtze River downstream of the TGD (Feng et al. 2007; Müller et al. 2008; Tang et al. 2008; He et al. 2011; Yan et al. 2013). Polycyclic aromatic hydrocarbons (PAH), polybrominated diphenyl ethers (PBDE), and polychlorinated biphenyls (PCB) were detected in analyses of sediments from the Yangtze River estuary and Wuhan reach and found to originate mainly from heavy rains and surface runoff (Yang et al. 2009; Ou et al. 2010; Gao et al. 2013), waste (Chen et al. 2006) and sewage discharge points (Liu et al. 2001; Hui et al. 2009a; Hui et al. 2009b; Yang et al. 2009; Ou et al. 2010), and combustion (Liu et al. 2001; Ou et al. 2010; Li et al. 2012). Generally, the concentrations of organic pollutants were found to increase from the remote west to the industrialized east (Liu et al. 2011). Only a few studies document organic pollutants in the TGR and focus mainly on PAH, PCB, organochlorine pesticides (OCP), phthalate acid esters (PAE), and polychlorinated dibenzodioxins and dibenzofurans (PCDD/F) (Gao et al. 2007; So et al. 2007; Chen et al. 2008; Cui et al. 2009; Wang et al. 2009; Luo et al. 2011; Liu et al. 2011; Wang et al. 2012; Chen et al. 2013).

2 Water resources and water treatment in China

Statistics show an increasing water shortage in China since the 1970s due to rapid socio-economic growth. In the past 10 years, for example, the demand of fresh water increased from 553 to 611 billion m^3 (NBoS 2011). Thus, water resources that account for 1,913 and 413 billion m^3 for surface water and groundwater, respectively, became increasingly short

(NBoS 2011). Especially in the catchments of the Hai River, Yellow (in Chinese: Huang) River, and Huai River in the drier northern part of China suffer from water scarcity as acute as in any major world region (Bergkoff 2003). The Yangtze River catchment, however, is rich in water. It accounts for 33.7% (784 of 2326 billion m^3) of China’s freshwater resources and, therefore, is considered for the provision of fresh water to the northern part of China within the frame of the South-North Water Transfer Project (SNWTP) (Bergkoff 2003; Chang et al. 2011; NBoS 2011). The middle route of this project diverts water from the Red River Mouth (in Chinese: Danjiangkou) Reservoir on the Chinese (in Chinese: Han) River to the North, and plans an additional water supply from the Three Gorges Reservoir. Concurrently, TGR surface water is the major source for public water supply in the TGR area (95.6% of treated raw water) since bank filtration as a first purification step is often not feasible (U.S. Department of Commerce 2005; NBoS 2011).

Generally can be stated that the quality of the TGR surface water is of major concern and there is an increasing consciousness for water protection in China. However, there are various kinds of pollution sources in the catchment such as agricultural and residential areas, industries, hospitals, and wastewater treatment plants (WWTPs). Wastewater discharge of industries and households increased in the past 10 years by 19% and 94%, respectively (NBoS 2011). By balancing China´s water demand of 611 billion tons and wastewater discharge of 66 billion tons, a calculated difference of 545 billion tons of water does not reach WWTPs. Taking into account that 386 billion tons are applied to agricultural areas and the ecological environment (NBoS 2011), it can be assumed that up to 159 billion tons of wastewater per year, that is 26% of the total water supply, are not treated and flow directly into the rivers. This is due to a deficit in the connection of households to WWTPs, especially in the TGR´s smaller cities and remote areas. It may also occur that, in summer, heavy rainfalls additionally provide huge amounts of wastewater that often result in an overflow of existing wastewater treatment plants and subsequent incomplete treatment of incoming wastewater and input into connected rivers. A study at four municipal WWTPs in Chongqing detected 21 pharmaceutically active compounds in individual treatment unit effluents and sludge (Yan et al. 2014) and found especially antibiotic concentrations comparable to or even higher than those reported in developed countries. Further, Yan et al. (2014) figured out that pollutants were not completely eliminated in the treatment steps and state that further regulatory control is needed to prevent the input of pharmaceutically active compounds into the environment.

In China, the use of surface water for drinking water production is regulated by the Environmental Quality Standards for Surface Water GB 3838 (SAEP 2002), which classifies surface water in five categories according to different environmental functions and protection targets wherein surface waters of the classes I-III are feasible for drinking water production. The compounds of relevance for classification are mostly inorganic (Table III-1). However, 80 organic compounds were included in the standard in a separate table of so-called “specific items” but without relevance for classification. The application of the standards for “specific items” is up to local governments at or above the county level, such as the government of province, autonomous region, or municipality. Furthermore, if the requirement of the Standards for Drinking Water Quality GB 5749 (MoPH 2006) are achieved after treatment, the standard allows the use of surface water as a drinking water source even if the surface water exceeds the limits.

Table III-1: Standard limits of basic items of the Chinese Environmental Quality Standards for Surface Water GB 3838 (SAEP 2002).

No	Standard value Categories Items	class I	class II	class III	class IV	class V
1	**Temperature (°C)**	Anthropogenic change of water temperature should be limited: Mean maximum rising value (each week) ≤ 1; Mean maximum falling value (each week) ≤ 2				
2	**pH value (-)**	6 - 9	6 - 9	6 - 9	6 - 9	6 - 9
3	**DO ≥ (mg L^{-1})**	Saturated rate 90% (or 7.5)	6	5	3	2
4	**Potassium permanganate index ≤ (mg L^{-1})**	2	4	6	10	15
5	**COD ≤ (mg L^{-1})**	15	15	20	30	40
6	**BOD_5 ≤ (mg L^{-1})**	3	3	4	6	10
7	**NH_3-N ≤ (mg L^{-1})**	0.15	0.5	1	1.5	2
8	**TP (Calculated with P) ≤ (mg L^{-1})**	0.02 (0.01 in lakes and reservoirs)	0.1 (0.025 in lakes and reservoirs)	0.2 (0.05 in lakes and reservoirs)	0.3 (0.1 in lakes and reservoirs)	0.4 (0.2 in lakes and reservoirs)
9	**TP (Calculated with N in lakes & reservoirs) ≤ (mg L^{-1})**	0.2	0.5	1	1.5	2
10	**Cu ≤ (mg L^{-1})**	0.01	1	1	1	1
11	**Zn ≤ (mg L^{-1})**	0.05	1	1	2	2
12	**F^- ≤ (mg L^{-1})**	1	1	1	1.5	1.5
13	**Se ≤ (mg L^{-1})**	0.01	0.01	0.01	0.02	0.02
14	**As ≤ (mg L^{-1})**	0.05	0.05	0.05	0.1	0.1
15	**Hg ≤ (mg L^{-1})**	0.00005	0.00005	0.0001	0.001	0.001
16	**Cd ≤ (mg L^{-1})**	0.001	0.005	0.005	0.005	0.01

The National Bureau of Statistics of China states that the Yangtze River surface water is mostly of class II and III and therefore usable for drinking water production (NBoS 2008, 2011) (Table III-2). Further, Yangtze River surface water quality is slightly better than the national mean. The Yangtze River insofar is viewed favorably due to its high discharge and sediment load that dilutes and adsorbs the input pollutants, respectively. Generally, water quality increased from 2008 to 2011. This increase might be related to a new law that forced industries to install WWTPs. Nowadays over 95% of the observed industrial wastewater meets the discharge standards. In 2000 it was just 77%.

Table III-2: Surface water quality classification of Yangtze River compared to the national mean. Quality assessment was performed after the Environmental Quality Standards for Surface Water GB 3838 (SAEP 2002). Source: NBoS (2008); (NBoS 2011).

	Class I %	Class II %	Class III %	Class IV %	Class V %	Inferior class V %
China 2008	3.5	31.8	25.9	11.4	6.8	20.6
China 2011	4.6	35.6	24.0	12.9	5.7	17.2
Yangtze River 2008	3.7	36.2	29.2	9.0	7.5	14.4
Yangtze River 2011	5.1	39.4	25.9	11.8	5.3	12.5

New Chinese Drinking Water Standards (GB 5749) were enacted in 2006 to reflect worldwide drinking water standards. The standards are mainly based on international and national standards, guidelines, and directives for drinking water quality. Within the enactment the number of regulated compounds was increased substantially from 35 (MoPH 1985) to 101, of which 48 are organic. Due to water treatment plant observations the compliance with the new standard in actual practice, however, is not always given. In the Wanzhou district at the TGR, for example, water works still apply conventional treatment technologies, such as sedimentation, filtration, and subsequent disinfection (Gao et al. 2007; Luo et al. 2011), although 90% of the investigated water works were built after the implementation of the new standards by 2006 (Luo et al. 2011). The purified water of the plants was tested with respect to the new standards and only 7 (1.75%) out of 400 samples passed (Luo et al. 2011). Amongst others, Luo et al. (2011) attributed this to a contamination of the raw water sources by domestic waste and a lack of the awareness of water protection. In China, commonly it is distinguished between tap water in the house of an end-consumer and drinking water in bottles.

3 Scope

The overall aim of this study is the assessment of water quality of the Three Gorges Reservoir (TGR) with respect to its suitability for drinking water production. The main focus is industrial, pharmaceutical, and agricultural organic trace substances, which are released into the surface water by various sources and mechanisms.

Hence, central questions are:

- What contaminants are of relevance in the TGR surface water with respect to legal limits and ecotoxicity?
- What are potential sources of contamination within the catchment area and how can they be located and quantified?
- Which drinking water treatment steps are necessary to remove the relevant substances?

In the first phase of the project, the TGR surface water and sediment are analyzed for dissolved ions and a variety of organic trace substances. Further, active and passive sampling methods are applied for the parallel determination of temporal changes and representative yearly average concentration, respectively. For this, four field campaigns were performed to collect water and sediment samples and to install and retrieve passive sampling devices.

In completing surface water screening, *IWW Water Centre* normally follows an emission approach in which (i) the emission sources are located and identified, (ii) the surface water samples are taken at or downstream of potential emission sources, and (iii) the samples are analyzed for source-specific inorganic and organic pollutants. However, access to information about location of and requirements for potential pollution sources at the TGR, such as industrial complexes, wastewater treatment plants (WWTPs), and agricultural sites, was limited. Thus, within this project an immission approach is followed in which (i) grab samples are taken randomly in profiles along the TGR and selected tributaries, (ii) the samples are analyzed for typical inorganic and organic pollutants due to IWW´s experiences with surface waters in Germany, and (iii) the distribution of the detected pollutant concentrations, then, is traced back to potential sources. The detected substances, finally, are used for an evaluation with regard to limit values given by Chinese standards and European directives, as well as to their ecotoxicological risk.

In the second phase of the project water treatment options are evaluated that are tailored to reduce especially those substances that had been shown to be of relevance. Therefore, laboratory batch experiments on the adsorption and oxidation behavior of selected organic trace substances are performed using deionized water and TGR surface water. In the adsorption experiments sorption kinetics are analyzed and sorption isotherms established. In oxidation experiments, first, TGR surface water is tested for its reaction behavior with ozone and hydroxyl radicals. Second, the oxidation effect of ozone and hydroxyl radicals on selected contaminants is estimated. Based on the results, finally, suggestions for adequate drinking water treatment steps are given.

4 Materials & Methods

4.1 Analytical parameters and grab sampling

Analytical parameters were mainly chosen based on the experience of IWW Water Centre on the occurrence of contaminants in German and European surface water. The main parameters in the assessment of surface water quality are the (i) on-site parameters, (ii) dissolved ions, dissolved organic carbon (DOC), and isotopes, (iii) pesticides, (iv) common pharmaceuticals and x-ray contrast media, (v) various groups of industrial organic compounds, and (vi) volatile organic compounds (VOC) (Figure III-6 left). The chosen organic substance groups cover 213 individual substances and a wide range of substance specific physico-chemical properties (Figure III-6 right and supplementary material in).

All grab water samples were taken in a water depth of 0 to 1 m and mostly at the river bank. During the first sampling campaign in April 2011, however, samples (n = 19) were taken exclusively from a boat at three locations at the TGR close to the cities of Chongqing, Kaixian, and Wushan (**Figure III-4**). This campaign was conducted during conditions of a water level of about 161 m and mean low discharge of 7220 m^3 s^{-1}, after winter stagnation (personal communications Wei HU). Grab samples from tap water (n = 3), i.e. a water sample from the water tap of an end-consumer, were taken in Chongqing, Kaixian, and Wushan.

The second campaign in September 2011 was intended to sample at the lowest water level, assuming high pollutant concentrations due to less dilution. The sampling, however, was affected by high precipitation of up to 144 mm per day on September 12th in a region of the 160000 km^2 wide catchment area of the tributary Jialing (Wanyuan station) (NOAA 2011-2013). The following flood in Jialing River (Bebei station) caused a rise in water level of 30 m to a high of 199 m and a ten times elevated discharge of 35,600 m^3 s^{-1} on September 19th (personal communications Wei HU). Entering the Yangtze River, the flood elevated the water level about 10 – 15 m (Cuntan station). Due to the incoming water volume and subsequent erosion, the sediment load was high and the dilution was assumed to be intense. The sampling locations for surface water (n = 24) were chosen in a profile along the upper part of the TGR from Chongqing to Yunyang and in the tributaries Jialing and Pengjie mainly up- and downstream of major cities, i.e. Chongqing, Changshou, Fuling, Fengdu, Zhongxian, Wanzhou, Yunyang, and Kaixian. The cities were presumed to embody potential sources of pollution. Additionally, tap water samples (n = 2) were taken in the cities Fuling and Wanzhou.

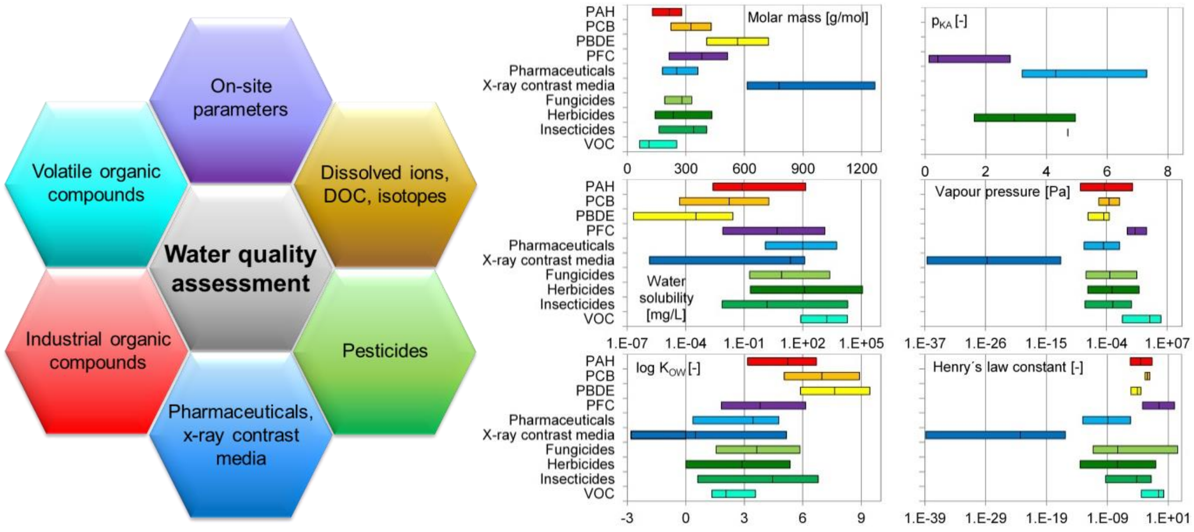


Figure III-6: Programs Interface (EPI) Suite™ developed by the EPA's Office of Pollution Prevention Toxics and Syracuse Research Corporation.

The third campaign was conducted during June 2012, just before the beginning of the rainy season. In this month the dilution was the lowest as indicated by a low water level of 145 to 150 m and sparse monthly precipitation of < 60 mm in the previous months (NOAA 2011-2013). The surface water samples (n = 16) were taken in a profile along the TGR, and in the tributaries Jialing, Shennong, and Xiangxi.

In this campaign samples from WWTP effluents (n = 5) were obtained. In addition, sediment samples (n = 18) were taken. A tap water sample was taken in the city of Wushan. The last sampling campaign at the TGR was performed at a low water level in June 2013 with the main intention of choosing a location downstream of the industrial city of Chongqing for the sampling of 50 L of surface water that was transferred to Germany for water treatment experiments (Figure III-4). Additional surface water samples (n = 15) were taken for the analyses of dissolved organic carbon (DOC).

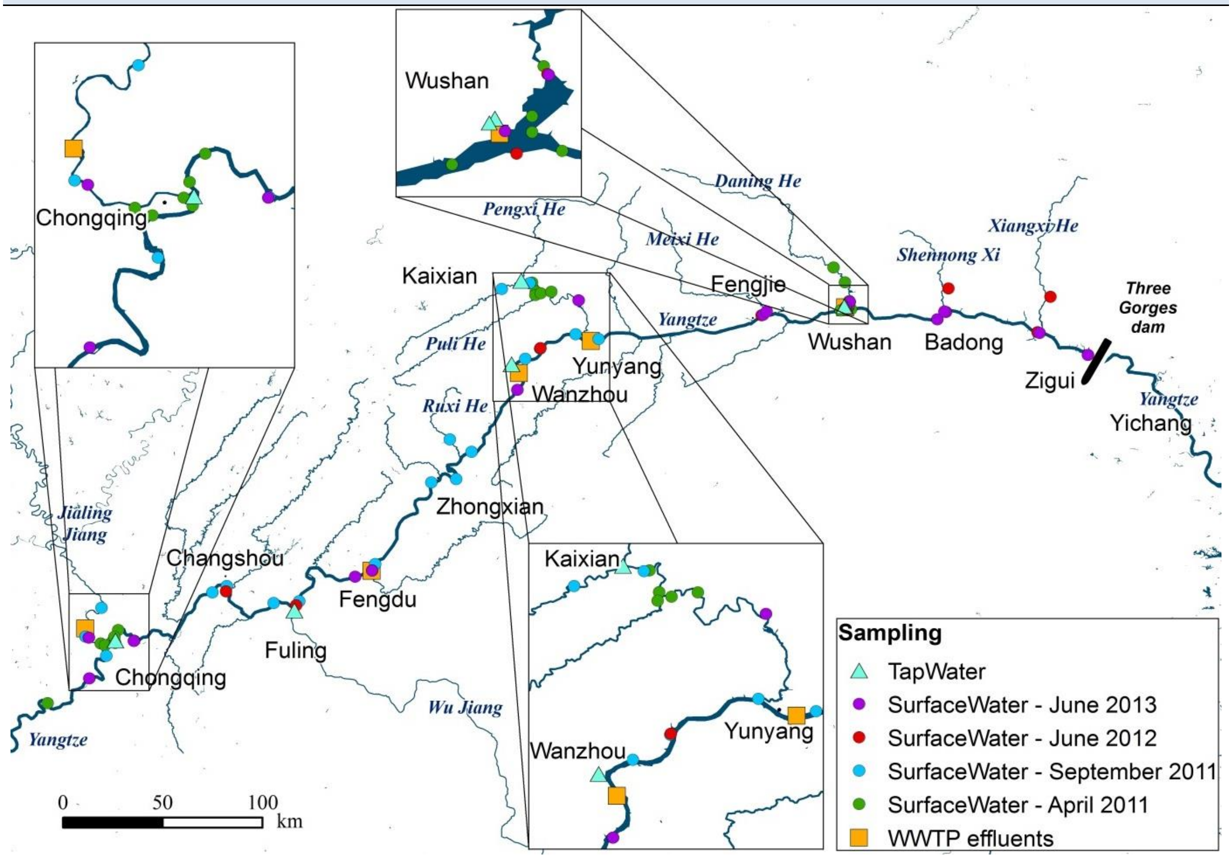


Figure III-7: Map of the water sampling locations of four sampling campaigns at the TGR.

4.2 Time integrated sampling

The above mentioned active water sampling method provides snapshots on the environmental state of the TGR at a certain time while concentration changes over time are not considered. An integrated water sampling with passive samplers, however, delivers average concentrations over defined time periods, hence, peak values are leveled and additional compounds may be captured that are not present in grab samples (Metcalfe et al. 2014). Further, the small and light samplers may be easily transported even to remote areas and require no technical devices and maintenance.

The applied passive samplers consist of a tube, acting as a membrane, filled with a sorbent of high capacity. A suitable membrane for the construction of the passive sampling devices should allow high diffusive fluxes to increase the mass of contaminants captured by the sampling device over time. This is especially important due to the expected very low concentrations of the compounds in the sampled water sources. In this study silicone samplers and ceramic dosimeters are used (Martin 1997; Piepenbrink 1998; Martin 2000; Grathwohl et al. 2001).

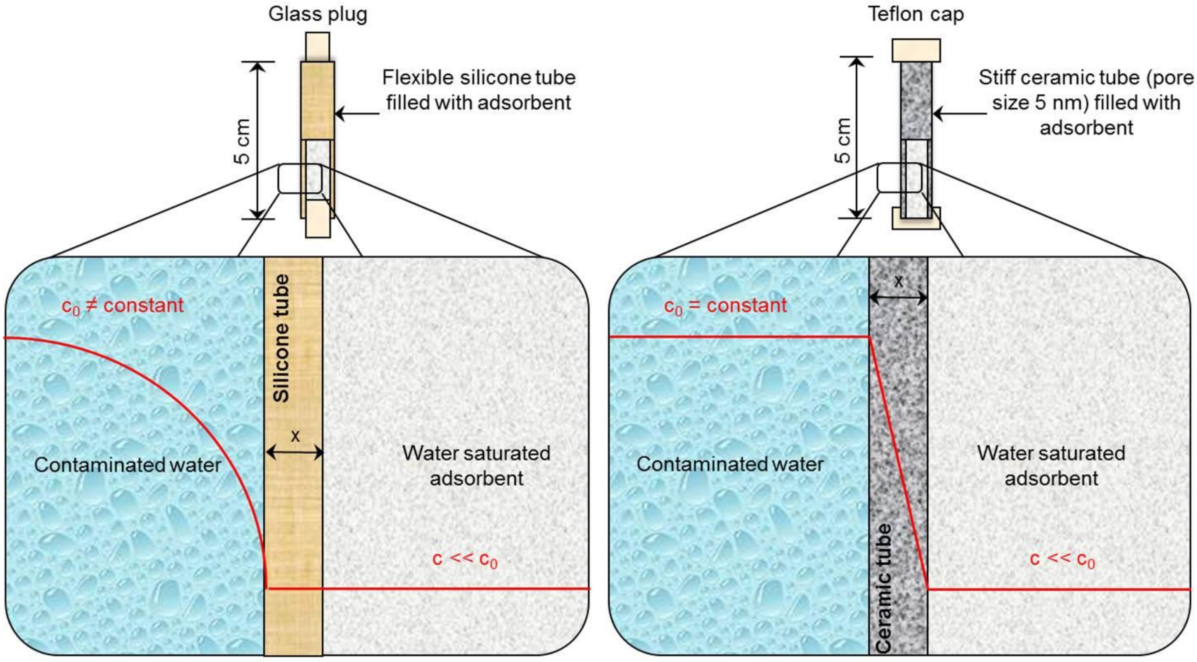


Figure III-8Schematic construction and cross section of the silicone samplers (left) and the ceramic dosimeters (right). The red line illustrates the concentration gradient (c) due to diffusion through a membrane of thickness (x). Modified after Piepenbrink (1998)

The ceramic tubes, that consist of chemical resistant ceramic membrane filter elements (Pall Corporation, Dreieich) made of pure α-Al_2O_3 with an embedded membrane film of TiO_2 (thickness x) as the inner layer, are limited in contaminant uptake fluxes by its small pores (5 nm) while silicon tubes have significantly higher uptake rates as diffusion rates in silicone are orders of magnitude faster compared to the ceramic tubes (Figure III-8). The quick uptake of the silicone samplers, however, is supposed to result in a depletion of the pollutant concentration (c_0) in the surrounding surface water while it will remain stable applying ceramic samplers (Figure III-8 (Piepenbrink 1998)). Due to these stable boundary conditions of ceramic samplers it is possible to calculate average concentrations in the surrounding surface water from the measured concentration in the adsorbent (c) whereas silicone samplers are useful to achieve low detection limits. The diffusion process and function of ceramic dosimeters are explained in more detailed in the following paragraph.

Table III-3: **Schumasiv 1-channel filter element (Pall Corporation, Dreieich, Germany) technical Information.**

Matrix	α-Al_2O_3	**Length**	5 cm
Membrane	TiO_2	**Membrane pore size**	5 nm (ultrafiltration)
Ø outside	10 mm	**Sealing**	Polytetrafluoroethylene
Ø inside	7 mm	**Porosity (support)**	Approximately 33%

Diffusion is a mass flux due to the *Brownian motion* (Einstein 1905) and always directed to the lower concentration. A diffusion process can be described mathematically with *Fick´s 1*st *law* (Fick 1855):

$$F = D_{aq} \cdot \frac{\delta c}{\delta x} \qquad (1)$$

F: Mass flux [ng·s^{-1}·cm^{-2}]
D$_{aq}$: Diffusion coefficient in water [cm^2 s^{-1}]
δc δx^{-1}: Concentration gradient [ng cm^{-4}]

Herein, the mass flux (F) of a compound is described as the product of the diffusion coefficient in water (D$_{aq}$) and the concentration gradient (δc δx^{-1}). Applying *Fick´s 1st law* to the ceramic dosimeters, the pore water in the membrane is handled as a stationary water film with thickness (x) of the membrane. The diffusion through a membrane, however, depends on its texture, i.e. primarily the pore size, tortuosity, and adsorption capacity. Thus, the D$_{aq}$ has to be adjusted and is substituted by an effective diffusion coefficient (D$_e$) that is valid for the diffusion through a membrane. This is done with *Archie's Law* (Archie 1942):

$$D_e = D_{aq} \cdot n_e^{\alpha} \qquad (2)$$

D$_e$: Effective diffusion coefficient [cm^2 s^{-1}]
D$_{aq}$: Diffusion coefficient in water [cm^2 s^{-1}]
n$_e$: Effective pore number (here: 30.5%, Piepenbrink (1998)) [-]
α: Archies law constant (in porous media usually between 1.5 and 2.5, here: 1.8, Piepenbrink (1998)) [-]

The D$_{aq}$ is multiplied by the effective pore number (n$_e$) to the power of the *Archie´s law* constant (α), which is a medium-specific value that does not depend on the compound or the concentration. For data set consistency, the D$_{aq}$ for the observed compounds are not taken from literature but calculated after Worch (1993):

$$D_{aq} = \frac{3.595 \cdot 10^{-7} \cdot T}{\eta \cdot M^{0.53}} \qquad (3)$$

D$_{aq}$: Diffusion coefficient in water [cm^2 s^{-1}]
T: Temperature [K]
η: Dynamic viscosity of water [centiPoise]
M: Molar mass [g·mol^{-1}]

The D$_{aq}$ depends on the temperature (T) and compound-specific physico-chemical properties such as the dynamic viscosity (η) and the molar mass (M). Hence, in the field the diffusion process is highly sensitive to periodically temperature fluctuations.

Under the assumption that the concentration in the adsorbent material is orders of magnitude lower than in the surrounding water body as described above, δc in equation (1) can be described as the concentration in the surrounding water body (c) and can now be calculated as:

$$c = \frac{F \cdot x}{D_e} = \frac{F \cdot x}{D_{aq} \cdot n_e^{\alpha}} \qquad (4)$$

c: Concentration in surrounding water body [ng cm^{-3}]
F: Mass flux [ng·s^{-1}·cm^{-2}]
x: Thickness of dosimeter wall [cm]
D$_e$: Effective diffusion coefficient [cm^2 s^{-1}]
D$_{aq}$: Diffusion coefficient in water [cm^2 s^{-1}]
n$_e$: Effective pore number [-]
α: Archies law constant
(in porous media usually between 1.5 and 2.5, here: 1.8, Piepenbrink (1998)) [-]

The mass flux (F) is also described as the diffusing compound mass (m) per time (t) and surface area (A):

$$F = \frac{m}{t \cdot A} \tag{5}$$

m: Diffusing contaminant mass [ng]
t: Time [s]
A: Surface area [cm^2]

Substituting F in equation (4) the integrated pollutant concentration in the surrounding water body (c) can finally be described as:

$$c = \frac{m \cdot x}{t \cdot A \cdot D_{aq} \cdot n_e^{\alpha}} \tag{6}$$

c: Concentration in surrounding water body [µg cm^{-3}]
m: Adsorbed contaminant mass in dosimeter [µg]
x: Thickness of dosimeter wall [cm]
t: Exposure time [s]
A: Membrane surface area [cm^2]
D_e: Effective diffusion coefficient [cm^2 s^{-1}]
n_e: Effective pore number [-]
α: Archies law constant
(in porous media usually between 1.5 and 2.5, here: 1.8, Piepenbrink (1998)) [-]

Above it is assumed that the concentration gradient in the membrane is stable over time. This implies the use of an adequate adsorbent. Due to investigations of Piepenbrink (1998) and (Martin 2000) the chelating ion exchange resin (AMBERLITE™ IRA743, *Rohm and Haas Industrial Processes,* Frankfurt, Germany), shortly referred to as IRA, is chosen as adsorbent in both, the silicone samplers and ceramic dosimeters. The beige-colored beads (Ø 0.5 - 0.7 mm) consist of macroporous polystyrene with a n-methylglucamine group and are specifically designed and used to remove boric acid and borate from water, magnesium brine, or other solutions (Table III-7).

Three ceramic dosimeters and three 3 - 5 cm long silicone samplers (outer diameter 7 mm, inner diameter 5 mm) were installed side by side at each sampling point for a time period of 12 months. The first generation passive samplers were installed in February 2012 at five locations in Chongqing and three locations around Yunyang on fixed swimming vessels. In June 2012, additional samplers of the second generation were installed at the February locations and five more locations were chosen close to the dam.

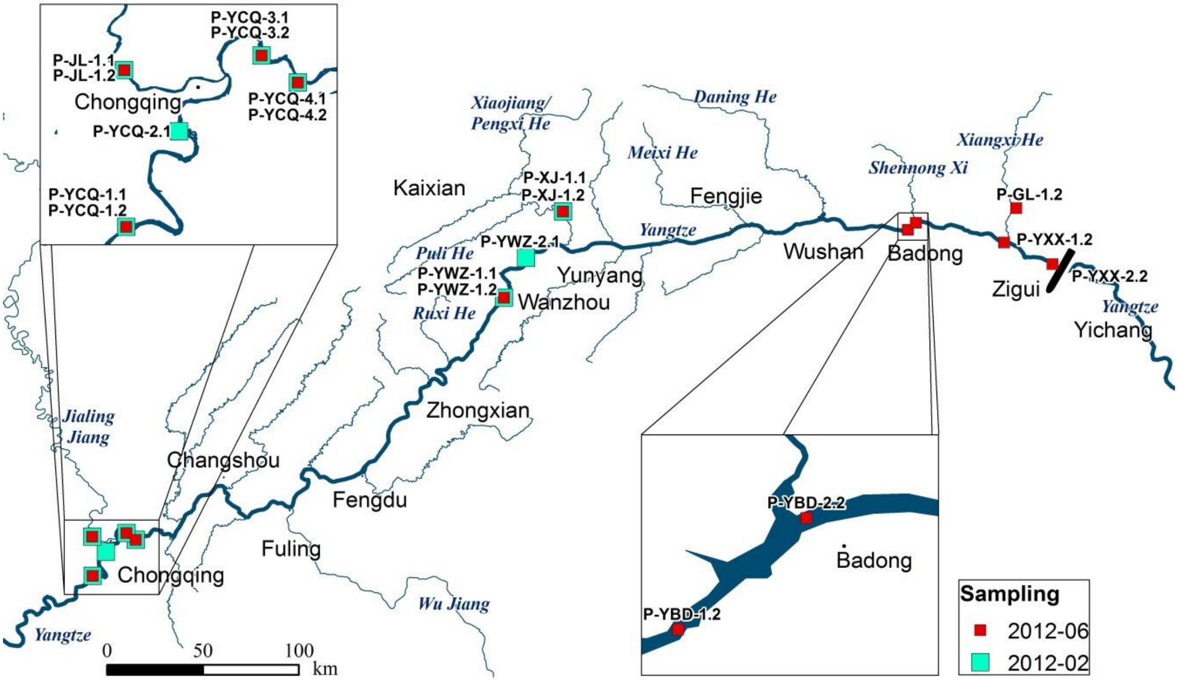


Figure III-9Map of the passive sampler install locations and dates.

4.3 Water Analyses

4.3.1 On-site sample pre-treatment

The on-site parameters in water were measured with a multi parameter probe (Professional Plus, YSI). The sediment samples were filled in aluminum containers (100 mL) and sealed tightly for transport. At each sampling point two glass vials (20 mL, headspace, screw cap, SigmaAldrich) were filled airless for the analysis of VOC. For the analysis of inorganic parameters water was filtered with cellulose acetate filters (pore size 0.45 µm, Ø 28 mm, Sartorius) and filled in two polyethylene vials (50 mL, screw cap, Sarstedt). Then, one vial was acidified with nitric acid (HNO_3) to pH < 2 for the analysis of cations. A Headspace and a Sarstedt vial were also taken for the analysis of isotopes and DOC, respectively. The DOC samples were stabilized with hydrochloric acid (HCl, pH < 2) after filtration with teflon filters (0.45 µm, ca. Ø 30 mm, non-sterile, Hydrophilic PTFE Membrane, Millipore). Additionally, four 1-L narrow-necked glass grinding bottles were filled with pre-filtered (glass fiber filters, Sartorius) water for the analysis of industrial organic compounds, pesticides, pharmaceuticals, and x-ray contrast media. The water, then, was extracted using solid-phase extraction (SPE) columns (Isolute ENV+, 200 mg, 3 mL, Biotage; preconditioned three times with 3 mL ethyl acetate and 5 mL distilled water) and a SPE vacuum device (Mallinkrodt Baker). The water flow rate during extraction was about 1 L h^{-1} and SPE columns were dried in the air stream thereafter. Since some acidic compounds (e.g. carbonic acids) require a low pH value for being extracted from water one 1-L sample was acidified to pH 2 ± 0.2 with hydrochloric acid prior to extraction.

4.3.2 Inorganic substances

The inorganic parameters in water were mainly determined at IWW inorganic laboratory according to European and/or German norms (EN, DIN) Table III-4). Cations were analyzed from the acidified Sarstedt vial after DIN EN ISO 11885 (DIN 2009b) vial by inductively coupled plasma optical emission spectrometry (ICP-OES, Vista Pro, Agilent Technologies) equipped with an auto-sampler SPS3 (Agilent Technologies). An aliquot of the sample was additionally used for the analysis of arsenic by atomic absorption spectroscopy (AAS, AAnalyst 600 with FIAS 400, Perkin Elmer) after DIN EN ISO 11969 (DIN 1996b) and gadolinium by inductively coupled plasma mass spectrometry (Perkin Elmer ELAN DRC II ICP-MS) equipped with an AS90 auto-sampler as described by Cyris (2013). The rare earth element gadolinium can be used as a pseudo-natural tracer for the anthropogenic influence on a water body (Moller et al. 2000). Therefore, the so-called gadolinium anomaly was determined that was defined as the ratio (R_a) of the detected (c_{det}) and the expected (geogenic) normalized molar concentration (c_{exp}) (Bau and Dulski 1996):

$$R_a = \frac{c_{\text{det}}}{c_{\text{exp}}} \tag{7}$$

R_a: Anomaly-ratio of Gd [-]
c_{det}: Detected normalized molar Gd concentration [M]
c_{exp}: Expected normalized molar Gd concentration [M]

For normalization the Post Achaean Australian Shell (PAAS) was chosen as reference material. The expected concentration was derived from an interpolation of normalized concentrations of other rare earth elements as described in detail by Cyris (2013).

The anions were analyzed from the neutral Sarstedt vial by ion chromatography (IC) after DIN EN ISO 10304-1 (DIN 2009a). Therefore, an ion chromatograph DX 500 (Dionex, separation column AS 14, front column AG 14) with GP 40 and conductivity detector CD 20 (Dionex), was used. The dissolved organic carbon (DOC) content in water was detected from CO_2 formation after burning in a Vario TOC select (Elementar Analysensysteme) at Chongqing University. The laboratory of Chongqing University was chosen because of a shorter transport time; hence, the probability for DOC degradation after sampling was minimized. Two DOC analyses were performed at IWW after DIN EN 1484 (DIN 1997a) with a TOC V (Shimadzu) and auto-sampler ASI V. Detection limits of all standard methods were carried out after DIN 32645 (DIN 2008).

Table III-4: **Procedures used for the analysis of inorganic compound groups. The analytical methods were performed mainly according to European and/or German norms (EN, DIN).**

Target group	**Corresponding EN and/or DIN regulation / applied analytical method**
Cations	**DIN EN ISO 11885 (DIN 2009b)** Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)
Arsenic	**DIN EN ISO 11969 (DIN 1996b)** Water quality - Determination of arsenic - Atomic absorption spectrometric method (hydride technique)
Gadolinium	**Cyris (2013)**
Anions	**DIN EN ISO 10304-1 (DIN 2009a)** Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate
DOC	**DIN EN 1484 (DIN 1997a)** Water analysis - Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)

4.3.3 Organic substances

The methods for the analysis of organic compounds in water were carried out in IWW´s organic laboratory according to modified European and/or German norms (Table III-4). For the analysis of industrial organic compounds, pesticides, pharmaceuticals, and x-ray contrast media, the SPE columns (see chapter 4.3.1) were eluted three times with 3 mL of solvent. For each SPE column a different solvent was chosen: (i) acetone for the analysis of PAH, PCB, OCP, and PBDE (ii) ethyl acetate for the analysis of PFC, x-ray contrast media, and polar (acidic) pesticides and pharmaceuticals from the acidified SPE column (pH 2 ±2), (iii) acetonitrile for the analysis of non-polar pesticides, e.g. triazine and phenyl urea pesticides, and (iv) methanol for the analysis of non-polar pharmaceuticals. The extracts were then concentrated to a volume of 200 µL using a Turbo Vap LV Evaporation System from Caliper Life Sciences (T = 40 °C; Hopkinton) in a gentle stream of nitrogen.

Volatile organic compounds were analyzed after DIN 38407-41 (DIN 2011b) directly from the headspace vial by gas chromatography and coupled mass spectrometry (7890A GC System, 5975C Inert XL MSD, Agilent) after headspace solid phase micro-extraction (HS-SPME). The system was connected to a multi-purpose sampler (MPS 2, Gerstel).

The acetone extract was analyzed with an Agilent gas chromatograph (6890 GC) and mass selective detector (5973 MSD, single quadrupole mass analyzer) (DIN 1996a, 2009c, 2011a). Additionally, a multi-purpose sampler (MPS 2, Gerstel) and cooled injection system (CIS 4, Gerstel) were connected to the system. The ethyl acetate extract was first divided in half and afterwards each part concentrated to 200 µL. Then, polar pesticides and pharmaceuticals in one extract were derivatized with diazomethane (DIN 2003). Diazomethane was produced in the reaction of diazald with sodium hydroxide (Figure III-10 (a)). Derivatization means, the molecules hydrophilic hydroxyl groups were substituted by a methyl group (methylization) that makes the compounds non-polar and, therefore, analyzable in the above mentioned Agilent GC-MS system (DIN 2003) (Figure III-10 (b)).

Table III-5 Procedures used for the analysis of organic compound groups. The analytical determinations were carried out according to modified European and/or German norms.

Target group	Corresponding DIN regulation / applied analytical method
VOC	**DIN 38407-41 (DIN 2011b)** Determination of selected easily volatile organic compounds in water - Method using gas chromatography (GC-MS) after headspace solid-phase micro extraction (HS-SPME)
PAH	**DIN 38407-39 (DIN 2011a)** Determination of selected polycyclic aromatic hydrocarbons (PAH) - Method using gas chromatography with mass spectrometric detection (GC-MS)
OCP and PCB	**DIN EN ISO 6468 (DIN 1996a)** Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes - Gas-chromatographic method after liquid-liquid extraction
PBDE	**DIN EN ISO 22032 (DIN 2009c)** Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge - Method using extraction and gas chromatography/mass spectrometry
PFC	**DIN 38407-42 (DIN 2011c)** Determination of selected polyfluorinated compounds (PFC) in water - Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction
Polar (acidic) pharmaceuticals and pesticides	**DIN EN ISO 15913 (DIN 2003)** Determination of selected phenoxyalkanoic herbicides, including bentazones and hydroxybenzonitriles by gas chromatography and mass spectrometry after solid phase extraction and derivatization
Pharmaceuticals and triazine pesticides	**DIN EN ISO 10695 (DIN 2000)** Determination of selected organic nitrogen and phosphorus compounds - Gas chromatographic methods
Phenylurea pesticides	**DIN EN ISO 11369 (DIN 1997b)** Determination of selected plant treatment agents - Method using high performance liquid chromatography with UV detection after solid-liquid extraction
Other pesticides and x-ray contrast media	**E DIN 38407-36 (DIN draft)** Determination of selected plant treatment agents and further organic compounds in water – Method using high performance liquid chromatography and mass spectrometric detection (HPLC-MS/MS) after direct injection

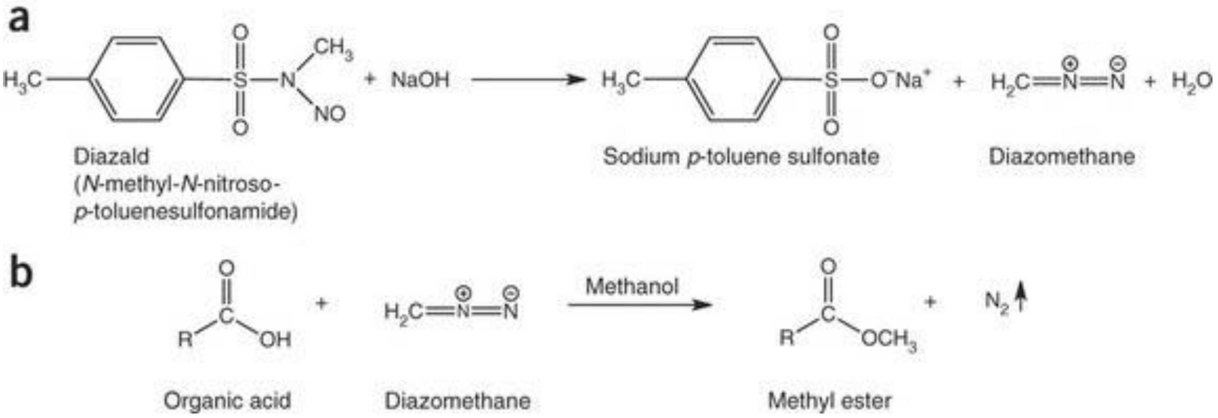


Figure III-10 (a) Formation of diazomethane from Diazald (N-methyl-N-nitroso-p-toluenesulfonamide) in a basic solution. (b) Methylation of an organic acid by diazomethane. Source: Werres and Balsaa (2012)

Perfluorinated compounds were analyzed from the other extract half using ultra performance liquid chromatography and tandem-quadrupol-mass spectrometry (Acquity UPLC-TQD, Waters) coupled with an electrospray ionization tandem mass spectrometric system (Milford) (DIN 2011c). After analysis the extract was dried completely and the residues dissolved in 200 µl methanol. The resulting extract was used for the analysis of x-ray contrast agents using the above mentioned UPLC-TQD method (DIN draft). The same norm was modified for the detection of neutral pesticides with UPLC-TQD from the acetonitrile extract (DIN draft). Phenylurea pesticides, however, were analyzed with UPLC and a coupled photodiode array detector (Aquity PDA detector, Waters) (DIN 1997b). An additional GC-MS

(Agilent) method was used for the detection of triazine pesticides and neutral pharmaceuticals (DIN 2000). Data acquisition, processing, and evaluation were carried out using Agilent ChemStation software combined with Gerstel Maestro software package. The limit of detection (LOD) was defined after DIN 32645 by a signal to noise ratio of 3:1 for all applied methods (DIN 2008). For blanks deionized water was additionally treated in an ultrapure water purification system (Simplicity UV, Millipore).

4.3.4 Sediment and IRA analyses

Sediments and the ion exchange resin IRA were analyzed in the hydrochemical laboratory of the Institute of Applied Geosciences in Darmstadt, Germany (Table III-6). First, the sediment samples were dried with an Alpha 1-4 (Christ) freeze dryer and homogenized for 30 sec in a swing mill (Siebtechnik). Second, the mineral composition was determined in a wavelength dispersive x-ray fluorescence (WD-XRF) spectrometer (S8 Tiger, Bruker). The results were processed with the software Quant Express Best-Detection-34 mm Vac (Bruker). The total organic carbon content (C_{org}), total inorganic carbon (C_{inorg}), and elementary carbon (C_{el}) content were each calculated by observed CO_2 emissions after burning in a three step method (Liqui TOC II 35112013, Elementar Analysensysteme).

Table III-6 : Procedures used for the analysis of sediment and IRA.

Target group	Corresponding analytical method
Mineral composition	**WD-XRF,** Wavelength dispersive x-ray fluorescence spectrometer
TOC, TIC and C_{el}	**LiquiTOC,** Observed CO_2 emission after burning in a three step method
Extraction	**ASE,** Accelerated solvent extraction

For the determination of organic pollutants the freeze-dried samples were extracted in the accelerated solvent extractor ASE 300 (Dionex, method: 100% acetone, 100 °C, 100 bar, 1 cycle, 20 min static, 5 min purge) connected with a Dionex solvent controller. Afterwards the extracts were concentrated to 2 mL in a Dry Vap concentrator system (Horizon Technology). Then, the extracts were filled in vials and sent to IWW´s laboratory for the analysis of highly adsorbable organic compounds, such as PAH, PCB, PBDE, and OCP. Additionally, selected pesticides that had been found frequently in surface water were analyzed. All analyses for organic compounds were performed as described in chapter 4.3.3.

4.4 Ozonation batch experiments

For the ozonation batch experiments pre-filtered (glass fiber filters, Sartorius) TGR surface water, sampled downstream Chongqing in June 2013, was used. In the experiments 250 mL TGR surface water is first spiked with 0.125 µmol (19.57 µg) para-chlorobenzoic acid (pCBA) while the pH value is buffered with borate (10 mM boric acid) and controlled steadily (target value 7.5). Then, the solution is exposed successively to ozone concentrations of 1, 2, 3, 4, and 5 mg L^{-1}. This is done with the aid of an ozone stock solution that was prepared passing a continuous and constant ozone gas stream through a flask containing Millipore water

(Purelab Flex, Elga) cooled in an ice-water bath. The ozone is produced in advance in the ozone-generator COM-AD01 (Anseros). The ozone concentration in the stock solution was determined by wave length (λ_{Oz} = 258 nm) in a two-beam UV/VIS spectrophotometer (UV 1650 PC, Shimadzu). Then, samples of each 10 mL are taken in defined time-intervals (Hoigne and Bader 1975) in which the ozone reaction is stopped quickly due to ozone consumption by 750 µL excessively added indigotrisulfonate (indigo) stock solution (1.25 mM) (Hoigne and Bader 1980) (Figure III-11). This Indigo method was invented by Bader and Hoigné (1981) and is principally based on the bleaching of indigo (absorption coefficient ~20000 $M^{-1}\cdot cm^{-1}$ at λ_{ind} = 600 nm, visible spectrum blue) due to its quick reaction with ozone (k = 9.4E07 $M^{-1}\cdot s^{-1}$) (Munoz and von Sonntag 2000). The intensiveness of bleaching hereby depends on how much ozone is reacting. Thus, a monitoring of indigo in the spectrophotometer can be used to trace back to the residual ozone concentration in the sample.

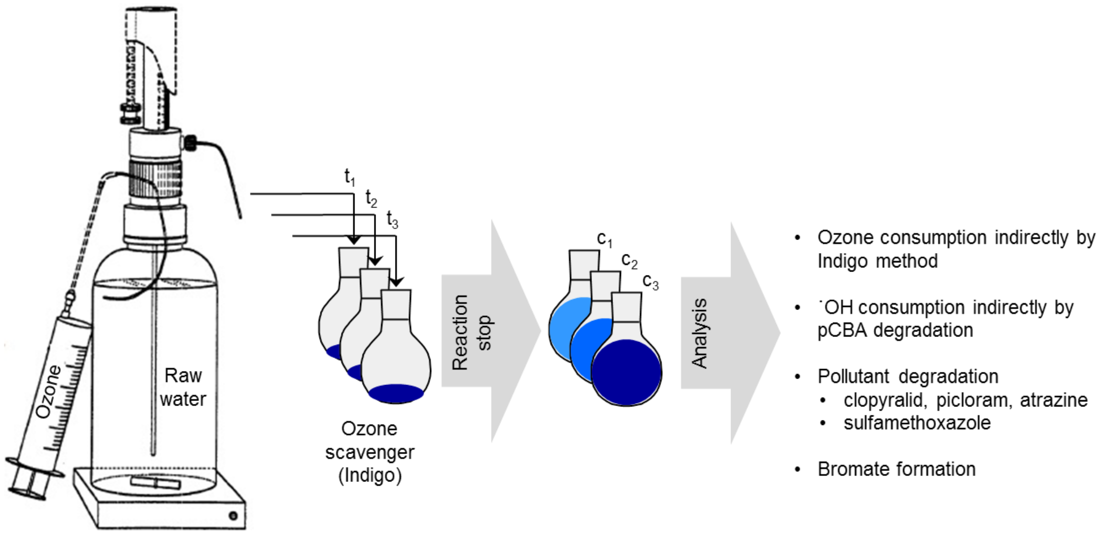


Figure III-11: **Scheme of the oxidation batch experiments with ozone. Modified after Hoigne and Bader (1994)**

The $OH^{\cdot}$ decomposition cannot be measured directly due to the extremely low concentrations below detection limit of formed OH radicals. It is measured by the degradation of pCBA in the sample as pCBA is not degraded by ozone but $OH^{\cdot}$. Analytics for pCBA are performed by high pressure liquid chromatography (LC-20AT prominence, Shimadzu) and mass spectrometry in a UV/UVS detector (SPD-20A prominence, Shimadzu) (HPLC-UV/UVS). It is equipped with an auto sampler (SIL-20A prominence, Shimadzu), a degasser (DGU-20A$_5$ prominence, Shimadzu), and a communications bus module (CBM-20A prominence, Shimadzu). A CTO-10AS VP (Shimadzu) column oven and a ProntoSil column 120-5-C18H (5.0 µm, Dim NC-04 (250 x 4.0 mm), P/N: 2504 F185PS050, S/N: 01021G003, German Engineered Performance, Bischoff Chromatography) is used. The results are analyzed using LabSolutions analytical software (LCsolution Version 1.25 SP4, Shimadzu). Additionally, samples are analyzed for bromate by an ion chromatograph DX 500 (Dionex, separation column AS 14, front column AG 14) with GP 40 and conductivity detector CD 20 (Dionex) after DIN EN ISO 10304-1 (DIN 2009a) in IWW laboratories in Mülheim. Finally, the whole experimental setup is repeated once with filtered (cellulose acetate filter, 0.45 µm, Ø 28 mm, Sartorius) TGR surface water and once with filtered TGR surface water that was spiked with hydrogen peroxide (peroxone, H_2O_2). The amount of added H_2O_2 is determined by the half-stoichiometric amount of added O_3 in a batch experiment and taken from a H_2O_2 stock solution of 50 mM.

4.5 Adsorption batch experiments

The mass distributions between an aqueous phase, here water, and a solid phase in equilibrium is generally described by the partitioning coefficient *(K_d)*, that relates the concentration of a compound in the solid phase *(c_S)* to the concentration of the compound in water *(c_W)* (Figure III-12):

$$K_d = \frac{c_s}{c_w} \tag{8}$$

K_d: Partitioning coefficient [$L^3 M^{-1}$]
c_S: Concentration in the solid phase [$M M^{-1}$]
c_w: Concentration in water [$M L^{-3}$]

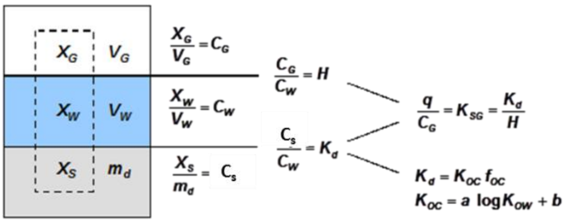
$$c_s = K_d \cdot c_w \tag{9}$$

An adsorption isotherm represents the amount of the sorbate as a function of the sorptive in equilibrium between these phases at a constant temperature. Equations (8) and (9) describe the adsorption as a linear relation of c_S to c_W (Figure III-14). Experimental studies, however, often show deviating results, especially for large concentration ranges. Therefore, Freundlich (1909) developed an empirical isotherm model that fits the data in form of an exponential function determining the *Freundlich* exponent n_{Fr} [-]:

$$c_s = K_{Fr} \cdot {c_w}^{n_{Fr}} \tag{10}$$

K_{Fr}: Freundlich partitioning coefficient [$L^3 M^{-1}$]
c_S: Concentration in the solid phase [$M M^{-1}$]
c_w: Concentration in water [$M L^{-3}$]
n_{Fr}: Freundlich exponent [-]

$$\log c_s = n_{Fr} \cdot \log c_w + \log K_{Fr} \tag{11}$$



X_G; X_W; X_S	Contaminant mass in the gas phase (X_G), water (X_W) and soil (X_S)
V_G; V_W; m_d	Volume of the gas phase (V_G), water (V_W) and mass of soil (m_d)
C_G; C_W; C_s	Contaminant concentration in the gas phase (C_G), water (C_W) and soil (q)
H	Partition coefficient gas phase - water (Henry's constant)
K_d	Partition coefficient soil - water
K_{SG}	Partition coefficient soil - gas phase
K_{OC}	Partition coefficient soil organic carbon - water
K_{OW}	Partition coefficient octanol - water
f_{OC}	Mass of organic carbon in the soil with respect to the total mass of the soil
a; b	Empirical constants

Figure III-12 Partitioning of organic pollutants in gas-, liquid- and solid phases. Modified from Grathwohl (1989).

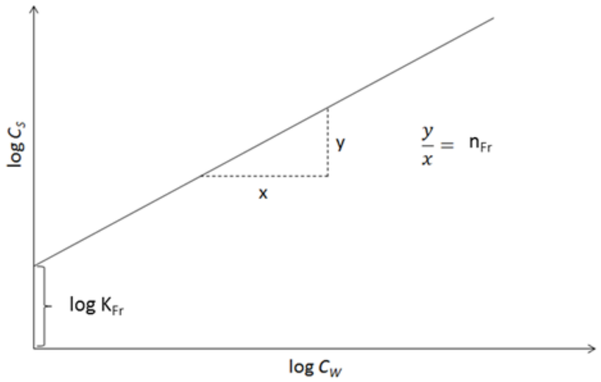


Figure III-13 Freundlich-isotherm plot of $\log C_W$ versus $\log C_S$ with derivation of the Freundlich exponent (n_{Fr}) and the Freundlich correlation coefficient (K_{Fr})

K_{Fr} [-] is the *Freundlich* constant and equals K_d if the exponent n_F is 1 and the isotherm therefore linear. A graph of log c_W versus log c_S would give the *Freundlich* parameters n_{Fr} from the slope and K_{Fr} from the intercept (Figure III-13).

Two types of batch experiments have been executed, those on adsorption isotherms for single compounds and those on adsorption kinetics. The latter are essential for the determination of correlation coefficients since they distinguish the time span, needed for the establishment of equilibrium of a contaminant in a 3-phase-system.

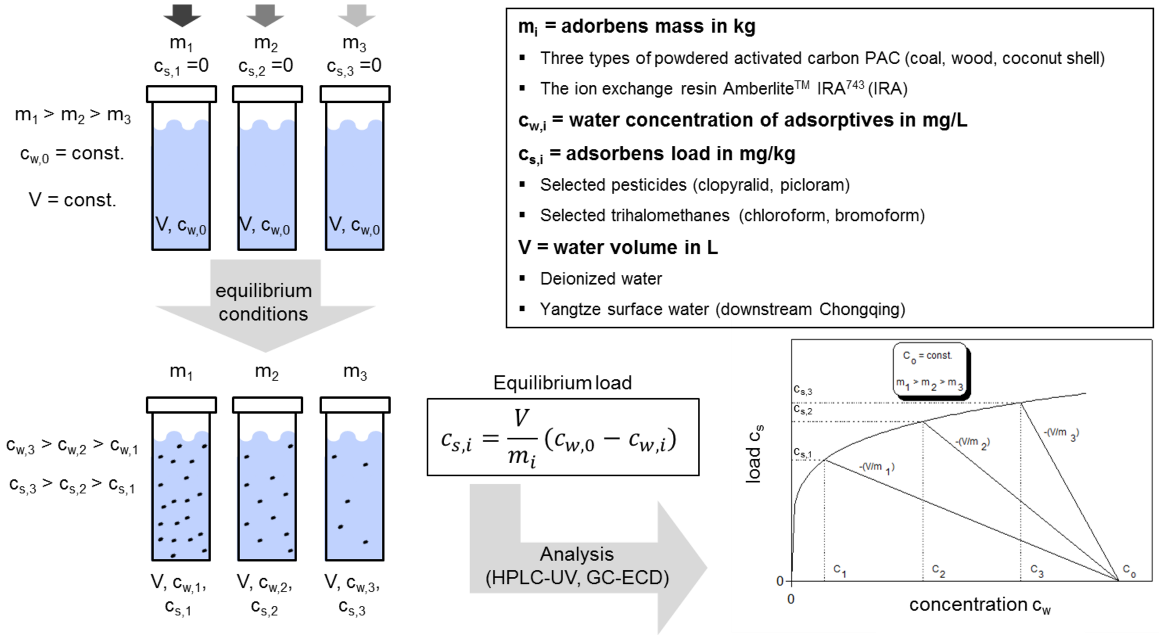


Figure III-14 **Scheme of the batch experiments for the determination of adsorption isotherms.**

For the experimental procedure, multiple samples of a known contaminant concentration are prepared in vials of a constant volume and exposed to different PAC and IRA masses (Figure III-14). Then the vials are shaken for a defined time span and afterwards analyzed. The load on the PAC and IRA can then be determined as shown in Figure III-14. The analytical procedure is different for THM and pesticides. As far as THM kinetic experiments are concerned, the concentration in the gas phase of a single sample is measured multiple times after different time intervals by gas chromatography (GC) combined with an electron-capture detector (ECD) (Agilent). Pesticides are analyzed in double experiments by an UltiMate 3000 HPLC and coupled UV/VIS DAD detector (Thermo Fisher). An Acclaim (OA 5 µ, 4,0 x 250 mm) column and a solvent solution of methanol and water (60 : 40, isocratic) is used for analysis. The results are compiled with the Chromeleon 7.1 software.

The three powdered activated carbons (PACs) investigated in this research were produced and provided by Jacobi Carbons GmbH, Frankfurt am Main, Germany and are all available in China. PACs of different basic raw materials (coal, wood, coconut shell) were selected. The material AMBERLITE™ IRA743 (Rohm and Haas) that here is shortly called IRA is an ion exchange resin specifically designed and used to remove boric acid and borate from water, magnesium brine or other solutions under a variety of conditions. An overview of the physical and chemical properties of the PACs and IRA, taken from the manufacturer's data, is given in Table III-7.

Table III-7 Overview on the physical and chemical properties of the PAC and IRA. Source: Product data sheets.

	AquaSorb BP2	AquaSorb CP1	ColorSorb G9	AMBERLITE™ IRA743
Origin	China	Sri Lanka	China	-
Basis	Bituminous coal	Coconut shell charcoal	Selected grades of wood	Macroporous polystyrene with n-methylglucamine
Physical form	Powder	Powder	Powder	Beige-colored beads
Density	580 kg m^{-3}	510 kg m^{-3}	-	700 kg m^{-3}
pH-value	8 – 10	8 – 11	9 – 11	-
Surface area	-	1050 m^2 g^{-1}	1050 m^2 g^{-1}	-
Pore volume	-	0.62 cm^3 g^{-1}	-	-
Particle size	-	< 0.045 mm (65 – 80 wt%)	< 0.045 mm (65 – 85 wt%)	0.5 – 0.7 mm
Main application	Medium and high molecular weight contaminants; Treatment of municipal drinking water as well as municipal and industrial wastewater	Low molecular weight compounds;Treatment of municipal drinking and wastewater as well as dechlorination and deozonation	Light organic molecules; Purification of organic acids and decolourising of chemicals	Treatment of irrigation water, drinking water, ultra-pure water, and waste

5 Results & discussion

5.1 Monitoring results

5.1.1 Inorganic parameters

The inorganic composition of the TGR surface water reflects its surrounding geology and the weathering of local bedrock (Figure III-15). High concentrations of sodium (4.6 - 68 mg L^{-1}), calcium (30 - 59 mg L^{-1}), chloride (4.6 - 85 mg L^{-1}), and sulfate (23 - 91 mg L^{-1}) refer to the mainly sedimentological background of the TGR area and its catchment. Silicium is found in lower concentrations and might be mainly related to aluminum, iron, and manganese ions forming silicates that are present in the region of the upper part of the reservoir. This water concentration pattern and ratio are carried through all water compartments indicating a drinking water supply from TGR surface water.

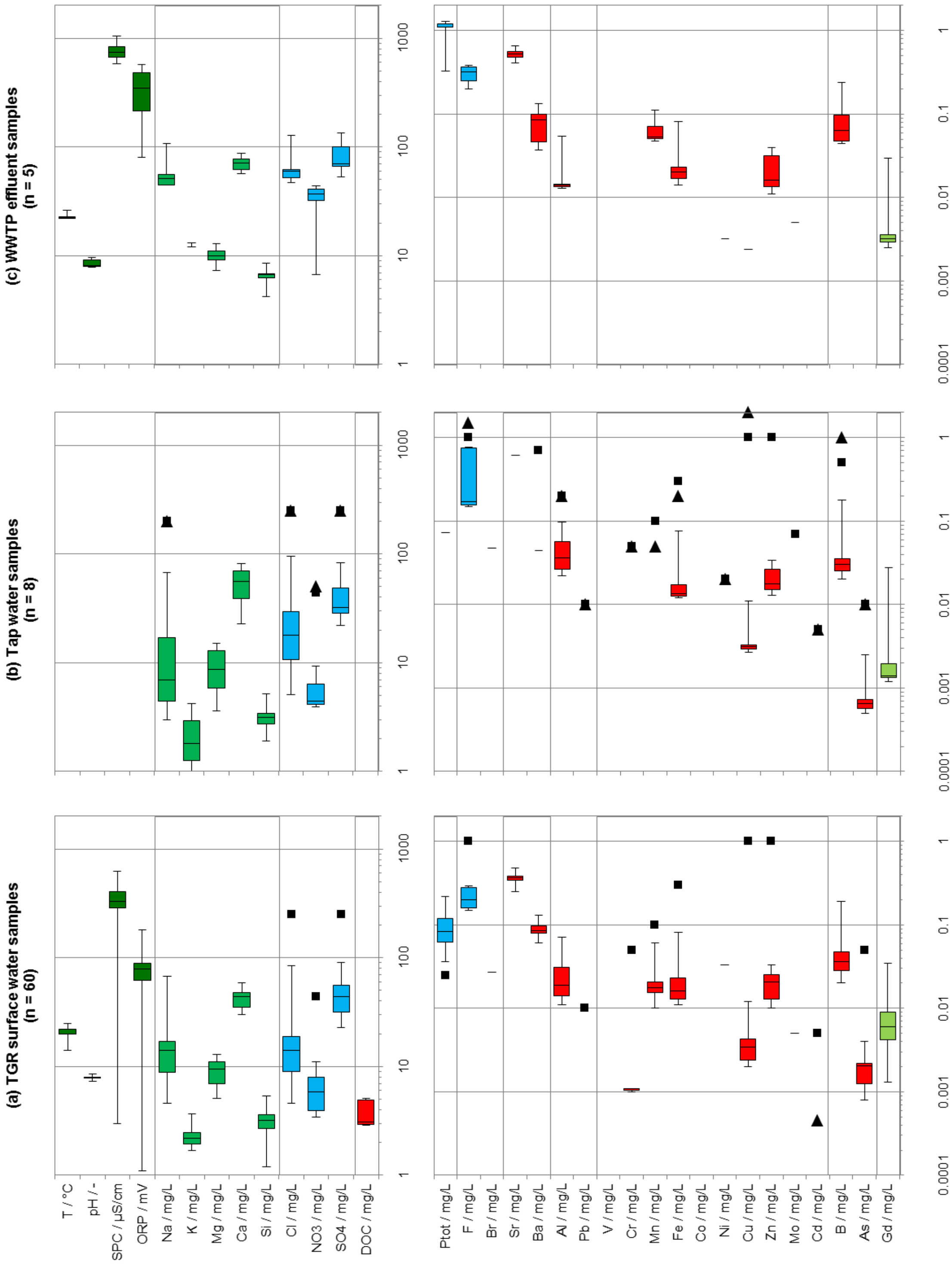


Figure III-15 Results of the on-site measurements and inorganic analyses of (a) surface water, (b) tap water, and (c) WWTP effluent samples and comparison to the Chinese standards (squares) and European directives (triangles) for (a) surface water (Chinese class II plotted) (SAEP 2002; EU 2000, 2008) and (b) drinking water (EU 1998; MoPH 2006).

Nitrate and total phosphorus are also present in surface water at concentrations of 3.4 to 11 mg L^{-1} and 0.036 to 0.22 mg L^{-1}, respectively. They might result from runoff from agricultural areas, untreated wastewater, and WWTP effluents. Additionally, some heavy metals can be found in surface water, tap water, and WWTP effluents in similar concentrations. This also supports the expectation that surface water is the main source for drinking water production in the TGR. Arsenic was also found in surface and tap water.

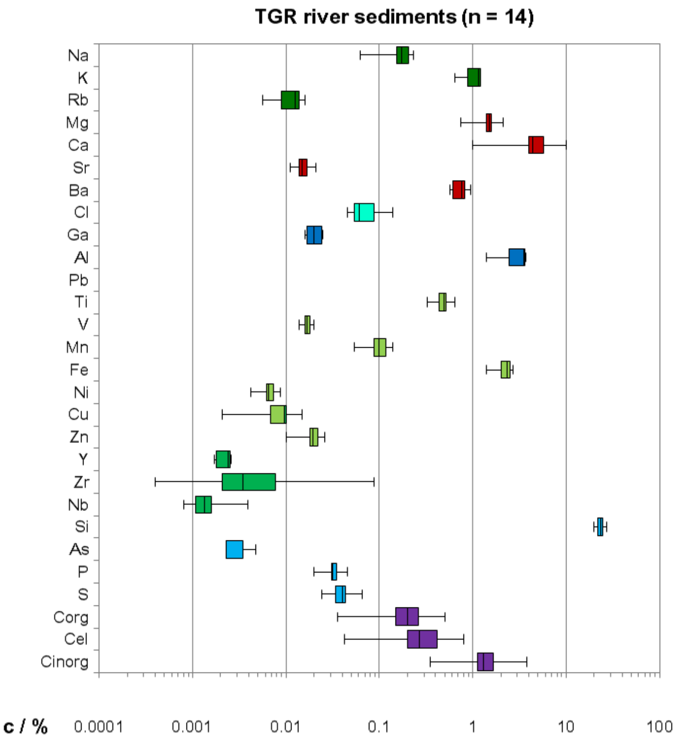


Figure III-16 **Results of the inorganic analyses of the TGR river sediments.**

The composition of the TGR surface sediments shows a similar pattern of inorganic compounds to the TGR surface water (Figure III-16). Due to the relatively high percentages of silicium, calcium, aluminum, iron, and manganese, silicates are assumed to build the major part of the sediments. The other part is built by evaporates, such as carbonates, dolomites, gypsum, and halides. The fraction of organic carbon, which includes organic carbon (C_{org}) and elementary carbon (C_{el}), in the samples is low with < 1%.

5.1.2 Pesticides

Ten out of 103 analyzed pesticides were found in surface waters (Figure III-17 (a)). Most frequently, clopyralid and picloram were detected with 45 positives for each, in a total of 60 samples from different campaigns. The highest concentrations with 3.5 µg L^{-1} and 2.1 µg L^{-1} for clopyralid and picloram, respectively, were detected in samples from the tributary Jialing. The pesticides belong to the family of pyridine herbicides and are of similar structure (Abramovic et al. 2007). They are commonly used in conjunction, explaining their concurrent appearance. The high detection frequency (DF = number of positive detections n^{-1}) and concentrations might indicate that they are applied on a regular basis in the area of the TGR. Also, the pesticides atrazine (DF: 22%, 0.020 - 0.060 µg L^{-1}), fluroxypyr (DF: 10%, 0.060 - 0.20 µg L^{-1}), fenuron (DF: 5.2%, 0.22 – 5.7 µg L^{-1}), and triclopyr (DF: 3.5%, 0.25 - 0.29 µg L^{-1}) were detected in surface water samples from the reservoir (Figure III-17 (a)).

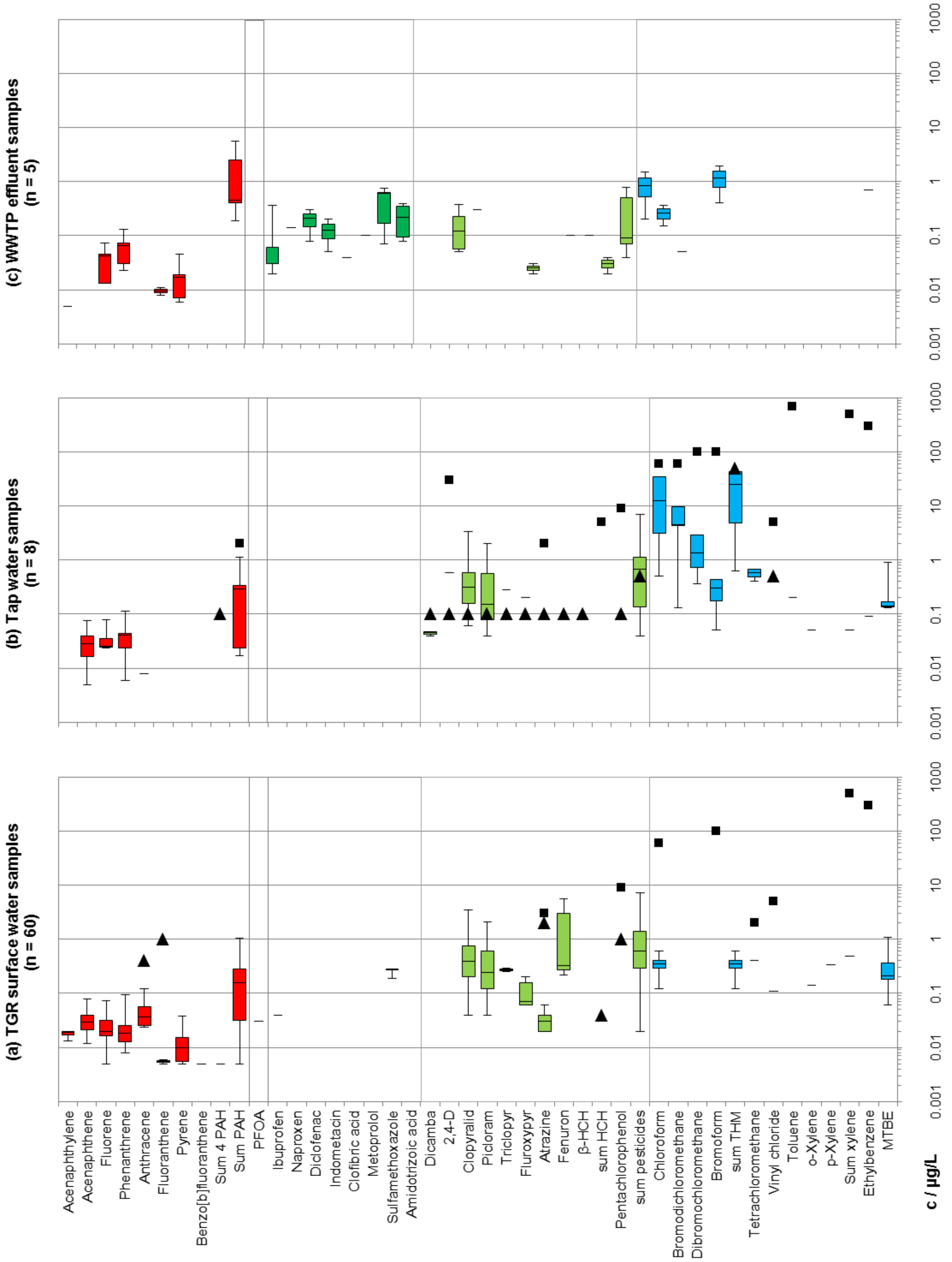


Figure III-17 Results of the organic analyses of (a) surface water, (b) tap water, and (c) WWTP effluent samples and comparison to the Chinese standards (squares) and European directives (triangles) for (a) surface water (SAEP 2002; EU 2000, 2008) and (b) drinking water (EU 1998; MoPH 2006).

In a comparable study downstream of the TGD, the pesticides picloram, triclopyr, and atrazine were below LOD, i.e. 1.0 µg L^{-1}, 0.50 µg L^{-1}, and 0.50 µg L^{-1}, respectively (Müller et al. 2008). In tap water, the two pesticides clopyralid and picloram were detected in five out of seven samples with concentrations of 0.060 - 4.0 µg L^{-1} and 0.040 - 2.4 µg L^{-1}, respectively (Figure III-17 (b)). Chongqing tap water concentrations are comparable to those found in surface water from the adjacent Jialing River, indicating its water supply for drinking water production for at least one part of the city. Further, the results show that local water treatment technologies are insufficient to remove the herbicides, i.e. compounds with high water solubilities (7,850 mg L^{-1} and 430 mg L^{-1} for clopyralid and picloram, respectively). Additionally, each of the pesticides 2,4-D (0.59 µg L^{-1}), triclopyr (0.28 µg L^{-1}), fluroxypyr (0.20 µg L^{-1}), and dicamba (0.045 µg L^{-1}) were detected in one of six samples. Some residual pesticides (clopyralid, picloram, atrazine, beta-HCH, and pentachlorophenol) were also detected in effluents of WWTPs in concentrations with a range of 0.020 – 0.38 µg L^{-1}. In sediments from the river bank and close to WWTP effluents, however, the analyzed pesticides were completely absent (Figure III-18 (a,b)). This might be due to their relatively low K_{OW} values and high water solubilities (Figure III-6, right).

5.1.3 VOC

Eleven out of 30 analyzed VOC were detected in the three water sources (surface water, tap water, and WWTP effluent) in the TGR, amongst these demonstratively the trihalomethanes (chloroform, bromoform, dibromochloromethane, and bromodichloromethane) in tap water (Figure III-17 (b)). They are frequently found as disinfection by-products, mainly due to the reaction of the disinfection agent chlorine with natural organic matter in the raw water (Rook 1977, 1974). The by-product with highest concentrations (0.50 µg L^{-1} - 79 µg L^{-1}) was chloroform. Similar concentrations were detected, e.g. in tap water from three sites in the United States (< LOD - 85 µg L^{-1}) (Rivera-Nunez et al. 2012) and from three Romanian cities (9.0 – 78 µg L^{-1}) (Thach et al. 2012). In Germany, however, chloroform concentrations in drinking water, in general, are low due to a comparatively low application of chlorine. Samples from WWTP effluents in the TGR area contain bromodichloromethane, dibromochloromethane, and chloroform in low concentrations of 0.050 – 1.5 µg L^{-1} (Figure III-17 (c)). In surface water chloroform could be detected in ten out of 58 samples with a maximum concentration of 0.61 µg L^{-1} but no other chlorination by-products were found (Figure III-17 (a)). An explanation might be the intense chlorination in drinking and wastewater treatment and deductive presence in all water sources. Disinfection by-products, however, may appear, as well, due to atmospheric deposition, release by vegetation, or production directly in the soil (Laturnus et al. 2002). Downstream of the TGD chloroform was also found in the Yangtze River surface water with concentrations ranging between 0.60 and 1.3 µg L^{-1} while other trihalomethanes were also below the LOD (Müller et al. 2008). Specific for the surface water, additionally, was the occurrence of methyl-tert-butyl-ether (MTBE), a gasoline additive (Figure III-17) ((a)). While some other VOC were detected in just one out of 60 samples, MTBE was detected in 18 samples. Samples from the tributary Daning reached concentrations of up to 1.1 µg L^{-1}. MTBE replaced lead as fuel oxygenate and consumption in China is still increasing (Global Industry Analysts 2011). However, due to concerns related to the detection of MTBE in groundwater, lakes, and reservoirs worldwide (Squillace et al. 1996; Reuter et al. 1998; van Wezel et al. 2009), other additives, such as ethanol or tert-amyl methyl ether (TAME), are recently favored, especially in the USA. Other detected VOC in surface and tap water were tetrachloromethane, vinyl chloride, xylene, ethylbenzene and toluene. Due to their high Henry´s law constants and low K_{OW} values VOC were not analyzed in sediments (Figure III-6, right).

5.1.4 Pharmaceuticals and x-ray contrast media

Eight out of 25 analyzed pharmaceuticals and contrast agents were detected (Figure III-17 (a,b,c)). They dominate in samples from WWTP effluents. The antibiotic sulfamethoxazole (0.070 - 0.76 µg L^{-1}) and the analgesic ibuprofen (0.020 – 0.37 µg L^{-1}) were found in all five WWTP effluent samples. Other analgesics, diclofenac, indometacin, and naproxen, were less frequent ranging from 0.050 to 0.30 µg L^{-1}. In four out of five effluent samples, amidotrizoic acid was detected in concentrations from 0.080 to 0.39 µg L^{-1}. It is the only x-ray contrast medium found in the samples. The agonist metabolite clofibric acid and the beta blocker metoprolol were found in the sample from Fengdu. In a study for the German Federal Environment Agency, Bergmann et al. (2011) collocated European monitoring data on environmental concentrations of x-ray contrast media, pharmaceuticals, and their metabolites in various environmental matrices with a special focus on Germany. They report the appearance of 274 compounds, of which 156 could be detected in samples from Germany. Due to their results the median concentrations for sulfamethoxazole (0.12 µg L^{-1}), indometacin (0.029 µg L^{-1}), and naproxen (0.071 µg L^{-1}) are lower in German WWTP effluents compared to the TGR while the concentrations for ibuprofen (0.094 µg L^{-1}), diclofenac (1.5 µg L^{-1}), and metoprolol (0.65 µg L^{-1}) are higher (German Federal Committee for Chemical Safety BLAC (2003) cited in Bergmann et al. (2011)).

While tap water was free of pharmaceuticals two pharmaceutical compounds were found in surface water (Figure III-17 (a,b)). The analgesic ibuprofen was detected with a concentration of 0.040 µg L^{-1} in a sample taken from Jialing tributary close to Chongqing while sulfamethoxazole (0.19 – 0.28 µg L^{-1}) was found in surface water samples from Wushan bay taken in April. A grab sample of a WWTP effluent in Wushan additionally contained ibuprofen, diclofenac, indometacin, amidotrizoic acid, and sulfamethoxazole (Figure III-17 (c)). Holbach et al. (2012a) and Holbach et al. (2012b) published the results of a hydrological model of the TGR with special focus on Wushan bay. The model predicts circulating currents in the bay with inhibited access to the Yangtze main stream. Additionally, the effluent of the sampled WWTP in Wushan was modeled and found to enter Wushan bay, indicating this as a potential pathway for the occurrence of pharmaceuticals in Wushan surface water. In the samples randomly taken from the bay, however, only sulfamethoxazole was detected. This might be related to its lower adsorption onto suspended particulate matter, as it has a higher water solubility and a lower K_{OW} value compared to the other pharmaceuticals found in the WWTP effluent (Bergmann et al. 2011). In German surface water, ibuprofen, diclofenac, indometacin, and sulfamethoxazole are found in mean concentrations ranging from 0.013 to 0.38 µg L^{-1}, which are concentrations comparable to TGR surface water but higher frequency than in TGR surface water (German Federal Committee for Chemical Safety BLAC (2003) cited in Bergmann et al. (2011)).

5.1.5 Industrial organic compounds

The group of industrial organic compounds includes the substance groups of PAH (n = 16), PCB (n = 21), PBDE (n = 8), and PFC (n = 10). The PAH naphthalene, however, had to be excluded from the list due to a high background in blank samples. PAH were detected in several surface water samples (DF: 3.4 - 42%) with concentrations in general below 0.12 µg L^{-1} (Figure III-17 (a)). Other studies at the TGR detected PAH in surface water in the same range or lower (Müller et al. 2008; Cui et al. 2009; Wang et al. 2009). PAH were also present in tap water and WWTP effluent samples ranging from 0.005 to 0.050 µg L^{-1} (Figure III-17 (b,c)). There are numerous potential sources for the occurrence of PAH as they are formed during any incomplete combustion process. PAH are one of the best studied organic substance groups and are found to be ubiquitously distributed all over the world (Hites et al. 1977; Richter and Howard 2000). In the TGR surface water, 3- and 4-ring PAH were both detected frequently, while the poorly-soluble 5- and 6-ring members were in general absent (Figure III-17 (a)). Due to their physico-chemical properties, the high molecular weight compounds have a high tendency for adsorption onto suspended particulate matter and sediments (Figure III-6, right). Although, the Yangtze River sediment contains very low organic (C_{org}) and elementary carbon (C_{el}) of less than 1% (Figure III-16 (a)), high molecular PAH can be detected in the sediment in mean concentrations of about 1.9 – 89 µg kg^{-1} (Figure III-18). Generally, no PFC, PCB, and PBDE were found in water samples of this study while Wang et al. (2009) were able to detect them in concentrations below the LOD of this study (i.e. 0.01 µg L^{-1}). The TGR sediments were analyzed for PBC and PBDE while just 5 PCB (PCB: 28, 52, 101, 118, 153, 180) could be detected. Those, however, were found frequently in mean concentrations of about 1.2 – 16 µg kg^{-1}.

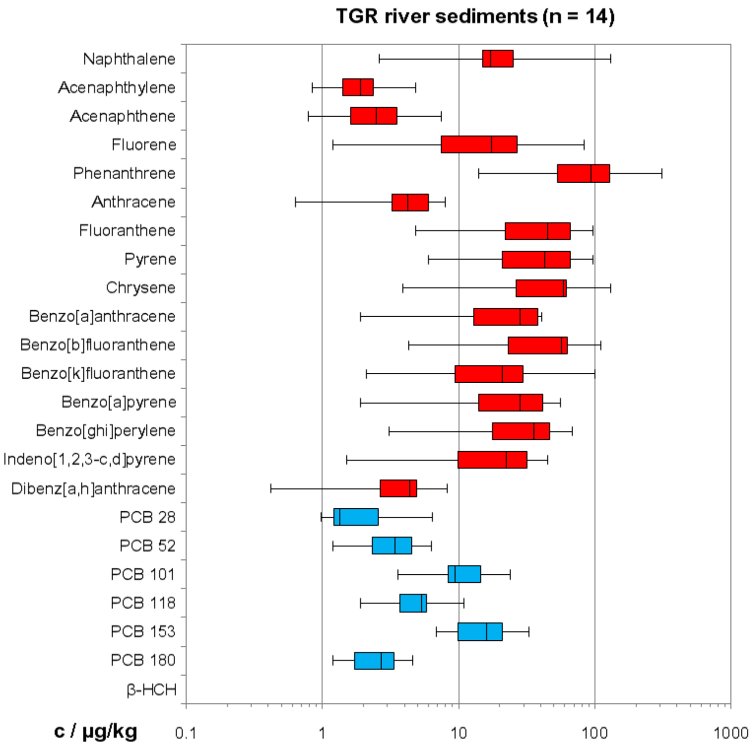


Figure III-18 Results of the organic analyses of the TGR river sediments.

Comparing the PAH concentrations from surface water samples with the surface water concentrations calculated with the results from the ceramic passive samplers (one year exposure time), huge differences are found (see chapter 4.2 and

Figure III-19 (b)). The water samples show 5.7 – 26 times higher PAH concentrations than the passive samplers. This might be related to the extremely slow uptake of the ceramic dosimeters that probably requires exposure times of more than one year. The silicone samplers, however, show a much better uptake of PAH (2.1 – 9.9 times higher) Figure III-19 ((a))

Overall, in the three sampled water sources typical contaminant patterns were found, i.e. pesticides and PAH in surface water, disinfection by-products in tap water, and pharmaceuticals in WWTP effluents (Figure III-17). However, there are some exceptions.

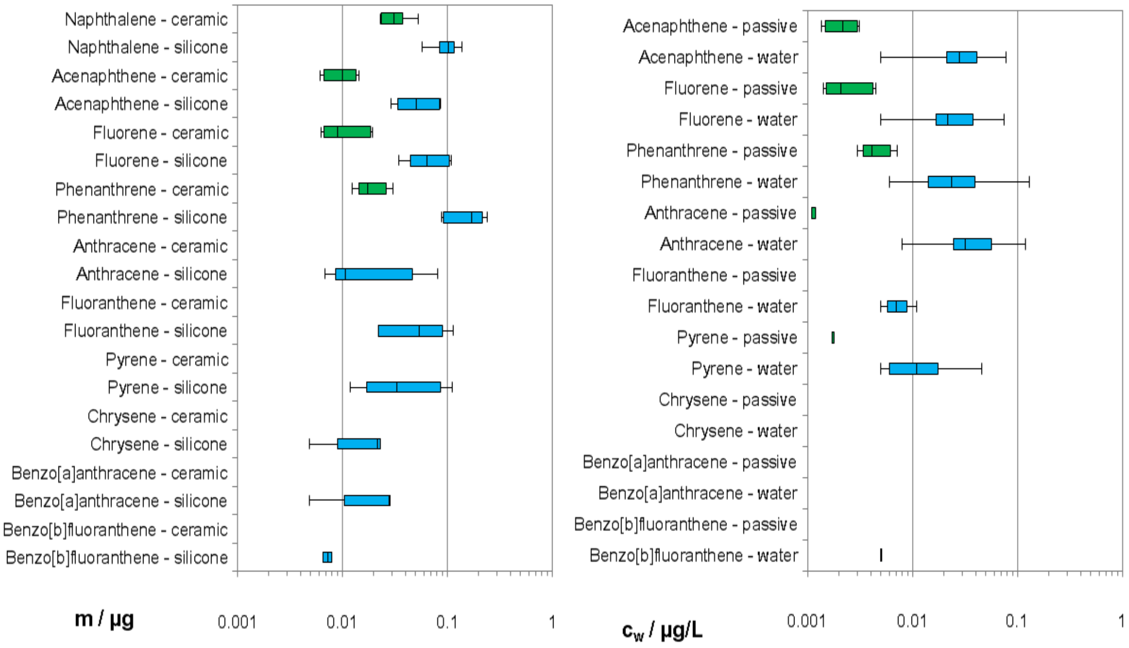


Figure III-19 Comparison of the results of the organic analyses of (a) the silicone and ceramic passive samplers and (b) the ceramic passive samplers and the surface water samples.

The occurrence of PAH and pesticides in tap water might be a relic from surface water contamination due to a scarce elimination in drinking water treatment (Gao et al. 2007; Luo et al. 2011). Residual concentrations of pesticides in WWTP effluents, in contrast, might be related to high precipitation during the sampling in June 2012, resulting in contaminated surface runoff and subsequent overflow of the WWTPs. PAH concentrations in WWTP effluents, however, may enter the WWTP effluents through various pathways, e.g. atmospheric or particle bonded deposition, precipitation, wastewater, and runoff, due to their ubiquitous distribution.

5.1.6 Evaluation due to given standards and directives

A comparison of the data with limit values in standards and directives is questionable since only random grab samples at four not necessarily representative sampling campaigns were taken. However, it still provides an indication on the water quality at the TGR.

Surface water samples achieve insofar as existent all limit values given by the Chinese Environmental Quality Standard for Surface Water (black squares in Figure III-17 (a), SAEP

(2002)) and the EU Directive on environmental quality standards in the field of water policy (black triangles in Figure III-17 (a), EU (2008)). Tap water samples, however, are different and exceed the limit values given by the Chinese Drinking Water Standard (black squares in Figure III-17 (b), MoPH (2006)) and the EU Drinking Water Directive (black triangles in Figure III-17 (b), EU (1998)). The Chinese Drinking Water Standard for chloroform of 60 µg L^{-1} is exceeded in the tap water sample from Wanzhou. Here a concentration of 79 µg L^{-1} was detected. Due to the high chloroform concentration, the limit value for the sum of trihalomethanes (THM) of the EU Drinking Water Directive of 50 µg L^{-1} is also exceeded in one tap water sample. Detections of pesticides in tap water are even worse in exceeding the EU limit values. Here, the directive specifies a limit value for single pesticides (0.1 µg L^{-1}) and one for the sum of pesticides (0.5 µg L^{-1}) and both are exceeded. Especially the aforementioned herbicides clopyralid and picloram, which were detected in median concentrations of 0.37 and 0.32 µg L^{-1}, can be blamed for this transgression. The limits for single compounds are exceeded 3 - 4 times and the limit for the sum of pesticides for 30%.

5.1.7 Ecotoxicological risk assessment

In this chapter the risk potential of the aforementioned detected substances in water will be evaluated. Risk potential hereby means the risk that appears if organisms are exposed to toxic substances due to contact with contaminated water. In ecotoxicology the risk (R) is calculated by dividing the measured environmental concentration (MEC) by the predicted no effect concentration (PNEC):

$$R = \frac{MEC}{PNEC} \tag{12}$$

R: Ecotoxicological risk [-]
MEC: Measured environmental concentration [µg L^{-1}]
PNEC: Predicted no effect concentration [µg L^{-1}]

If R then is below 1 usually there is no risk while for values above 1 there is a potential risk. The needed MEC value can be easily taken from the maximum detected concentrations for each detected compound in surface water, tap water, and WWTP effluents, respectively, while the PNEC value is usually assessed from ecotoxicological studies due to the Technical Guidance Document (TGD) on Risk Assessment from the European Commission (EC 2003). It is defined as the maximum concentration of a compound with effect on organisms in an aquatic ecosystem. Thus, there is to find the lowest concentration of each substance that was investigated in existing ecotoxicological studies to have effect on aquatic organisms. In this study PNEC values were taken directly from the newly existing ecotoxicological Aquatic Impact Indicators Database (AiiDA) version 3.0 of Jerome Payet (AiiDA 2014). This global database groups together the 8 most important ecotoxicity databases (OPP, Fathead, Aquire, ECHA, CERC-USGS, EAT, OECD, IUCLID) and automatically calculates different ecotoxicological endpoints.

Table III-8 List of the PNEC values (EC 2003; AiiDA 2014) and calculated ecotoxicological risk (R) (EC 2003) for median and maximum concentrations in surface water (n = 60), tap water (n = 8), and WWTP effluents (n = 5).

x		PNEC	Surface water	Tap water	WWTP effluents
Substance	**Substance group**	**µg L^{-1}**	**R_{max} / -**	**R_{max} / -**	**R_{max} / -**
Acenaphthylene	PAH	n.a.	n.a.	n.a.	n.a.
Acenaphthene	PAH	1	0.078	0.05	n.d.
Fluorene	PAH	1	0.073	0.046	0.074
Phenanthrene	PAH	0.00002	**4800**	**2300**	**6500**
Anthracene	PAH	0.2	0.6	0.04	n.d.
Fluoranthene	PAH	0.06	0.1	n.d.	0.18
Pyrene	PAH	0.12	0.32	n.d.	0.38
Benzo[b]fluoranthene	PAH	0.054	0.093	n.d.	n.d.
PFOA	PFC	n.a.	n.a.	n.a.	n.a.
Ibuprofen	Analgesic	0.001	**40**	n.d.	**370**
Naproxen	Analgesic	0.32	n.d.	n.d.	0.44
Diclofenac	Analgesic	0.5	n.d.	n.d.	0.6
Indometacin	Analgesic	100	n.d.	n.d.	0.002
Clofibric acid	Agonist metabolite	2.5	n.d.	n.d.	0.016
Metoprolol	Betablocker	n.a.	n.a.	n.a.	n.a.
Sulfamethoxazole	Sulfonamide antibiotic	0.013	**21**	n.d.	**58**
Amidotrizoic acid	X-ray contr. medium	n.a.	n.a.	n.a.	n.a.
Dicamba	Aromatic acid herb.	n.a.	n.a.	n.a.	n.a.
2,4-D	Phenoxy herbicide	n.a.	n.a.	n.a.	n.a.
Clopyralid	Pyridine herbicide	69	0.051	0.058	0.0055
Picloram	Pyridine herbicide	70	0.03	0.034	0.0043
Triclopyr	Pyridine herbicide	0.91	0.32	0.31	n.d.
Fluroxypyr	Pyridine herbicide	18	0.011	0.011	n.d.
Atrazine	Triazine herbicide	0.000011	**5500**	n.d.	**2700**
Fenuron	Urea herbicide	7	0.81	n.d.	n.d.
β-HCH	Organochlorine	0.32	n.d.	n.d.	0.31
Pentachlorophenol	Organochlorine	0.4	n.d.	n.d.	0.1
Chloroform	Trihalomethane	15	0.04	**5.2**	0.099
Bromodichloromethane	Trihalomethane	24	n.d.	0.46	0.015
Dibromochloromethane	Trihalomethane	10	n.d.	0.58	0.0048
Bromoform	Trihalomethane	170	n.d.	0.0032	n.d.
Tetrachloromethane	Halogen. hydrocarbon	1.4	0.28	0.54	n.d.
Vinyl chloride	Halogen. hydrocarbon	240	0.00046	n.d.	n.d.
Toluene	Arom. hydrocarbon	680	n.d.	0.00029	n.d.
o-Xylene	Arom. hydrocarbon	250	0.00056	0.0002	n.d.
p-Xylene	Arom. hydrocarbon	250	0.0014	n.d.	n.d.
Ethylbenzene	Arom.hydrocarbon	100	n.d.	0.0009	n.d.
MTBE	Oxygenate gasoline add.	520	0.0021	0.00038	0.0013

The results in Table III-8 show mainly ecotoxicological risk potentials in the TGR surface water, tap water, WWTP effluents below 1, i.e. no risk. However, there are some exceptions that often result from very low PNEC values. The first is the 3-ring PAH phenanthrene with maximum risk potentials of 4800, 2300, and 6500 for surface water, tap water, and WWTP effluents, respectively, while there is no risk of other PAH in the TGR area. Due to low PNEC values the pharmaceuticals ibuprofen and sulfamethoxazole also are supposed to pose a potential risk in surface water and WWTP effluents of up to 370 and 58, respectively. Within the pesticides, it is the triazine herbicide atrazine that shows a huge risk potential of 5500 and 2700 in surface water and WWTP effluents, respectively. Clopyralid and picloram, however, have relatively high PNEC values of about 70 µg L^{-1} that are able to buffer the high detected concentrations with respect to risk assessment. They are measured in high concentrations but have just a low ecotoxicological risk of 0.0043 – 0.058 in all three water sources. Chloroform in tap water that exceeds the Chinese and European drinking water limit values also shows a potential but low risk of maximum 5.2 in Wushan tap water.

5.2 Ozonation batch experiments

The reactions of ozone in water depend strongly on the type and composition of the water matrix and have to be determined experimentally. In that regard, ozone depletion and intrinsic formation of hydroxyl radicals (˙OH), which act as powerfull secondary oxidants, are the key factors to assess the efficiency of the ozonation process. With these data at hand, one can predict the degradation of pollutants if their reaction rates towards ozone and ˙OH are known (cf. compilation of rate constants in von Gunten (2003a), and von Sonntag and von Gunten (2012)).

5.2.1 TGR surface water kinetics

There are various methods for the determination of ozone depletion, ˙OH formation, and reaction rates in experimental studies. In this study, ozone was determined by a colorimetric method (*Indigo Method*, Bader and Hoigne (1981), see chapter 4.4). The formation of ˙OH, available for pollutant degradation, was determined by monitoring the degradation of the ozone refractory compound para-chlorobenzoic acid (pCBA). Its reaction with ˙OH, however, is quick with a reaction rate constant (*k*) of 5.0 10^9 $M^{-1}\cdot s^{-1}$ (further details can be obtained from von Gunten (2003a)). Besides the oxidation efficiency, by-product formation must also be carefully assessed. A major drawback in ozonation is the formation of bromate, a potential cancerogen, that is limited to an allowed maximum of 10 µg L^{-1} in drinking water by both the *EU Drinking Water Directive* (98/83/EC) and *Chinese Drinking Water Standard* (GB 5749-2006) (EU 1998; MoPH 2006). One option to control the bromate formation is the addition of hydrogen peroxide (H_2O_2, peroxone process). This also increases the rate of ˙OH formation allowing to minizie the hydraulic retention time of ozone reactors.

Figure III-20 (left) gives the pCBA degradation versus the applied ozone dose for TGR surface water that was either unfiltered (◊), filtered (□), or filtered and exposed to peroxone (Δ). It is shown, that an ozone dose of both 1 and 2 mg L^{-1} leads to an incomplete degradation of ozone refractory pollutants, such as pCBA. However, it should be noted, that the TGR surface water sample, used for all experiments, was pre-filtered in field with glass-fiber filters to enable a storage over several weeks. The overall degradation capacity by ˙OH of the peroxone process resembles the conventional ozonation, however, the rate of ˙OH is increased (accelerated pCBA degradation).

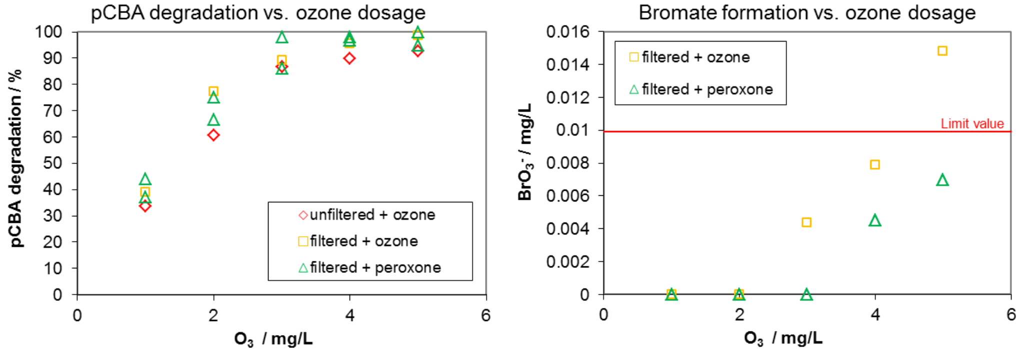


Figure III-20 Degradation of para-chlorobenzoic acid (pBCA) (left) and bromate formation (right) after applying 1 - 5 mg L^{-1} of ozone on either unfiltered (◊), filtered (□), or filtered and exposed to peroxone (O3+ H2O2, Δ) TGR surface water. The red line (right plot) gives the limit value of 10 µg L^{-1} for the concentration of carcinogenic bromate by the *EU Drinking Water Directive* (98/83/EC) and *Chinese Drinking Water Quality Standard* (GB 5749-2006) (EU 1998; MoPH 2006). The raw water basic parameters were determined as pH 7.9, hydrogen carbonate 2.3 mmol L^{-1}, DOC 3.3 mg L^{-1}, bromide 0.027 mg L^{-1}.

The plot in Figure III-20 (right) gives the formation of bromate due to the application of ozone on TGR surface water. Bromate formation depends on the composition of the water matrix, such as the pH-value, the concentration of bromide and bicarbonate/carbonate, and the kind and concentration of DOC. Due to the carcinogenicity and subsequent limitation to a maximum allowed concentration of 10 µg L^{-1} in drinking water (see above), bromate can be seen as a disqualifier for ozone use. This limit value is exceeded if an ozone dose of 5 mg L^{-1} is applied on filtered TGR surface water. The bromate formation, however, appears at lower concentrations in the peroxone process (Figure III-20, right). This is due to the fact, that H_2O_2 reduces one of the intermediates in the reaction mechanism of bromate formation (von Gunten 2003b).

Figure III-21 and Figure III-22 illustrate the ozone depletion and pCBA degradation, respectively, over time with applied ozone doses of 1, 3, and 5 mg L^{-1}. The plots show that filtered and unfiltered TGR surface water show comparable depletion curves while the addition of H_2O_2 reduces highly the oxidation strength.

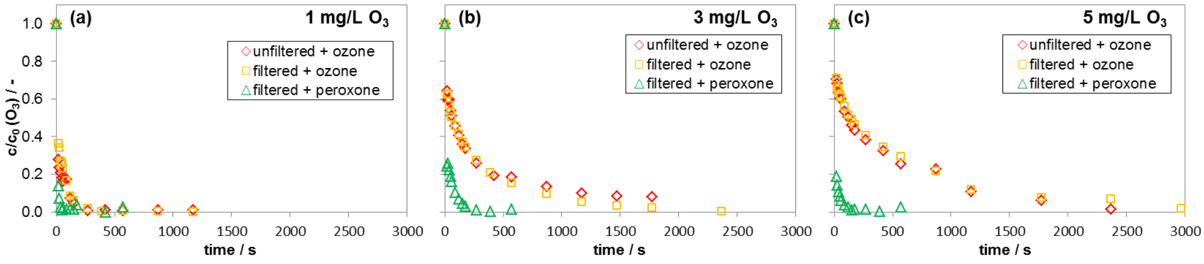


Figure III-21 Ozone depletion over time after applying 1, 3, and 5 mg L^{-1} of ozone in (a), (b), and (c), respectively, on either unfiltered (◊), filtered (□), or filtered and exposed to peroxone (O_3+ H_2O_2, Δ) TGR surface water.

The results indicate that the application of an ozone dose of 3 mg L^{-1} may lead to a degradation of > 90% of recalcitrant pollutants, while in case of a peroxone process no bromate is formed. The formation of bromate in conventional ozonation, however, is also still below the drinking water standards (see above) but little fluctuations in bromide concentration may lead to an exceedance of the bromate drinking water limit values.

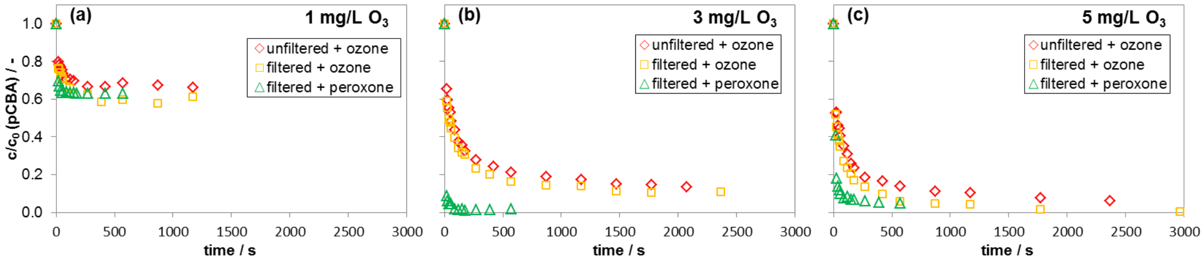


Figure III-22 Degradation of pCBA over time after applying 1, 3, and 5 mg L^{-1} of ozone in (a), (b), and (c), respectively, on either unfiltered (◊), filtered (□), or filtered and exposed to peroxone (O_3+ H_2O_2, Δ) TGR surface water.

5.2.2 *Pollutant degradation kinetics*

In this chapter the degradation of selected organic substances by oxidation due to ozone and OH$^{\cdot}$ will be estimated. The selection of pollutants was based on the results of the monitoring. Thus, the herbicides clopyralid, picloram, and atrazine were selected, as well as the antibiotic sulfamethoxazole, which was detected with high frequency in Wushan bay. In contrast to the other substances, by now, relatively little is known about clopyralid and kinetic constants for its reaction with O_3 and $^{\cdot}$OH have not yet been determined. Hence, its degradation cannot be estimated and experimental studies are needed to develop the oxidation of clopyralid in an ozonation process (currently under study within the frame of this project).

Table III-9 shows a different reactivity of the compounds under study towards ozone. Thereby, atrazine represents an ozone refractory compound, picloram is a compound with low reactivity, and sulfamethoxazole reacts fast with ozone. However, the $^{\cdot}$OH reaction rates of the three compounds are similar. Hence, sulfamethoxazole is degraded efficiently by direct ozone reactions, whereas picloram and atrazine are increasingly degraded by $^{\cdot}$OH. Further, it has to be noted that the concentration of $^{\cdot}$OH is typically in the pico-molar range. Hence, ozone refractory compounds are much less efficiently degraded than compounds with a moderate to high reaction rate towards ozone.

Table III-9 Reaction rate constants [$M^{-1}s^{-1}$] for atrazine, picloram, and sulfamethoxazole with O_3 and OH$^{\cdot}$.

Oxidant	Atrazin	Picloram	Sulfamethoxazole
k (O_3)	6 (Yao & Haag 1990)	140 (Yao & Haag 1990)	$2.5 \cdot 10^{6}$ (Yao & Haag 1990)
k (OH$^{\cdot}$)	$2.6 \cdot 10^{9}$ (Haag & Yao 1992)	$3.4 \cdot 10^{9}$ (Haag & Yao 1992)	$5.5 \cdot 10^{9}$ (Haag & Yao 1992)

In Figure III-23 (a-i) it is shown that sulfamethoxazole is degraded within the first seconds after ozone application, even for low applied doses, while atrazine cannot be completely removed even if applying a high ozone dose of 5 mg L^{-1} for up to 50 min. Figure III-24 summarizes the degradation of sulfamethoxazole, picloram, and atrazine. With an ozone dose of 3 mg L^{-1} these compounds can be degraded to > 84%. This dose requires the addition of H_2O_2 to minimize the formation of bromate. Furthermore, the oxidation capacity can be achieved in a shorter reaction time, since the complete depletion of ozone was achieved in the peroxone process within 5 min, whereas > 30 min are required in conventional ozonation.

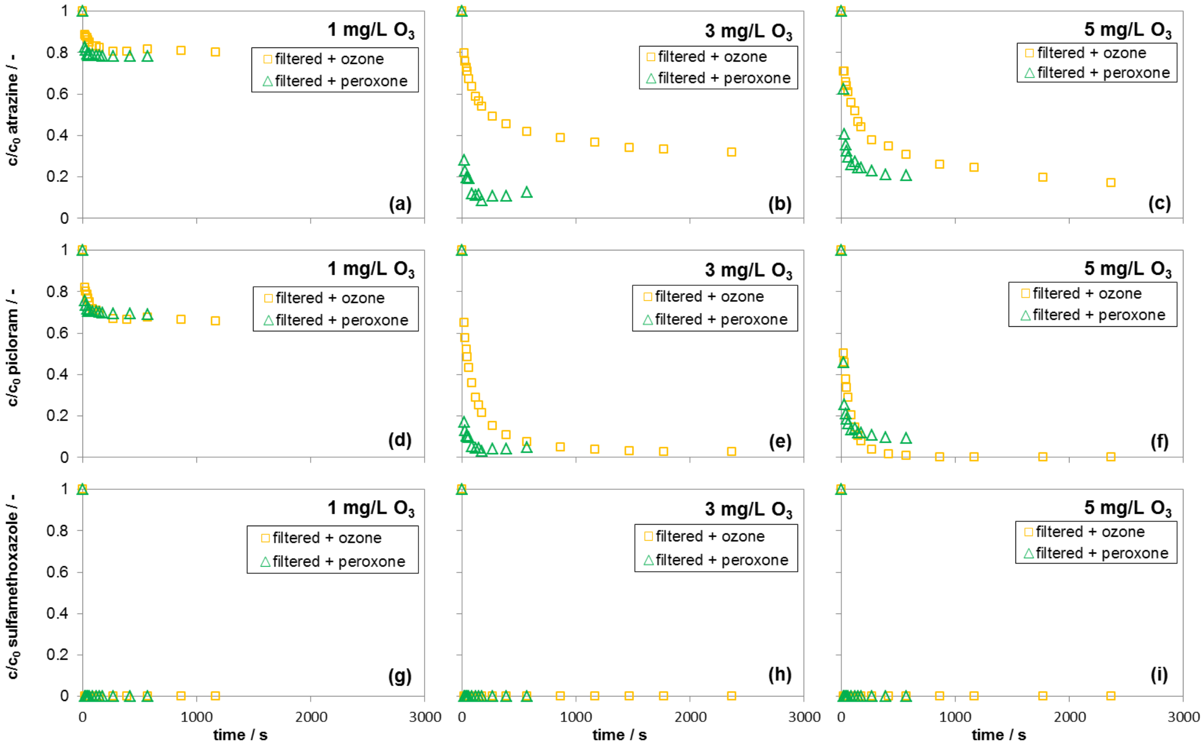


Figure III-23 Estimated degradation of atrazine (a-c), picloram (d-f), and sulfamethoxazole (g-i) in the TGR surface water by their reaction rate constants (Table III-9) applying 1 (a, d, g), 3 (b, e, h), and 5 mg L^{-1} (c, f, i) of ozone.

Additionally, it has to be mentioned that the short life time of ozone can limit the disinfection capacity of the ozone based processes, as ozone is a stronger disinfectant than ˙OH in most cases (von Gunten 2003b).

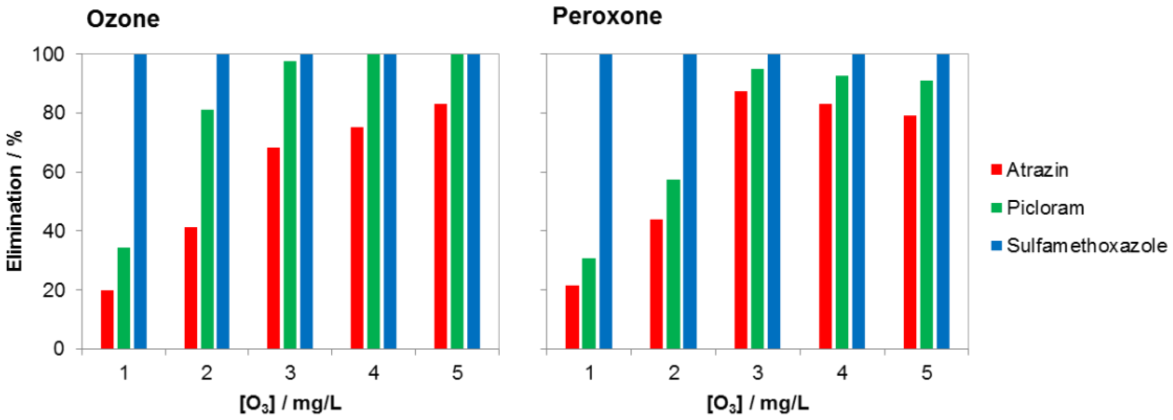


Figure III-24 Percentile degradation endpoints (after 50 min) of the estimated reactions of atrazine, picloram, and sulfamethoxazole with 1 – 5 mg L^{-1} of ozone (left) and peroxone (right).

5.3 Adsorption batch experiments

In addition to oxidation experiments, selected pollutants were tested for their adsorption behavior on the surface areas of three PAC and the ion exchange resin IRA. Therefore, two THM, chloroform and bromoform, and two pesticides, clopyralid and picloram, were chosen. The selection of pollutants was based on their demonstrative occurrence in the samples of all three water sources at the TGR. The substances represent two organic substance groups, trihalomethanes (THM) and polar pesticides, with relatively high volatility and water solubility, respectively (Figure III-6, right). This comes along with low K_{OW} values, which indicate a poor adsorption to organic solvents and organic matter. For the THM and picloram various studies on the adsorption behavior on different adsorbers can be found in literature but not for clopyralid. The adsorption strength, however, depends highly on the water type, especially on the DOC content in water. Studies on the adsorption of the above mentioned organic compounds on PAC and IRA have not been performed yet for the TGR or Yangtze surface water and will be presented in this chapter.

5.3.1 Kinetics

Kinetic experiments give the reaction velocity of an adsorption process that is due to *van der Waals forces* and a concurrent increase of the entropy of a system, if a nonpolar hydrophobic substance migrates from the water phase to the solid phase because a hydrophobic substance in water usually accumulates a hydration shell of polar water molecules (*"iceberg formation"*) that decreases the entropy (Frank and Evans 1945). The reaction rate of an adsorption process can be slowed by the mass transport and the physical process of bonding

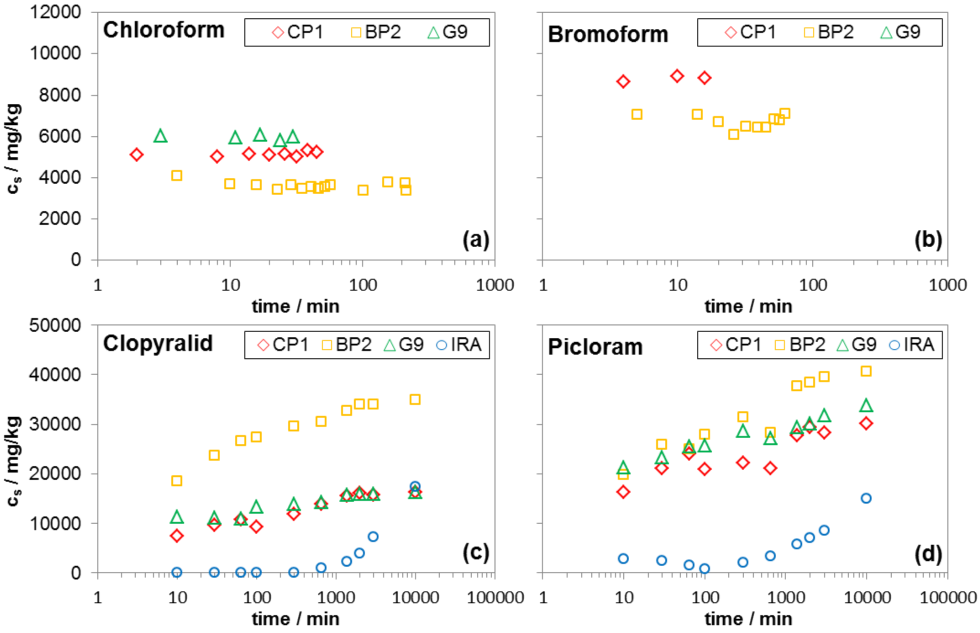


Figure III-25 Kinetic plots (adsorbed concentration on the solid phase c_s vs. time) of chloroform (a), bromoform (b), clopyralid (c), and picloram (d) on three different PAC and IRA. The initial concentration in the water solution (C_0) for experiments with powdered activated carbons (PAC) was 0.5 mg L^{-1} for bromoform and chloroform, 3 mg L^{-1} for clopyralid, and 4 mg L^{-1} for picloram. In experiments with IRA lower C_0 of 2 mg L^{-1} were used.

while the bonding can be neglected as the needed amount of adsorption activation energy is very small (Pignatello 1989). Hence, the molecular size and weight both play an important role in the adsorption process.

The plots in Figure III-25 give the adsorbed concentration on the solid phase (c_S) of chloroform (a), bromoform (b), clopyralid (c), and picloram (d) over time. The results show a very quick adsorption (within a few minutes) of the relatively small molecular substances chloroform and bromoform while the higher molecular pesticides need about one week to achieve equilibrium between the concentration in the water and solid phases. Also the used PAC and IRA react differently with different compounds due to their specific surfaces and properties. For the THM, the reaction velocity for the PAC cannot be compared due to the extremely quick adsorption but one can separate the adsorption strength of the PAC. For the tested THM the wood-based PAC ColorSorb G9 sorbs best and the coal-based PAC AquaSorb BP2 worst. The results of the herbicides, however, indicate that AquaSorb BP2 sorbs best and more quickly than the other two PAC. The ion exchange resin IRA was just tested for the hydrophilic herbicides because it is known to be well suited for the adsorption of polar organic compounds. The results, however, show a comparatively slow adsorption kinetic of the herbicides on the IRA pellets that might be explained by an assumed lower surface area due to the larger grain size. The adsorption capacity and velocity of the coconut shell based PACs AquaSorb CP1 and ColorSorb G9 are comparable and plot in between BP2 and IRA.

5.3.2 Isotherms

For the illustration of the adsorption capacity of the PAC for the selected compounds the *Freundlich isotherm model* was used (Freundlich 1909). In this chapter the adsorption isotherms for THM are given while those for the pesticides are still in progress within the

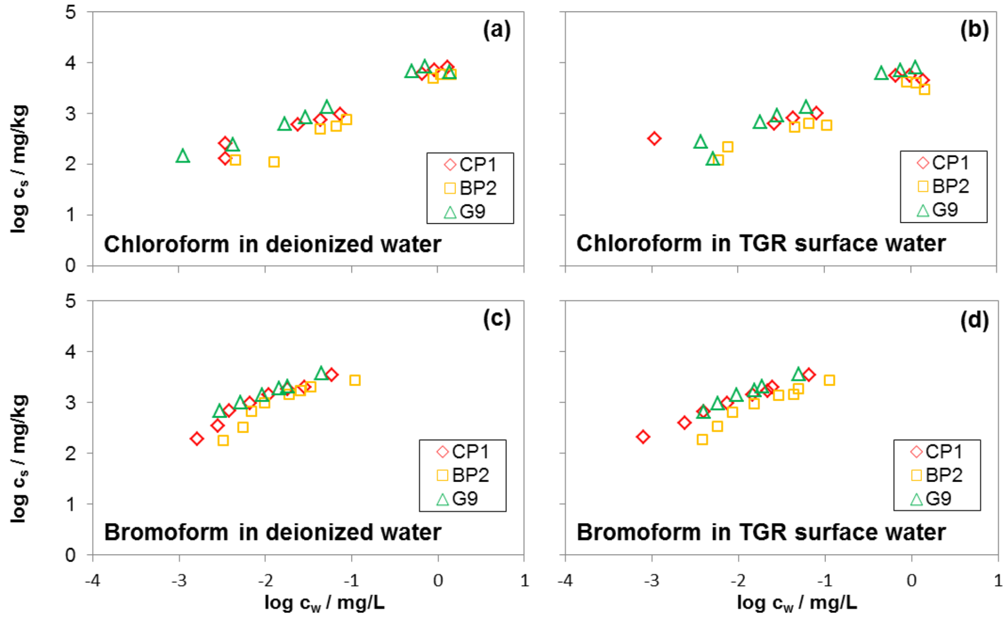


Figure III-26 Logarithmized isotherm plots after the *Freundlich* model (Freundlich 1909) of chloroform (a, b) and bromoform (c, d) on three different PAC in deionized water (a, c) and TGR surface water (b, d).

frame of this study. The double logarithmic plots in Figure III-26 (a-d) show the adsorbed concentration on the PAC (c_S) versus the concentration in the water phase (c_W) after equilibrium is set.

The *Freundlich* model assumes a potential function that explains the distribution of the compounds between the two phases. Hence, the double logarithmic plots should show linear relations in which the slope gives the *Freundlich* exponent (n_{Fr}) and the intercept the *Freundlich* coefficient (K_{Fr}). Exponents and K_{Fr} of the plots in Figure III-26 are listed in Table III-10. Additionally,Table III-10 lists the coefficients (R^2) of the correlation and the probability (p) that the hypothesis of the correlation is wrong.

The results generally showed (R^2 > 86% and p < 0.1%) linear correlations for all PAC and both substances in deionized (DW) and TGR surface water (TGRW). *Freundlich* correlation constants for bromoform are generally about one order of magnitude higher than those for chloroform indicating a better adsorption of the brominated THM. This can also be proven by bromoform´s higher K_{OC} value of 126 L kg^{-1} (chloroform 53 L kg^{-1}). ColorSorb G9, with one exception, is the best adsorbing amongst the tested PAC and AquaSorb BP2 the worst. Generally, however, all three PAC adsorb in the same order of magnitude and are all feasible for the extraction of THM from water. Hereby, however, the water composition is of importance as THM in deionized water are sorbed 50 - 76% better than in the TGR surface water on the PAC CP1 and BP2. For the PAC G9, the results show 10% less adsorption for deionized water compared to the TGRW. This, however, might be due to experimental inaccuracies while a worse adsorption in the TGRW can reasonably be explained by the competition of THM with other water ingredients, such as highly adsorbable DOC, on adsorption spaces.

Table III-10 **Parameters and corresponding correlation coefficients (R^2)and probabilities that the correlation does not exist (p_{uncorr}) of the *Freundlich* isotherm model (Freundlich 1909) on the in Figure III-26 illustrated isotherm plots for chloroform and bromoform in deionized water (DW) and TGR surface water (TGRW).**

			Freundlich model			Correlation	
			K_{Fr} / L kg^{-1}	log K_{Fr} / L kg^{-1}	n_{Fr} / -	R^2 / -	p_{uncorr} / -
Chloroform	DW	CP1	6870	3.84	0.661	0.979	< 0.001
		BP2	4691	3.67	0.754	0.975	< 0.001
		G9	8055	3.91	0.609	0.979	< 0.001
	TGRW	CP1	4318	3.64	0.441	0.916	< 0.001
		BP2	3114	3.49	0.602	0.964	< 0.001
		G9	8982	3.95	0.684	0.961	< 0.001
Bromoform	DW	CP1	37120	4.57	0.771	0.942	< 0.001
		BP2	23754	4.38	0.777	0.868	< 0.001
		G9	25821	4.41	0.620	0.998	< 0.001
	TGRW	CP1	20951	4.32	0.644	0.994	< 0.001
		BP2	16022	4.20	0.741	0.941	< 0.001
		G9	28518	4.46	0.664	0.987	< 0.001

6 Summary & conclusions

The water sampling campaigns in the area of the TGR showed that organic compounds can be found in surface water, tap water, and WWTP effluents. Altogether, 48 substances out of 213 analyzed organic substances were detected. The occurrence, however, is low and substances are often detected in < 5 samples out of 73. Tap water and WWTP effluents are characterized by typical compound patterns, such as disinfection by-products in tap water and pharmaceuticals in WWTP effluents. Furthermore, pesticide concentrations in surface water seem to reflect the surface runoff from agricultural areas or flooding of agricultural sites in the TGR water fluctuation zone. In particular, clopyralid and picloram were found in surface water in significant concentrations that are comparable to those found in tap water samples, indicating a scarce elimination of these compounds in drinking water treatment. Analyzed tap water samples, therefore, exceed the limit values for pesticides given by the EU Drinking Water Directive (EU 1998). The Chinese Drinking Water Standard (MoPH 2006), however, is not exceeded since no limit values are specified, either for clopyralid and picloram or for pesticides. Although the pesticides were found in relatively high concentrations, their ecotoxicological risk is estimated to be low. The results show that the compounds with a greater potential risk, despite their lower concentrations, are the PAH phenanthrene, the pharmaceutical sulfamethoxazole in Wuhan bay, the toxic herbicide atrazine, and chloroform in Wushan drinking water. It should be noted that metabolites have not been analyzed in this study but may play a decisive role in the quality assessment of the surface water.

With the exception of the two pesticides clopyralid and picloram, concentrations of the investigated organic pollutants in the TGR are, in general, in the same range or even lower compared to surface waters in western industrialized countries. This might be related to a high discharge and sediment load of the Yangtze River and concurrent dilution, adsorption, and desorption effects. Contaminant loads, however, can still be high due to the high discharge, as it was shown by others, and the detrimental effects on down gradient ecosystems is of major concern (Müller et al. 2008; Müller et al. 2012).

Since the detected surface water concentrations meet the Chinese surface water standard, the suggested use of surface water from the TGR for drinking water purposes is a valid option. However, the observed spatial variations in contaminant concentrations, the limited number of grab samples taken during this study, and the limited number of regulated compounds in Chinese standards should be taken into account. In addition, the currently applied methods for the purification of drinking water as well as for wastewater treatment seem to be inadequate for some compounds. For drinking water treatment, chlorination seems to lead to the occurrence of significant concentrations of disinfection by-products, and pharmaceuticals are not effectively removed in wastewater treatment. Moreover, the two pesticides clopyralid and picloram can be found in the reservoir, drinking water, and treated wastewater, indicating that no effective removal is achieved, either naturally or during the treatments.

The tested drinking water treatment steps (i) ozonation and (ii) powdered activated carbon adsorption are both feasible for an application in the TGR area since the observed pollutants are removed satisfactorily and the formation of the toxic by-product bromate is below the limits. Ozonation, however, cannot be used unescorted for disinfection purposes since water distribution networks are long and ozone decomposes quickly. Further, the subtropical Chinese climate, additionally, enhances the reproduction and expansion of water organisms and bacteria. Hence, chlorination is still necessary for disinfection but by-product formation can be avoided by first installing activated carbon filtration, for the removal of dissolved organic matter.

7 References

Abramovic BF, Anderluh VB, Sojic DV, Gaal FF (2007) Photocatalytic removal of the herbicide clopyralid from water. J Serb Chem Soc 72 (12):1477-1486. doi:10.2298/jsc0712477a

AiiDA (2014) The Aquatic Impact Indicator Database (AiiDA). http://aiida.tools4env.com/home Accessed: 2014-06-17.

Archie GE (1942) The electrical resistivity log as an aid in determining some reservoir characteristics. Trans AIME 146:54-62

Asarin AE, Lapin GG (2001) Social and Ecological Aspects of the Three Gorges Project. Power Technology and Engineering 35 (5):265-267. doi:10.1023/a:1012338430294

Bader H, Hoigné J (1981) Determination of ozone in water by the indigo method. Water Res (15):449-456

Bao LJ, Maruya KA, Snyder SA, Zeng EY (2012) China's water pollution by persistent organic pollutants. Environ Pollut 163:100-108. doi:10.1016/j.envpol.2011.12.022

Bau M, Dulski P (1996) Anthropogenic origin of positive gadolinium anomalies in river waters. Earth Planet Sc Lett 143 (1-4):245-255. doi:Doi 10.1016/0012-821x(96)00127-6

Bergkoff J (2003) China: The South-North Water Transfer Project - is it justified? Water Policy 5:1-28

Bergmann A, Fohrmann R, Weber F-A (2011) Collocation of monitoring data on environmental concentrations of pharmaceuticals (in German). Report: IWW for German Federal Environment Agency Survey Report FKZ 360 14 013

Chai C, Yu ZM, Shen ZL, Song XX, Cao XH, Yao Y (2009) Nutrient characteristics in the Yangtze River Estuary and the adjacent East China Sea before and after impoundment of the Three Gorges Dam. Sci Total Environ 407 (16):4687-4695

Chang JX, Wang YM, Huang QA (2011) Water Dispatch Model for Middle Route of a South-to-North Water Transfer Project in China1. J Am Water Resour As 47 (1):70-80. doi:10.1111/j.1752-1688.2010.00478.x

Chemspider (2014) Royal Society of Chemistry free chemical structure database. www.chemspider.com (accessed March 2012)

Chen JA, Luo JH, Qiu ZQ, Xu C, Huang YJ, Jin YH, Saito N, Yoshida T, Ozawa K, Cao J, Shu WQ (2008) PCDDs/PCDFs and PCBs in water samples from the Three Gorge Reservoir. Chemosphere 70 (9):1545-1551

Chen JS, Wang FY, Xia XH, Zhang LT (2002) Major element chemistry of the Changjiang (Yangtze River). Chem Geol 187 (3-4):231-255

Chen L, Bi Y, Zhu K, Hu Z, Zhao W, Henkelmann B, Bernhoft S, Temoka C, Schramm KW (2013) Contamination status of dioxins in sediment cores from the Three Gorges Dam area, China. Environmental science and pollution research international. doi:10.1007/s11356-012-1447-2

CIESIN (2000) Global gridded population database. Center for International Earth Science Information Network, Earth Institute, Columbia University

Cui ZH, Liu JY, Li P, Cao B, Luo CH, Cao J (2009) Biomonitoring of Detoxifying Activity as Measured by CYP1A1 Induction in Yangtze and Jialing Rivers in Chongqing City in China. J Toxicol Env Heal A 72 (11-12):782-788. doi:Pii 911876798

Doi 10.1080/15287390902841680

Cyris M (2013) Behavior of Gadolinium-based Diagnostics in Water Treatment. University Duisburg-Essen (Dissertation)

DIN (1996a) German Institute for Standardization (DIN). DIN EN ISO 6468 Water quality - Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes - Gas-chromatographic method after liquid-liquid extraction (ISO 6468:1996); German version EN ISO 6468:1996. German National Standard 1997-02

DIN (1996b) German Institute for Standardization (DIN). DIN EN ISO 11969 Water quality - Determination of arsenic - Atomic absorption spectrometric method (hydride technique) (ISO 11969:1996); German version EN ISO 11969:1996. German National Standard 1996-11

DIN (1997a) German Institute for Standardization (DIN). DIN EN 1484 Water analysis - Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC); German version EN 1484-1997. German National Standard 1997-08

DIN (1997b) German Institute for Standardization (DIN). DIN EN ISO 11369 Water quality - Determination of selected plant treatment agents - Method using high performance liquid chromatography with UV detection after solid-liquid extraction (ISO 11369:1997); German version EN ISO 11369:1997. German National Standard 1997-11

DIN (2000) German Institute for Standardization (DIN). DIN EN ISO 10695 Water quality - Determination of selected organic nitrogen and phosphorus compounds - Gas chromatographic methods (ISO 10695:2000); German version EN ISO 10695:2000. German National Standard 2000-11

DIN (2003) German Institute for Standardization (DIN). DIN EN ISO 15913 Water quality - Determination of selected phenoxyalkanoic herbicides, including bentazones and hydroxybenzonitriles by gas chromatography and mass spectrometry after solid phase extraction and derivatization (ISO 15913:2000); German version EN ISO 15913:2003. German National Standard 2003-05

DIN (2008) German Institute for Standardization (DIN). DIN 32645 Chemical analysis - Decision limit, detection limit and determination limit under repeatability conditions - Terms, methods, evaluation. German National Standard 2008-11

DIN (2009a) German Institute for Standardization (DIN). DIN EN ISO 10304-1 Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate (ISO 10304-1:2007); German version EN ISO 10304-1:2009. German National Standard 2009-07

DIN (2009b) German Institute for Standardization (DIN). DIN EN ISO 11885 Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885:2007); German version EN ISO 11885:2009. German National Standard 2009-09

DIN (2009c) German Institute for Standardization (DIN). DIN EN ISO 22032 Water quality - Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge - Method using extraction and gas chromatography/mass spectrometry (ISO 22032:2006); German version EN ISO 22032:2009. German National Standard 2009-07

DIN (2011a) German Institute for Standardization (DIN). DIN 38407-39 Determination of selected polycyclic aromatic hydrocarbons (PAH) - Method using gas chromatography with mass spectrometric detection (GC-MS) (F 39). German National Standard 2011-09

DIN (2011b) German Institute for Standardization (DIN). DIN 38407-41 Determination of selected easily volatile organic compounds in water - Method using gas chromatography (GC-MS) after headspace solid-phase micro extraction (HS-SPME) (F 41). German National Standard 2011-06

DIN (2011c) German Institute for Standardization (DIN). DIN 38407-42 Determination of selected polyfluorinated compounds (PFC) in water - Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction (F 42). German National Standard 2011-03

DIN (draft) German Institute for Standardization (DIN). E DIN 38407-36 Determination of selected plant treatment agents and further organic compounds in water – Method using high performance liquid chromatography and mass spectrometric detection (HPLC-MS/MS) after direct injection (F 36). german National Standard

EC (2003) Technical Guidance Document (TGD) in Risk Assessment in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances; Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances; Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. .

Einstein A (1905) Investigations on the theory of Brownian Movement (in German). Annalen der Physik 17 (8):549–560. doi:10.1002/andp.19053220806

EU (1998) The Council of the European Union. Council Directive 98/83/EC on the quality of water intended for human consumption. Official Journal of the European Communities December, 12 1998

EU (2000) The European Parliament and the Council of the European Union. Directive 2000/60/EC establishing a framework for community action in the field of water policy. Official Journal of the European Communities October, 23 2000

EU (2008) The European Parliament and the Council of the European Union. Directive on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. December, 14th 2008

Feng CL, Xia XH, Shen ZY, Zhou Z (2007) Distribution and sources of polycyclic aromatic hydrocarbons in Wuhan section of the Yangtze River, China. Environ Monit Assess 133 (1-3):447-458. doi:10.1007/s10661-006-9599-5

Fick A (1855) On liquid diffusion. Philosophical Magazine 294 (X):30-39

Frank HS, Evans MW (1945) Free volume and entropy in condensed systems. 3. Entropy in binary liquid mixtures - Partial molall entropy in dilute solutions - Structure and thermodynamics in aqueous electrolytes. J Chem Phys 13 (11):507-532. doi:10.1063/1.1723985

Freundlich H (1909) Capillary Chemistry (in German). Leipzig Akademische Verlagsgesellschaft mbH:591

Gao S, Chen J, Shen Z, Liu H, Chen Y (2013) Seasonal and spatial distributions and possible sources of polychlorinated biphenyls in surface sediments of Yangtze Estuary, China. Chemosphere (0). doi:http://dx.doi.org/10.1016/j.chemosphere.2013.01.085

Gao X, Wang X, Guo JS, Xiong Y, Cao J (2007) Varieties of PAHs distribution among water purification plants in Three Gorges Reservoir Region (Chinese). Journal for Safety and Environment 7 (4)

German Federal Committee for Chemical Safety BLAC (2003) Pharmaceuticals in the environment - Processing of monitoring data (in German). Agency for Environment and Health, Institute for Hygiene and Environment - Hamburg

Global Industry Analysts I (2011) Methyl Tert-Buthyl Ether (MTBE) - A Global Strategic Business Report.1-110

Grathwohl P, Martin H, Piepenbrink M (2001) Investigation of passive samplers for time-integrated monitoring of groundwater, surface water, and land fills: Ceramic dosimeter and deposition samplers (in German). FZKA-BWPLUS

He H, Hu GJ, Sun C, Chen SL, Yang MN, Li J, Zhao Y, Wang H (2011) Trace analysis of persistent toxic substances in the main stream of Jiangsu section of the Yangtze River, China. Environ Sci Pollut R 18 (4):638-648. doi:DOI 10.1007/s11356-010-0414-z

Heggelund G (2006) Resettlement programmes and environmental capacity in the Three Gorges dam project. Dev Change 37 (1):179-199

Hites RA, Laflamme RE, Farrington JW (1977) Sedimentary Polycyclic Aromatic-Hydrocarbons - Historical Record. Science 198 (4319):829-831. doi:10.1126/science.198.4319.829

Hoigne J, Bader H (1975) Ozonation of Water - Role of Hydroxyl Radicals as Oxidizing Intermediates. Science 190 (4216):782-784

Hoigne J, Bader H (1980) Determination of ozone and chlorine dioxide in water by the Indigo Method (in German). Vom Wasser - Special Issue 55:261-280

Hoigne J, Bader H (1994) Characterization of Water-Quality Criteria for Ozonation Processes .2. Lifetime of Added Ozone. Ozone-Science & Engineering 16 (2):121-134. doi:Doi 10.1080/01919519408552417

Holbach A, Wang L, Chen H, Hu W, Schleicher N, Zheng B, Norra S (2012a) Impact factors on water quality in the confluence zone of the Daning River and the Yangtze River at different hydrological conditions in the Three Gorges Reservoir. Geophysical Research Abstracts 14 (EGU2012-11782-3, EGU General Assembly 2012)

Holbach A, Wang L, Chen H, Hu W, Schleicher N, Zheng B, Norra S (2012b) 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. Environmental science and pollution research international. doi:10.1007/s11356-012-1373-3

Hui Y, Zheng M, Liu Z, Gao L (2009a) PCDD/Fs and dioxin-like PCBs in sediments from Yellow Estuary and Yangtze Estuary, China. Bull Environ Contam Toxicol 83 (4):614-619. doi:10.1007/s00128-009-9832-3

Hui YM, Zheng MH, Liu ZT, Gao LR (2009b) Distribution of polycyclic aromatic hydrocarbons in sediments from Yellow River Estuary and Yangtze River Estuary, China. Journal of Environmental Sciences-China 21 (12):1625-1631. doi:Doi 10.1016/S1001-0742(08)62465-1

Jackson S, Sleigh A (1998) Resettlement issues of China´s Three Gorges Dam. Economic Issues 2:1-19

Jiang T, Su B, Hartmann H (2007) Temporal and spatial trends of precipitation and river flow in the Yangtze River Basin, 1961-2000. Geomorphology 85 (3-4):143-154

Laturnus F, Haselmann KF, Borch T, Gron C (2002) Terrestrial natural sources of trichloromethane (chloroform, CHCl(3)) - An overview. Biogeochemistry 60 (2):121-139. doi:10.1023/A:1019887505651

Li B, Feng C, Li X, Chen Y, Niu J, Shen Z (2012) Spatial distribution and source apportionment of PAHs in surficial sediments of the Yangtze Estuary, China. Mar Pollut Bull 64 (3):636-643. doi:http://dx.doi.org/10.1016/j.marpolbul.2011.12.005

Li SY, Lu XX, He M, Zhou Y, Bei RT, Li L, Ziegler AD (2011) Major element chemistry in the upper Yangtze River: A case study of the Longchuanjiang River. Geomorphology 129 (1-2):29-42

Liu C, Yuan GL, Yang ZF, Yu T, Xia XQ, Hou QY, Chen L (2011) Levels of organochlorine pesticides in natural water along the Yangtze River, from headstream to estuary, and factors determining these levels. Environ Earth Sci 62 (5):953-960. doi:10.1007/s12665-010-0580-9

Liu M, Hou LJ, Yang Y, Zou HX, Lu JH, Wang XR (2001) Distribution and sources of polycyclic aromatic hydrocarbons in intertidal flat surface sediments from the Yangtze estuary, China. Environ Geol 41 (1-2):90-95

Luo H, Fu G, Peng M, Gong R, Xiang W, Wang H (2011) Centralized water supply in rural villages of Three Gorges Reservoir (in Chinese). Chinese Rural Health Service Administration 31 (9)

Ma LM, Rena D, Zhang M, Zhao JF (2010) Phosphorus fractions and soil release in alternately waterlogged and drained environments at the water-fluctuation-zone of the Three Gorges Reservoir. J Food Agric Environ 8 (3-4):1329-1335

Martin H (1997) Development of dosimeters for the sampling of contaminants in ground water (in German). Tübingen Geoscientific Works (Diploma Thesis)

Martin H (2000) Investigation of passive samplers for time-inetragted monitoring of land fills and groundwater: adsorbing columns and ceramic dosimeter (in German). Tübingen Geoscientific Works (Dissertation) C56:102

Metcalfe C, Hoque ME, Sultana T, Murray C, Helm P, Kleywegt S (2014) Monitoring for contaminants of emerging concern in drinking water using POCIS passive samplers. Environmental Science: Processes & Impacts 16 (3):473-481. doi:10.1039/c3em00508a

Moller P, Dulski P, Bau M, Knappe A, Pekdeger A, Sommer-von Jarmersted C (2000) Anthropogenic gadolinium as a conservative tracer in hydrology. J Geochem Explor 69:409-414. doi:Doi 10.1016/S0375-6742(00)00083-2

MoPH (1985) Ministry of Public Health of the People´s Republic of China (MoPH). National Standard of the People´s Republic of China - Sanitary Standard for Drinking Water (GB 5749-1985). Released 1985

MoPH (2006) Ministry of Public Health of China (MoPH) and Standardization Administration of China. National Standard of the People´s Republic of China - Standards for Drinking Water Quality (GB 5749-2006). Issued on December 29th, 2006. Implemented on July 1st, 2007 (Replacing GB 5749-1985)

Müller B, Berg M, Pernet-Coudrier B, Qi WX, Liu HJ (2012) The geochemistry of the Yangtze River: Seasonality of concentrations and temporal trends of chemical loads. Glob Biogeochem Cycle 26. doi:10.1029/2011gb004273. Artn Gb2028

Müller B, Berg M, Yao ZP, Zhang XF, Wang D, Pfluger A (2008) How polluted is the Yangtze river? Water quality downstream from the Three Gorges Dam. Sci Total Environ 402 (2-3):232-247. doi:10.1016/j.scitotenv.2008.04.049.

Munoz F, von Sonntag C (2000) Determination of fast ozone reactions in aqueous solution by competition kinetics. Journal of the Chemical Society, Perkin Transactions 2 (4):661-664. doi:10.1039/a909668j

NASA (2000) National Aeronautics and Space Administration. Digital Elevation Data. http://www.viewfinderpanoramas.org (accessed January 16, 2013)

NBoS (2008) National Bureau of Statistics of China (NBoS). Environmental Statistics (in Chinese). http://www.stats.gov.cn/tjsj/qtsj/hjtjzl/hjtjsj2008/. (accessed: December, 9 2013).

NBoS (2011) National Bureau of Statistics of China (NBoS). Environmental Statistics (in Chinese). http://www.stats.gov.cn/tjsj/qtsj/hjtjzl/hjtjsj2011/. (accessed: December, 9 2013).

NOAA (2011-2013) National Oceanic and Atmospheric Administration (NOAA). Climate data. Global Summary of the Day (GSOD). http://wwwclimategov/data/maps-and-data (accessed: February 29, 2012)

Ou DN, Liu M, Cheng SB, Hou LJ, Xu SY, Wang LL (2010) Identification of the sources of polycyclic aromatic hydrocarbons based on molecular and isotopic characterization from the Yangtze estuarine and nearby coastal areas. J Geogr Sci 20 (2):283-294. doi:10.1007/s11442-010-0283-x

Park YS, Chang JB, Lek S, Cao WX, Brosse S (2003) Conservation strategies for endemic fish species threatened by the Three Gorges Dam. Conserv Biol 17 (6):1748-1758. doi:DOI 10.1111/j.1523-1739.2003.00430.x

Piepenbrink M (1998) Investigation and use of passive samplers for time-integrated and depth horizonted groundwater monitoring (in German). Tübingen Geoscientific Works (Diploma Thesis)

Pignatello JJ (1989) Sorption dynamics of organic compounds in soils and sediments.- In: Reactions an Movements of Organic Chemicals in Soils. Sawhney BL, Brown K (Eds.) Soil Sci Soc Am Inc Am. Soc. Of Agronomy Inc, Madison, Wi.:45-80

Ran XB, Yu ZG, Yao QZ, Chen HT, Mi TZ (2010) Major ion geochemistry and nutrient behaviour in the mixing zone of the Changjiang (Yangtze) River and its tributaries in the Three Gorges Reservoir. Hydrol Process 24 (17):2481-2495. doi:10.1002/Hyp.7684

Reuter JE, Allen BC, Richards RC, Pankow JF, Goldman CR, Scholl RL, Seyfried JS (1998) Concentrations, sources, and fate of the gasoline oxygenate methyl tert-butyl ether (MTBE) in a multiple use lake. Environ Sci Technol 32 (23):3666-3672. doi:10.1021/Es9805223

Richter H, Howard JB (2000) Formation of polycyclic aromatic hydrocarbons and their growth to soot - a review of chemical reaction pathways. Prog Energ Combust 26 (4-6):565-608. doi:10.1016/S0360-1285(00)00009-5

Rivera-Nunez Z, Wright JM, Blount BC, Silva LK, Jones E, Chan RL, Pegram RA, Singer PC, Savitz DA (2012) Comparison of Trihalomethanes in Tap Water and Blood: A Case Study in the United States. Environ Health Perspect 120 (5):661-667. doi:10.1289/ehp.1104347

SAEP (2002) Chinese State Administration for Environmental Protection (SAEP). Chinese State Administration for Quality Supervision, Inspection, and Quarantine. National Standard of the People´s Republic of China - Environmental Quality Standards for Surface Water (GB 3838-2002). Released on April 28th, 2002 (Replacing GB 3838-1988, GHZB 1-1999)

Shen ZL, Liu Q (2009) Nutrients in the Changjiang River. Environ Monit Assess 153 (1-4):27-44. doi:10.1007/s10661-008-0334-2

So MK, Miyake Y, Yeung WY, Ho YM, Taniyasu S, Rostkowski P, Yamashita N, Zhou BS, Shi XJ, Wang JX, Giesy JP, Yu H, Lam PKS (2007) Perfluorinated compounds in the Pearl River and Yangtze River of China. Chemosphere 68 (11):2085-2095

Squillace PJ, Zogorski JS, Wilber WG, Price CV (1996) Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993-1994. Environ Sci Technol 30 (5):1721-1730. doi:10.1021/Es9507170

Tang ZW, Yang ZF, Shen ZY, Niu JF, Cai YP (2008) Residues of organochlorine pesticides in water and suspended particulate matter from the Yangtze River catchment of Wuhan, China. Environ Monit Assess 137 (1-3):427-439. doi:10.1007/s10661-007-9778-z

Thach TT, Gurzau AE, Russi M, Dimitrascu I, Pop C, Popa O (2012) An Analysis of Trihalomethane Levels in the Distribution Networks of Three Romanian Cities. Carpath J Earth Environ Sci 7 (1):81-88

U.S. Department of Commerce s (2005) Water Supply and Wastewater Treatment Market in China. US Department of Commerce - International Trade Administration Washington, DC www.ita.doc.gov: 1 - 105

USGS (1997) U.S. Geological Survey (USGS), Department of the Interior. Compiled by Steinshouer D W, Qiang J, McCabe P J, and Ryder R T. Maps showing geology, oil, and gas fields, and geologic provinces of the Asia Pacific Region. Open- File Report 97-470F. http://certmapper.cr.usgs.gov/geoportal/catalog/search/resource/details.page?uuid={8DB1A546-92DC-4230-B9E7-FF7F210383A5} (accessed February 21, 2014).

van Wezel A, Puijker L, Vink C, Versteegh A, de Voogt P (2009) Odour and flavour thresholds of gasoline additives (MTBE, ETBE and TAME) and their occurrence in Dutch drinking water collection areas. Chemosphere 76 (5):672-676. doi:10.1016/j.chemosphere.2009.03.073

Wang J, Bi Y, Pfister G, Henkelmann B, Zhu K, Schramm KW (2009) Determination of PAH, PCB, and OCP in water from the Three Gorges Reservoir accumulated by semipermeable membrane devices (SPMD). Chemosphere 75 (8):1119-1127. doi:10.1016/j.chemosphere.2009.01.016.

Wang J, Henkelmann B, Bi Y, Zhu K, Pfister G, Hu W, Temoka C, Westrich B, Schramm KW (2012) Temporal variation and spatial distribution of PAH in water of Three Gorges Reservoir during the complete impoundment period. Environmental science and pollution research international. doi:10.1007/s11356-012-1427-6

Werres F, Balsaa P (2012) Training course presentation, October 2012 in Bulgaria.

Wood A (1995-2014) Compendium of Pesticide Common Names. www.alanwood.net (accessed March 2012)

Worch E (1993) A new equation to calculate diffusion coefficients of dissolved compounds (in German). Vom Wasser 81:289-297

WorldClim (1950-2000) WorldClim - Global Climate Data. Free climate data for ecological modeling and GIS. Hijmans R J , Cameron S, Parra J, Museum of Vertebrate Zoology, University of California, Berkeley. Accessed: 2014-02- (http://www.worldclim.org/current).

Wu JG, Huang JH, Han XG, Gao XM, He FL, Jiang MX, Jiang ZG, Primack RB, Shen ZH (2004) The Three Gorges Dam: an ecological perspective. Front Ecol Environ 2 (5):241-248

WWF (2007) World Wide Fund for Nature International. World's top 10 rivers at risk. Authors: Wong C M, William C E, Pittock J, Colier U, Schelle P. Gland, Swizerland. URL http://wwf.panda.org/what_we_do/how_we_work/policy/wwf_europe_environment/initiatives/freshwater/publications/?108620/Worlds-Top-10-Rivers-at-Risk (accessed February 19, 2014)

Xing GX, Zhu ZL (2002) Regional nitrogen budgets for China and its major watersheds. Biogeochemistry 57 (1):405-427. doi:Doi 10.1023/A:1016508323200

Xu KH, Milliman JD (2009) Seasonal variations of sediment discharge from the Yangtze River before and after impoundment of the Three Gorges Dam. Geomorphology 104 (3-4):276-283

Xu XB, Tan Y, Yang GS, Li HP, Su WZ (2011) Impacts of China's Three Gorges Dam Project on net primary productivity in the reservoir area. Sci Total Environ 409 (22):4656-4662. doi:10.1016/j.scitotenv.2011.08.004

Yan CX, Yang Y, Zhou JL, Liu M, Nie MH, Shi H, Gu LJ (2013) Antibiotics in the surface water of the Yangtze Estuary: Occurrence, distribution and risk assessment. Environmental Pollution 175:22-29. doi:DOI 10.1016/j.envpol.2012.12.008

Yan Q, Gao X, Chen Y-P, Peng X-Y, Zhang Y-X, Gan X-M, Zi C-F, Guo J-S (2014) Occurrence, fate and ecotoxicological assessment of pharmaceutically active compounds in wastewater and sludge from wastewater treatment plants in Chongqing, the Three Gorges Reservoir Area. Science of The Total Environment 470–471 (0):618-630. doi:http://dx.doi.org/10.1016/j.scitotenv.2013.09.032

Yang M, Kostaschuk R, Chen ZY (2004) Historical changes in heavy metals in the Yangtze Estuary, China. Environ Geol 46 (6-7):857-864. doi:10.1007/s00254-004-1072-6

Yang SL, Gao A, Hotz HM, Zhu J, Dai SB, Li M (2005) Trends in annual discharge from the Yangtze River to the sea (1865-2004). Hydrolog Sci J 50 (5):825-836. doi:10.1623/hysj.2005.50.5.825

Yang ZF, Shen ZY, Gao F, Tang ZW, Niu JF (2009) Occurrence and possible sources of polychlorinated biphenyls in surface sediments from the Wuhan reach of the Yangtze River, China. Chemosphere 74:1522-1530. doi:10.1016

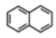
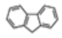
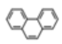
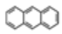
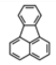
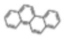
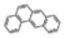
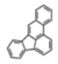
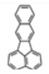
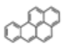
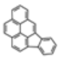
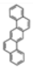
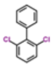
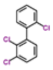
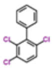
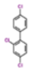
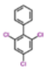
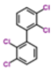
YWRPB (1999) Yangtze Valley Water Resources Protection Bureau (YWRPB). Questions and Answers on Environmental Issues for the Three Gorges Project. Science Press, Beijing and New York.

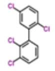
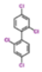
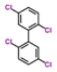
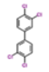
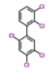
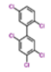
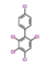
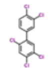
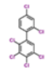
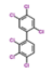
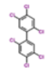
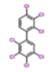
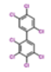
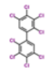
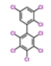
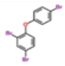
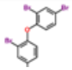
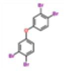
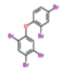
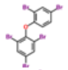
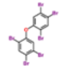
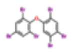
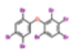
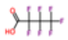
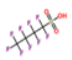
Zhang J, Zhang ZF, Liu SM, Wu Y, Xiong H, Chen HT (1999) Human impacts on the large world rivers: Would the Changjiang (Yangtze River) be an illustration? Glob Biogeochem Cycle 13 (4):1099-1105. doi:10.1029/1999gb900044

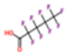
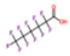
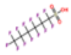
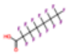
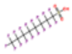
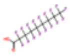
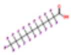
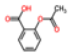
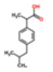
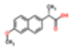
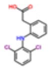
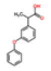
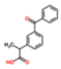
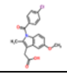
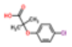
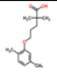
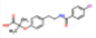
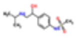
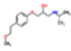
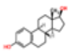
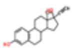
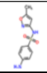
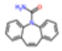
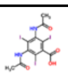
Zhu N, Zhao SH (1996) Research on the Three Gorges Resettlement and Reservoir Development (in Chinese). Wuhan University Publishing House. Cited in Heggelund G (2006) Resettlement programmes and environmental capacity in the Three Gorges dam project. Dev Change 37 (1):179-199.

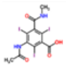
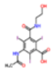
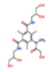
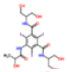
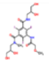
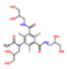
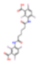
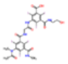
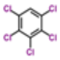
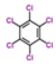
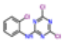
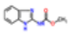
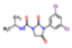
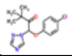
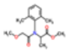
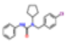
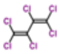
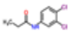
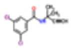
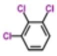
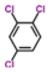
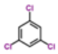
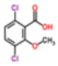
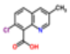
8 Supplementary material

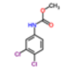
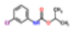
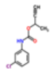
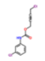
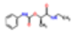
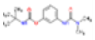
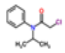
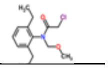
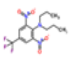
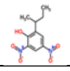
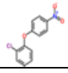
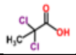
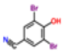
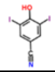
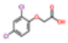
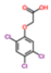
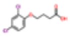
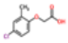
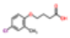
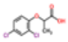
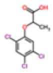
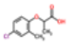
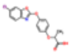
Table III-11 Supplementary material: List of analyzed organic trace substances. [1] Chemical Astract Services Registration Number (CAS-RN), [2] Pesticide classification after Wood (1995-2014), [3] Substance structures taken from Chemspider (2014)

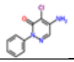
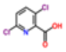
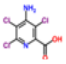
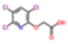
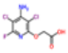
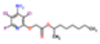
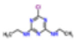
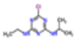
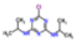
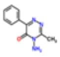
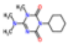
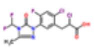
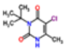
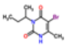
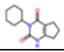
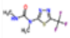
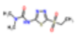
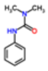
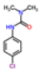
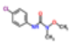
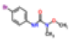
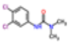
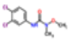
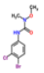
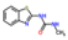
Sub. No	CAS RN[1]	Substance English name	Substance group[2]	Formula	Molar mass g mol^{-1}	Structure[3]
1	91-20-3	Naphthalene	PAH	$C_{10}H_8$	128.18	
2	208-96-8	Acenaphthylene	PAH	$C_{12}H_8$	152.20	
3	83-32-9	Acenaphthene	PAH	$C_{12}H_{10}$	154.21	
4	86-73-7	Fluorene	PAH	$C_{13}H_{10}$	166.22	
5	85-01-8	Phenanthrene	PAH	$C_{14}H_{10}$	178.24	
6	120-12-7	Anthracene	PAH	$C_{14}H_{10}$	178.24	
7	206-44-0	Fluoranthene	PAH	$C_{16}H_{10}$	202.26	
8	129-00-0	Pyrene	PAH	$C_{16}H_{10}$	202.26	
9	218-01-9	Chrysene	PAH	$C_{18}H_{12}$	228.29	
10	56-55-3	Benzo[a]anthracene	PAH	$C_{18}H_{12}$	228.29	
11	205-99-2	Benzo[b]fluoranthene	PAH	$C_{20}H_{12}$	252.32	
12	207-08-9	Benzo[k]fluoranthene	PAH	$C_{20}H_{12}$	252.32	
13	50-32-8	Benzo[a]pyrene	PAH	$C_{20}H_{12}$	252.32	
14	191-24-2	Benzo[g,h,i]perylene	PAH	$C_{22}H_{12}$	276.34	
15	193-39-5	Indeno[1,2,3-c,d]-pyrene	PAH	$C_{22}H_{12}$	276.34	
16	53-70-3	Dibenz[a,h]anthracene	PAH	$C_{22}H_{14}$	278.36	
17	33146-45-1	PCB 10	PCB	$C_{12}H_8Cl_2$	223.10	
18	38444-78-9	PCB 16	PCB	$C_{12}H_7Cl_3$	257.54	
19	55702-45-9	PCB 24	PCB	$C_{12}H_7Cl_3$	257.54	
20	7012-37-5	PCB 28	PCB	$C_{12}H_7Cl_3$	257.54	
21	35693-92-6	PCB 30	PCB	$C_{12}H_7Cl_3$	257.54	
22	38444-93-8	PCB 40	PCB	$C_{12}H_6Cl_4$	291.99	

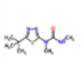
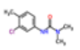
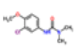
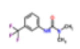
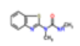
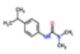
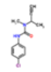
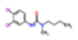
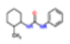
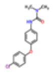
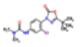
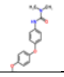
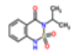
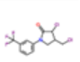
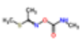
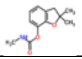
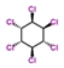
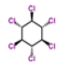
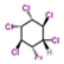
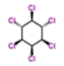
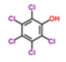
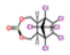
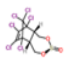
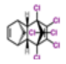
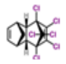
Sub. No	CAS RN[1]	Substance English name	Substance group[2]	Formula	Molar mass g mol^{-1}	Structure[3]
23	41464-39-5	PCB 44	PCB	$C_{12}H_6Cl_4$	291.99	
24	2437-79-8	PCB 47	PCB	$C_{12}H_6Cl_4$	291.99	
25	35693-99-3	PCB 52	PCB	$C_{12}H_6Cl_4$	291.99	
26	32598-13-3	PCB 77	PCB	$C_{12}H_6Cl_4$	291.99	
27	41464-51-1	PCB 97	PCB	$C_{12}H_5Cl_5$	326.44	
28	37680-73-2	PCB 101	PCB	$C_{12}H_5Cl_5$	326.44	
29	74472-38-1	PCB 115	PCB	$C_{12}H_5Cl_5$	326.44	
30	31508-00-6	PCB 118	PCB	$C_{12}H_5Cl_5$	326.44	
31	35694-06-5	PCB 137	PCB	$C_{12}H_4Cl_6$	360.88	
32	35065-28-2	PCB 138	PCB	$C_{12}H_4Cl_6$	360.88	
33	35065-27-1	PCB 153	PCB	$C_{12}H_4Cl_6$	360.88	
34	35065-30-6	PCB 170	PCB	$C_{12}H_3Cl_7$	395.32	
35	35065-29-3	PCB 180	PCB	$C_{12}H_3Cl_7$	395.32	
36	35694-08-7	PCB 194	PCB	$C_{12}H_2Cl_8$	429.77	
37	68194-17-2	PCB 198	PCB	$C_{12}H_2Cl_8$	429.77	
38	41318-75-6	PBDE 28	PBDE	$C_{12}H_7Br_3O$	406.90	
39	5436-43-1	PBDE 47	PBDE	$C_{12}H_6Br_4O$	485.79	
40	93703-48-1	PBDE 77	PBDE	$C_{12}H_6Br_4O$	485.79	
41	60348-60-9	PBDE 99	PBDE	$C_{12}H_5Br_5O$	564.69	
42	189084-64-8	PBDE 100	PBDE	$C_{12}H_5Br_5O$	564.69	
43	68631-49-2	PBDE 153	PBDE	$C_{12}H_4Br_6O$	643.58	
44	207122-15-4	PBDE 154	PBDE	$C_{12}H_4Br_6O$	643.58	
45	207122-16-5	PBDE 183	PBDE	$C_{12}H_3Br_7O$	722.48	
46	375-22-4	PFBA	PFC	$C_4HF_7O_2$	214.04	
47	375-73-5	PFBS	PFC	$C_4HF_9O_3S$	300.10	

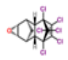
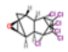
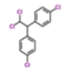
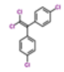
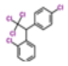
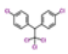
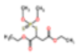
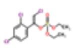
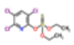
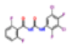
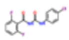
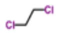
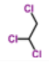
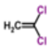
Sub. No	CAS RN[1]	Substance English name	Substance group[2]	Formula	Molar mass g mol^{-1}	Structure[3]
48	2706-90-3	PFPA	PFC	$C_5HF_9O_2$	264.05	
49	307-24-4	PFHxA	PFC	$C_6HF_{11}O_2$	314.05	
50	355-46-4	PFHxS	PFC	$C_6HF_{13}O_3S$	400.11	
51	375-85-9	PFHpA	PFC	$C_7HF_{13}O_2$	364.06	
52	335-67-1	PFOA	PFC	$C_8HF_{15}O_2$	414.07	
53	1763-23-1	PFOS	PFC	$C_8HF_{17}O_3S$	500.13	
54	375-95-1	PFNA	PFC	$C_9HF_{17}O_2$	464.08	
55	335-76-2	PFDA	PFC	$C_{10}HF_{19}O_3$	514.08	
56	50-78-2	Acetyl salicylic acid	Analgesic	$C_9H_8O_4$	180.16	
57	15687-27-1	Ibuprofen	Analgesic	$C_{13}H_{18}O_2$	206.29	
58	22204-53-1	Naproxen	Analgesic	$C_{14}H_{14}O_3$	230.27	
59	15307-86-5	Diclofenac	Analgesic	$C_{14}H_{11}Cl_2NO_2$	296.15	
60	31879-05-7	Fenoprofen	Analgesic	$C_{15}H_{14}O_3$	242.28	
61	22071-15-4	Ketoprofen	Analgesic	$C_{16}H_{14}O_3$	254.29	
62	53-86-1	Indometacin	Analgesic	$C_{19}H_{16}ClNO_4$	357.80	
63	882-09-7	Clofibric acid	Agonist metabolite	$C_{10}H_{11}ClO_3$	214.65	
64	25812-30-0	Gemfibrozil	Agonist	$C_{15}H_{22}O_3$	250.34	
65	41859-67-0	Bezafibrate	Agonist	$C_{19}H_{20}ClNO_4$	361.83	
66	3930-20-9	Sotalol	Betablocker	$C_{12}H_{20}N_2O_3S$	272.36	
67	37350-58-6	Metoprolol	Betablocker	$C_{15}H_{25}NO_3$	267.36	
68	50-28-2	Estradiol	Hormone	$C_{18}H_{24}O_2$	272.39	
69	57-63-6	17a-Ethinylestradiol	Hormone	$C_{20}H_{24}O_2$	296.40	
70	723-46-6	Sulfamethoxazole	Sulfonamide antibiotic	$C_{10}H_{11}N_3O_3S$	253.28	
71	298-46-4	Carbamazepine	Anticonvulsant	$C_{15}H_{12}N_2O$	236.28	
72	117-96-4	Amidotrizoic acid	X-ray contrast medium	$C_{11}H_9I_3N_2O_4$	613.91	

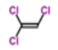
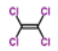
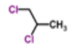
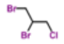
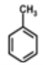
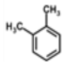
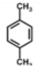
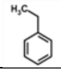
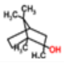
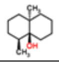
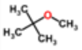
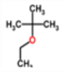
Sub. No	CAS RN[1]	Substance English name	Substance group[2]	Formula	Molar mass g mol^{-1}	Structure[3]
73	2276-90-6	Iothalamic acid	X-ray contrast medium	$C_{11}H_9I_3N_2O_4$	613.91	
74	28179-44-4	Ioxithalamic acid	X-ray contrast medium	$C_{12}H_{11}I_3N_2O_5$	643.78	
75	78649-41-9	Iomeprol	X-ray contrast medium	$C_{17}H_{22}I_3N_3O_8$	777.09	
76	60166-93-0	Iopamidol	X-ray contrast medium	$C_{17}H_{22}I_3N_3O_8$	777.09	
77	73334-07-3	Iopromide	X-ray contrast medium	$C_{18}H_{24}I_3N_3O_8$	791.11	
78	66108-95-0	Iohexol	X-ray contrast medium	$C_{19}H_{26}I_3N_3O_9$	821.14	
79	606-17-7	Iodipamide	X-ray contrast medium	$C_{20}H_{14}I_6N_2O_6$	1139.76	
80	59017-64-0	Ioxaglic acid	X-ray contrast medium	$C_{24}H_{21}I_6N_5O_8$	1268.88	
81	608-93-5	Pentachlorobenzene	Aromatic fungicide	C_6HCl_5	250.34	
82	118-74-1	Hexachlorobenzene	Aromatic fungicide	C_6Cl_6	284.76	
83	101-05-3	Anilazine	Triazine fungicide	$C_9H_5Cl_3N_4$	275.52	
84	10605-21-7	Carbendazim	Carbamate fungicide	$C_9H_9N_3O_2$	191.19	
85	36734-19-7	Iprodione	Imidazole fungicide	$C_{13}H_{13}Cl_2N_3O_3$	330.17	
86	43121-43-3	Triadimefon	Conazole and triazole fungicide	$C_{14}H_{16}ClN_3O_2$	293.75	
87	57837-19-1	Metalaxyl	Amide fungicide	$C_{15}H_{21}NO_4$	279.33	
88	66063-05-6	Pencycuron	Urea fungicide	$C_{19}H_{21}ClN_2O$	328.84	
89	87-68-3	Hexachlorobutadiene	Unclassified fungicide	C_4Cl_6	260.76	
90	709-98-8	Propanil	Amide herbicide	$C_9H_9Cl_2NO$	218.18	
91	23950-58-5	Propyzamide	Amide herbicide	$C_{12}H_{11}Cl_2NO$	256.13	
92	87-61-6	1,2,3-Trichlorobenzene	Aromatic herbicide	$C_6H_3Cl_3$	181.45	
93	120-82-1	1,2,4-Trichlorobenzene	Aromatic herbicide	$C_6H_3Cl_3$	181.45	
94	108-70-3	1,3,5-Trichlorobenzene	Aromatic herbicide	$C_6H_3Cl_3$	181.45	
95	1918-00-9	Dicamba	Aromatic acid herbicide	$C_8H_6Cl_2O_3$	221.04	
96	90717-03-6	Quinmerac	Aromatic acid herbicide	$C_{11}H_8ClNO_2$	221.64	
97	26225-79-6	Ethofumesate	Benzofuranyl alkylsulfonate herbicide	$C_{13}H_{18}O_5S$	286.34	

Sub. No	CAS RN[1]	Substance English name	Substance group[2]	Formula	Molar mass g mol^{-1}	Structure[3]
98	1918-18-9	Swep	Carbamate herbicide	$C_8H_7Cl_2NO_2$	220.05	
99	101-21-3	Chlorpropham	Carbamate herbicide	$C_{10}H_{12}ClNO_2$	213.66	
100	1967-16-4	Chlorbufam	Carbamate herbicide	$C_{11}H_{10}ClNO_2$	223.66	
101	101-27-9	Barban	Carbamate herbicide	$C_{11}H_9Cl_2NO_2$	258.10	
102	16118-49-3	Carbetamide	Carbamate herbicide	$C_{12}H_{16}N_2O_3$	236.27	
103	4849-32-5	Karbutilate	Carbamate herbicide	$C_{14}H_{21}N_3O_3$	279.33	
104	1918-16-7	Propachlor	Chloroacetanilide herbicide	$C_{11}H_{14}ClNO$	211.69	
105	15972-60-8	Alachlor	Chloroacetanilide herbicide	$C_{14}H_{20}ClNO_2$	269.77	
106	1582-09-8	Trifluralin	Dinitroaniline herbicide	$C_{13}H_{16}F_3N_3O_4$	335.28	
107	88-85-7	Dinoseb	Dinitrophenol herbicide	$C_{10}H_{12}N_2O_5$	240.22	
108	1836-75-5	Nitrofen	Diphenyl ether herbicide	$C_{12}H_7Cl_2NO_3$	284.09	
109	75-99-0	Dalapon	Halogenated aliphatic herbicide	$C_3H_4Cl_2O_2$	142.97	
110	1689-84-5	Bromoxynil	Nitrile herbicide	$C_7H_3Br_2NO$	276.91	
111	1689-83-4	Ioxynil	Nitrile herbicide	$C_7H_3I_2NO$	370.92	
112	94-75-7	2,4-D	Phenoxy herbicide	$C_8H_6Cl_2O_3$	221.04	
113	93-76-5	2,4,5-T	Phenoxy herbicide	$C_8H_5Cl_3O_3$	255.48	
114	94-82-6	2,4-DB	Phenoxy herbicide	$C_{10}H_{10}Cl_2O_3$	249.09	
115	94-74-6	MCPA	Phenoxy herbicide	$C_9H_9ClO_3$	200.62	
116	94-81-5	MCPB	Phenoxy herbicide	$C_{11}H_{13}ClO_3$	228.68	
117	120-36-5	Dichlorprop	Phenoxy herbicide	$C_9H_8Cl_2O_3$	235.07	
118	93-72-1	Fenoprop	Phenoxy herbicide	$C_9H_7Cl_3O_3$	269.51	
119	93-65-2	Mecoprop	Phenoxy herbicide	$C_{10}H_{11}ClO_3$	214.65	
120	95617-09-7	Fenoxaprop	Phenoxy herbicide	$C_{16}H_{12}ClNO_5$	333.72	
121	76578-14-8	Quizalofop-ethyl	Phenoxy herbicide	$C_{19}H_{17}ClN_2O_4$	372.80	
122	87237-48-7	Haloxyfop-ethoxyethyl ester	Phenoxy herbicide	$C_{19}H_{19}ClF_3NO_5$	433.70	

Sub. No	CAS RN[1]	Substance English name	Substance group[2]	Formula	Molar mass g mol^{-1}	Structure[3]
123	1698-60-8	Chloridazon	Pyridazinone herbicide	$C_{10}H_8ClN_3O$	221.66	
124	1702-17-6	Clopyralid	Pyridine herbicide	$C_6H_3Cl_2NO_2$	192.00	
125	1918-02-1	Picloram	Pyridine herbicide	$C_6H_3Cl_3N_2O_2$	241.46	
126	55335-06-3	Triclopyr	Pyridine herbicide	$C_7H_4Cl_3NO_3$	256.47	
127	69377-81-7	Fluroxypyr	Pyridine herbicide	$C_7H_5Cl_2FN_2O_3$	255.03	
128	81406-37-3	Fluroxypyr-1-methylheptyl ester	Pyridine herbicide	$C_{15}H_{21}Cl_2FN_2O_3$	367.24	
129	122-34-9	Simazine	Triazine herbicide	$C_7H_{12}ClN_5$	201.66	
130	1912-24-9	Atrazine	Triazine herbicide	$C_8H_{14}ClN_5$	215.69	
131	139-40-2	Propazine	Triazine herbicide	$C_9H_{16}ClN_5$	229.71	
132	41394-05-2	Metamitron	Triazinone herbicide	$C_{10}H_{10}N_4O$	202.21	
133	51235-04-2	Hexazinone	Triazinone herbicide	$C_{12}H_{20}N_4O_2$	252.31	
134	128621-72-7	Carfentrazone-ethyl metabolite	Triazolone herbicide	$C_{13}H_{10}Cl_2F_3N_3O_3$	384.14	
135	5902-51-2	Terbacil	Uracil herbicide	$C_9H_{13}ClN_2O_2$	216.66	
136	314-40-9	Bromacil	Uracil herbicide	$C_9H_{13}BrN_2O_2$	261.12	
137	2164-08-1	Lenacil	Uracil herbicide	$C_{13}H_{18}N_2O_2$	234.30	
138	25366-23-8	Thiazafluron	Urea herbicide	$C_6H_7F_3N_4OS$	240.21	
139	30043-49-3	Ethidimuron	Urea herbicide	$C_7H_{12}N_4O_3S_2$	264.33	
140	101-42-8	Fenuron	Urea herbicide	$C_9H_{12}N_2O$	164.21	
141	150-68-5	Monuron	Urea herbicide	$C_9H_{11}ClN_2O$	198.65	
142	1746-81-2	Monolinuron	Urea herbicide	$C_9H_{11}ClN_2O_2$	214.65	
143	3060-89-7	Metobromuron	Urea herbicide	$C_9H_{11}BrN_2O_2$	259.10	
144	330-54-1	Diuron	Urea herbicide	$C_9H_{10}Cl_2N_2O$	233.09	
145	330-55-2	Linuron	Urea herbicide	$C_9H_{10}Cl_2N_2O_2$	249.10	
146	13360-45-7	Chlorbromuron	Urea herbicide	$C_9H_{10}BrClN_2O_2$	293.96	
147	1929-88-0	Benzthiazuron	Urea herbicide	$C_9H_9N_3OS$	207.25	

Sub. No	CAS RN[1]	Substance English name	Substance group[2]	Formula	Molar mass g mol^{-1}	Structure[3]
148	34014-18-1	Tebuthiuron	Urea herbicide	$C_9H_{16}N_4OS$	228.31	
149	15545-48-9	Chlortoluron	Urea herbicide	$C_{10}H_{13}ClN_2O$	212.68	
150	19937-59-8	Metoxuron	Urea herbicide	$C_{10}H_{13}ClN_2O_2$	228.68	
151	2164-17-2	Fluometuron	Urea herbicide	$C_{10}H_{11}F_3N_2O$	232.20	
152	18691-97-9	Methabenzthiazuron	Urea herbicide	$C_{10}H_{11}N_3OS$	221.28	
153	34123-59-6	Isoproturon	Urea herbicide	$C_{12}H_{18}N_2O$	206.28	
154	3766-60-7	Buturon	Urea herbicide	$C_{12}H_{13}ClN_2O$	236.70	
155	555-37-3	Neburon	Urea herbicide	$C_{12}H_{16}Cl_2N_2O$	275.17	
156	1982-49-6	Siduron	Urea herbicide	$C_{14}H_{20}N_2O$	232.32	
157	1982-47-4	Chloroxuron	Urea herbicide	$C_{15}H_{15}ClN_2O_2$	290.75	
158	34205-21-5	Dimefuron	Urea herbicide	$C_{15}H_{19}ClN_4O_3$	338.79	
159	14214-32-5	Difenoxuron	Urea herbicide	$C_{16}H_{18}N_2O_3$	286.33	
160	25057-89-0	Bentazon	Unclassified herbicide	$C_{10}H_{12}N_2O_3S$	240.28	
161	61213-25-0	Flurochloridone	Unclassified herbicide	$C_{12}H_{10}Cl_2F_3NO$	312.12	
162	16752-77-5	Methomyl	Carbamate insecticide	$C_5H_{10}N_2O_2S$	162.21	
163	1563-66-2	Carbofuran	Carbamate insecticide	$C_{12}H_{15}NO_3$	221.23	
164	319-84-6	α-HCH	Organochlorine insecticide	$C_6H_6Cl_6$	290.83	
165	319-85-7	β-HCH	Organochlorine insecticide	$C_6H_6Cl_6$	290.83	
166	58-89-9	γ-HCH (Lindane)	Organochlorine insecticide	$C_6H_6Cl_6$	290.83	
167	319-86-8	δ-HCH	Organochlorine insecticide	$C_6H_6Cl_6$	290.83	
168	87-86-5	Pentachlorophenol	Organochlorine insecticide	C_6HCl_5O	266.34	
169	959-98-8	α-Endosulfan	Organochlorine insecticide	$C_9H_6Cl_6O_3S$	406.93	
170	115-29-7	β-Endosulfan	Organochlorine insecticide	$C_9H_6Cl_6O_3S$	406.93	
171	309-00-2	Aldrin	Organochlorine insecticide	$C_{12}H_8Cl_6$	364.91	
172	465-73-6	Isodrin	Organochlorine insecticide	$C_{12}H_8Cl_6$	364.91	

Sub. No	CAS RN[1]	Substance English name	Substance group[2]	Formula	Molar mass $g\ mol^{-1}$	Structure[3]
173	60-57-1	Dieldrin	Organochlorine insecticide	$C_{12}H_8Cl_6O$	380.91	
174	72-20-8	Endrin	Organochlorine insecticide	$C_{12}H_8Cl_6O$	380.91	
175	72-54-8	pp´-TDE	Organochlorine insecticide	$C_{14}H_{10}Cl_4$	320.04	
176	72-55-9	pp´-DDE	Organochlorine insecticide	$C_{14}H_8Cl_4$	318.03	
177	789-02-6	op´-DDT	Organochlorine insecticide	$C_{14}H_9Cl_5$	354.49	
178	50-29-3	pp´-DDT	Organochlorine insecticide	$C_{14}H_9Cl_5$	354.49	
179	121-75-5	Malathion	Organophosphorus insecticide	$C_{10}H_{19}O_6PS_2$	330.36	
180	470-90-6	Chlorfenvinphos	Organophosphorus insecticide	$C_{12}H_{14}Cl_3O_4P$	359.57	
181	2921-88-2	Chlorpyrifos-ethyl	Organophosphorus insecticide	$C_9H_{11}Cl_3NO_3PS$	350.58	
182	83121-18-0	Teflubenzuron	Insect growth regulators	$C_{14}H_6Cl_2F_4N_2O_2$	381.11	
183	35367-38-5	Diflubenzuron	Insect growth regulators	$C_{14}H_9ClF_2N_2O_2$	310.69	
184	75-09-2	Dichloromethane	VOC Halogenated hydrocarbon	CH_2Cl_2	84.93	
185	67-66-3	Chloroform	VOC Trihalomethane	$CHCl_3$	119.38	
186	75-27-4	Bromodichloromethane	VOC Trihalomethane	$CHBr_1Cl_2$	163.83	
187	124-48-1	Dibromochloromethane	VOC Trihalomethane	$CHBr_2Cl_1$	208.28	
188	75-25-2	Bromoform	VOC Trihalomethane	$CHBr_3$	252.73	
189	107-06-2	1,2-Dichloroethane	VOC Halogenated hydrocarbon	$C_2H_4Cl_2$	98.96	
190	71-55-6	1,1,1-Trichloroethane	VOC Halogenated hydrocarbon	$C_2H_3Cl_3$	133.40	
191	79-00-5	1,1,2-Trichloroethane	VOC Halogenated hydrocarbon	$C_2H_3Cl_3$	133.40	
192	56-23-5	Tetrachloromethane	VOC Halogenated hydrocarbon	CCl_4	153.82	
193	75-01-4	Vinyl chloride (chloroethene)	VOC Halogenated hydrocarbon	C_2H_3Cl	62.50	
194	75-35-4	1,1-Dichloroethene	VOC Halogenated hydrocarbon	$C_2H_2Cl_2$	96.94	
195	156-59-2	cis-1,2-Dichloroethene	VOC Halogenated hydrocarbon	$C_2H_2Cl_2$	96.94	
196	156-60-5	trans-1,2-Dichloroethene	VOC Halogenated hydrocarbon	$C_2H_2Cl_2$	96.94	
197	540-49-8	1,2-Dibromoethene	VOC Halogenated hydrocarbon	$C_2H_2Br_2$	185.85	

Sub. No	CAS RN[1]	Substance English name	Substance group[2]	Formula	Molar mass g mol^{-1}	Structure[3]
198	79-01-6	Trichloroethene	VOC Halogenated hydrocarbon	C_2HCl_3	131.39	
199	127-18-4	Tetrachloroethene	VOC Halogenated hydrocarbon	C_2Cl_4	165.83	
200	78-87-5	1,2-Dichloropropane	VOC Halogenated hydrocarbon	$C_3H_6Cl_2$	112.99	
201	96-12-8	1,2-Dibromo-3-chloropropane	VOC Halogenated hydrocarbon	$C_3H_5Br_2Cl$	236.33	
202	10061-01-5	Z-1,3-Dichloropropene	VOC Halogenated hydrocarbon	$C_3H_4Cl_2$	110.97	
203	10061-02-6	E-1,3-Dichloropropene	VOC Halogenated hydrocarbon	$C_3H_4Cl_2$	110.97	
204	71-43-2	Benzene	VOC Aromatic hydrocarbon	C_6H_6	78.11	
205	108-88-3	Toluene	VOC Aromatic hydrocarbon	C_7H_8	92.14	
206	95-47-6	o-Xylene	VOC Aromatic hydrocarbon	C_8H_{10}	106.17	
207	106-42-3	p-Xylene	VOC Aromatic hydrocarbon	C_8H_{10}	106.17	
208	100-41-4	Ethylbenzene	VOC Aromatic hydrocarbon	C_8H_{10}	106.17	
209	2371-42-8	2-Methylbornanol	VOC Odorous organic chemical	$C_{11}H_{20}0$	168.28	
210	19700-21-1	Geosmin	VOC Odorous organic chemical	$C_{12}H_{22}O$	182.30	
211	1634-04-4	MTBE	VOC Oxygenate gasoline additive	$C_5H_{12}O$	88.15	
212	637-92-3	ETBE	VOC Oxygenate gasoline additive	$C_6H_{14}O$	102.17	
213	994-05-8	TAME	VOC Oxygenate gasoline additive	$C_6H_{14}O$	102.17	

IV TRANSMIC - Mass transfer and microbiological degradation in the pollutant/water/sediment system

FKZ: 02WT1130

Water Technology Center, Department of Environmental Biotechnology, Karlsruhe, Germany

Irene Kranzioch

Andreas Tiehm

Figure IV-1: View from the dam upstream Photo: RD Wilken

1 Introduction

The main objective of the project was to extend the knowledge of interactions between the water body, sediment and the microbiological degradation of chlorinated pollutants within this system. One intention was to investigate the microbiological transformation processes of model substances during different reductive-oxidative-conditions. With this study the understanding of anaerobic microbiological conversion processes was improved and a risk assessment and prediction of pollutant behaviour within the water body and sediment is possible. The enhancement and application of up-to-date molecular biological techniques provided extended insight into the involved microorganisms and provides new methods for fast and precise detection of the degradation processes. The developed methods extend the existing toolbox and result in an improved process understanding. The project was settled within the frame of the Sino-German Yangtze Project and in the research field of water technologies. In this study the microbiological conversion processes of chlorinated pollutants and the detection of microorganisms and their catabolic enzymes in the Three Gorges Reservoir (TGR) were examined. The acquired results and developed methods are useful for environmental applications in both countries China as well as Germany.

2 Results and Discussion

2.1 Yangtze River and Three Gorges Reservoir

The Yangtze River is with a length of 6,300 km, a mean annual water discharge of 29,400 m^3/s and a sediment load of 500 million tons/year one of the largest rivers world wide (Zhang 1995). In the last decades, pollutant discharge into Chinese rivers has increased because of growing industrial development and the widespread application of fertilizers, pesticides and herbicides in agriculture (Müller et al. 2008). Additionally, changes in water quantity, quality, and the aquatic ecosystems have to be expected from large dam constructions, such as the Three Gorges Dam (TGD) at the Yangtze. With the impoundment of the 630 km long TGR, upstream the TGD huge industrial, residential and agricultural areas were flooded. In consequence notable amounts of organic and inorganic pollutants were released to the reservoir (Wolf et al. 2013). Within the joint Sino-German-research project the objective was to obtain more insight into environmental processes under these highly dynamic conditions (Bergmann et al. 2012). To achieve this aim the experiments were composed of following topics:

- Analysis of TGR sediment and water samples
- Anaerobic degradation of chlorinated ethenes with Yangtze River sediment and Yangtze River enrichment cultures
- Evaluation of the substrate spectrum of the TGR cultures
- Oxygen tolerance of the TGR cultures
- mRNA expression analysis with the TGR cultures

2.2 Analysis of TGR sediment and water samples

There are several groups of bacteria which are able to degrade chlorinated aliphatic and aromatic hydrocarbons under anaerobic conditions. Microorganisms which are known to be able to reductively dechlorinate pollutants are *Desulfomonile* spp., *Desulfitobacterium* spp., *Dehalobacter* spp., *Desulfuromonas* spp. and *Dehalococcoides* spp. But only bacteria of the genus *Dehalococcoides* spp. are capable for the complete degradation of tetrachloroethene (PCE) to ethene (Holliger et al. 1993; Schmidt et al. 2006; Aktaş et al. 2011). 57 samples were taken within a two years period and screened for the five dechlorinating microorganisms *Desulfomonile* spp., *Desulfitobacterium* spp., *Dehalobacter* spp., *Desulfuromonas* spp. and *Dehalococcoides* spp. An overview of the reservoir and the sampling locations from the first sampling campaign in March 2011 is given in Figure IV-2.

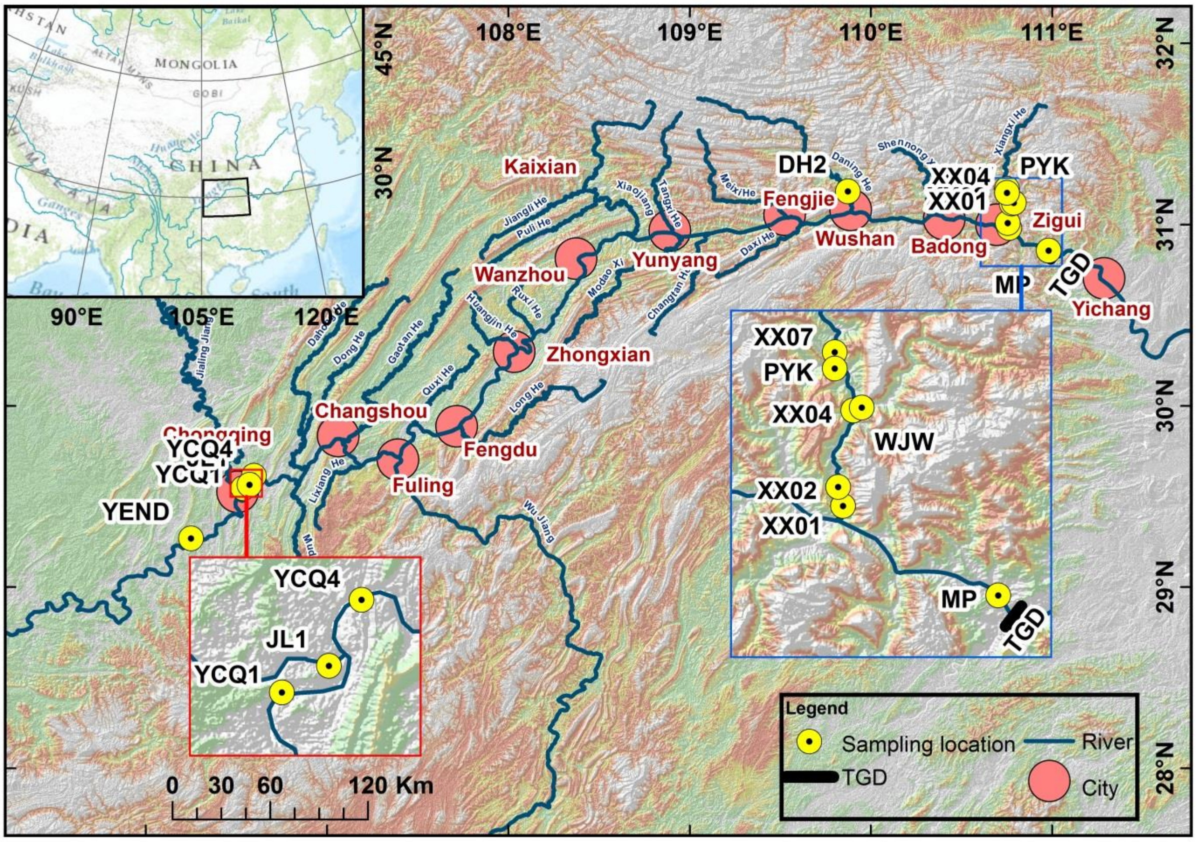


Figure IV-2: Sampling locations in the TGR (Sampling campaign 2011)

In March 2011, 18 sediment samples were taken. In August and December 2011, it was possible to obtain bacterial DNA from 17 water samples from different sampling locations within the TGR. Further in June 2012 it was possible to take sediment and water samples from different depths of the water body from the Yangtze River, the Daning He River and the Xiangxi River.

Table IV-1: Results of the screening for dechlorinating microorganisms

Sampling time	Sample name	Sample location	Sample type	Dechlorinating microorganism				
				Dhc	Dsb	DeSu	Deha	DeTi
March 2011	**MP1**	Maoping Dam Region	Sediment			+	+	
	MP2					+		
	MP3					+		+
	MP4					+		
	MP5					+		+
	MP6							
	MP7				+	+		+
	PYK	Xiangxi River						
	WJW					+		+
	XX01				+	+		
	XX02				+			+
	XX04							+
	XX07				+	+		+
	DH2	Daninghe River				+		+
	YCQ1	Chongqing Yangtze River				+		+
	YCQ4					+		+
	JL1	Chongqing Jialing River				+		
	YEnd	Yangtze Reservoir End				+		
August 2011	MB07 40m	Daninghe River	Water	+	+			
	MB08 20m			+				
	MB09 0m			+				
	MB13 20m							
	MB14 10m							
	MB15 0m							
December 2011	WSA1 50m	Wushan Lake and Daninghe River	Water					
	WSA2 25m				+			
	WSH3 45m				+			
	WSH4 20m				+			
	WSH5 0m				+			
	WSH6 50m				+			
	WSH7 25m							
	WSH8 0m							
	DaL1 40m				+			
	DaL2 15m				+			
	DaL3 0m				+			
June 2012	WL1 0m	Wushan Lake and Daninghe River	Water		+			
	WL1 18m				+			+
	WL2 0m							
	WL2 10m				+			
	WL2 25m				+		+	
	WL3 0m				+			+
	WL3 15m				+			
	WL3 30m				+			+
	DaH1 0m				+			
	DaH1 10m				+			
	DaH1 15m				+			+
	PYK 5m	Xiangxi River			+			
	XX01 0m				+			
	XX01 65m				+			+
	XX03 0m				+			
	XX03 10m				+			
	WL2	Wushan Lake and Daninghe River	Sediment		+	+		
	WL3				+	+		+
	DaH1				+	+		
	PYK	Xiangxi River			+	+		+
	XX01				+	+		+
	XX03				+	+		+
Sum of detections:	57			3	34	20	2	19

Overall 57 sediment or water samples were taken within the TGR region. In most of the samples at least one of the five dechlorinating bacteria could be found. In two sediment and seven water samples none of the analysed bacteria were detected. Within the 48 samples, where at least one of the dechlorinators was found, the distribution was as follows: 3 detections of *Dehalococcoides* spp., 34 detections of *Desulfitobacterium* spp., 20 detections of *Desulfuromonas* spp., two detections of *Dehalobacter* spp. and 19 detections of

Desulfomonile spp. In this part of the study, the presence of dechlorinating bacteria in Yangtze sediment and water samples was demonstrated, thus indicating their relevance for pollutant turnover in the catchment area. The applied PCR methods proved to be suitable for the detection of the different dechlorinating bacteria. The next step was to test if the detected dechlorinating bacteria are viable and have the capability to degrade chlorinated pollutants.

2.3 Dechlorination tests with chlorinated Ethenes

Nine of the 18 sediment samples taken in March 2011 were used to prepare batch degradation tests with PCE. Further, one sediment from June 2012 was used to proof the ability of the indigenous microorganisms from the sediment to dechlorinate PCE without any additions of auxiliary substrates.

For the dechlorination experiments with PCE and auxiliary substrates sediments were chosen in which at least one of the dechlorinating bacteria groups was detected. In none of the nine sediments *Dehalococcoides* spp. was detected so a complete dechlorination to the end product ethene was not expected at this point of the study. The following dechlorinators were detected in the sediments used for the dechlorination experiments with PCE:

MP1 *Desulfuromonas* spp. and *Dehalobacter* spp.;
MP3 *Desulfuromonas* spp. and *Desulfomonile* spp.;
MP7 *Desulfitobacterium* spp., *Desulfuromonas* spp. and *Desulfomonile* spp.;

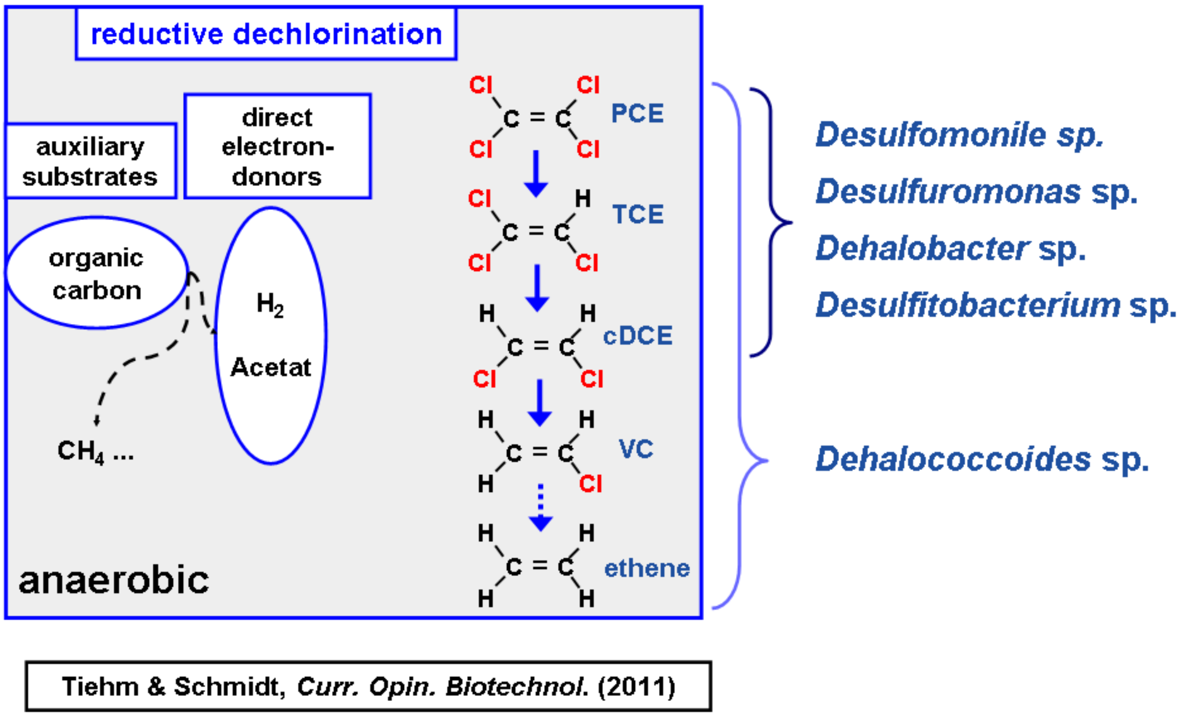


Figure IV-3: PCE degradation pathway

XX01 *Desulfitobacterium* spp. and *Desulfuromonas* spp.;
XX04 *Desulfitobacterium* spp., *Desulfuromonas* spp. and *Desulfomonile* spp.;
XX07 *Desulfitobacterium* spp., *Desulfuromonas* spp. and *Desulfomonile* spp.;
DH2 *Desulfuromonas* spp. and *Desulfomonile* spp.;
YCQ1 *Desulfuromonas* spp. and *Desulfomonile* spp.;
YCQ4 *Desulfuromonas* spp. and *Desulfomonile* spp.;
and
XX01 from year 2012 *Desulfitobacterium* spp., *Desulfuromonas* spp. and *Desulfomonile* spp.

In all batch experiments PCE was dechlorinated to less chlorinated Ethenes. The PCE dechlorination occurs via TCE and DCE to VC and the nonchlorinated endproduct Ethene (Figure IV-3). In the case of DCE there are three different isomers cDCE, tDCE and 1,1-DCE. cDCE is mainly found as an intermediate, or an end product, during the dechlorination of PCE.

The culture MP1 dechlorinated PCE to only cDCE as an end product, MP3 to VC and all other cultures were able to completely dechlorinate PCE to the end product Ethene. Interestingly the cultures XX04, XX07 and DH2 did not form cDCE as a major intermediate but tDCE. Despite *Dehalococcoides* spp. were below the detection limit in the initial sediment screening (Table IV-1) seven of the nine batch cultures were able to completely dechlorinate PCE to the end product ethene.

In the next step, the cultures were followed by molecular biological analysis of the genes of *Desulfomonile* spp., *Desulfitobacterium* spp., *Dehalobacter* spp., *Desulfuromonas* spp. and

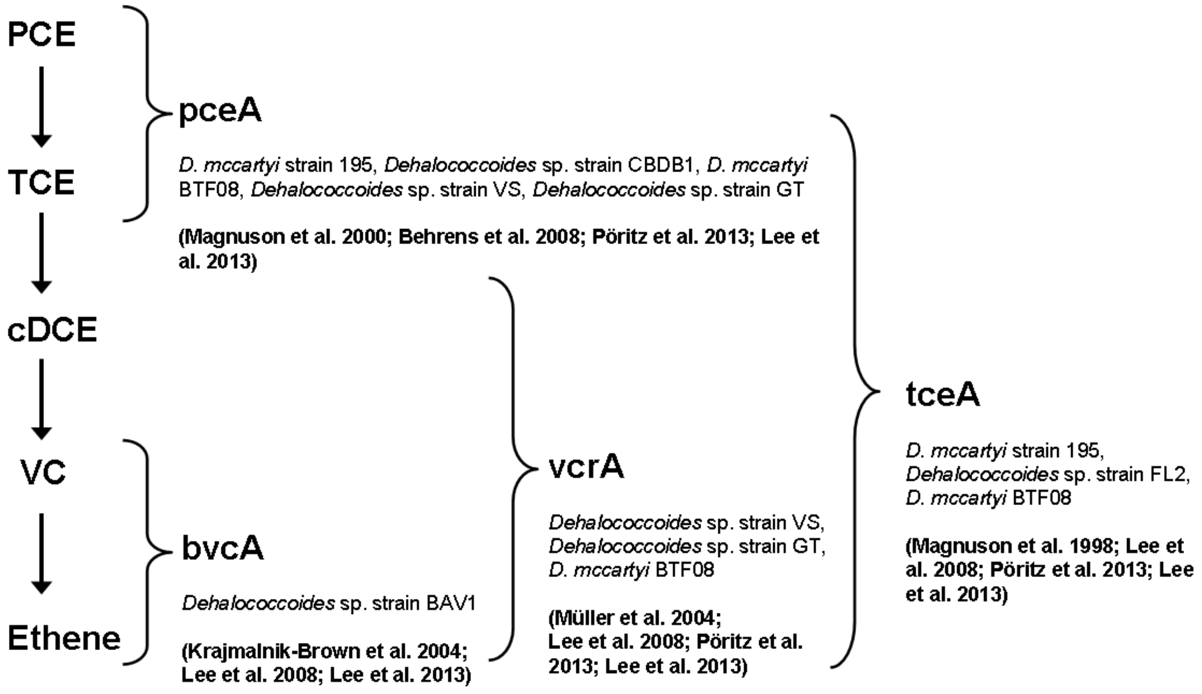


Figure IV-4: Dehalogenase genes of Dehalococcoides spp.

Dehalococcoides spp. Further for the group *Dehalococcoides* spp. the genes of the dehalogenase enzymes *pceA*, *tceA*, *vcrA* and *bvcA* were analysed with qPCR to follow their growth. An overview of the current knowledge with respect to the involved genes is shown in Figure IV-4.

In the cultures MP7, XX01, XX04, XX07, DH2, YCQ1 and YCQ4 an increase in *Dehalococcoides* spp. genes was found during the dechlorination of DCE via VC to Ethene. In the sediments and at the beginning of the experiments *Dehalococcoide*s spp. was below the detection limit of the method, but in the degradation experiments the gene copies increased beyond the detection limit. In the culture MP1 *Dehalococcoides* spp. was not found within the culture. Consistent with the PCR analysis, PCE dechlorination stopped at the level of cDCE. In Figure IV-4 exemplarily a degradation experiment with complete dechlorination to ethene is shown.

Desulfomonile spp. and *Desulfitobacterium* spp. showed an increase of about one order of magnitude during the dechlorination of PCE over TCE to DCE. Whereupon *Desulfitobacterium* spp. was mainly growing during the dechlorination of PCE to TCE and *Desulfomonile* spp. showed a more shallow slope but was increasing until all TCE was depleted. Further *Dehalococcoides* spp. showed an increase during the dechlorination step of TCE to DCE of about four orders of magnitude from below the quantification limit to about 10^6 copies/mL. The *Dehalococcoides* spp. genes were increasing until the end of the experiment after 28 weeks and reached a maximum value of nearly 10^8 copies/mL. Also *Dehalobacter* spp. was detected within the experiments, but it first showed a decrease of about one order of magnitude and then stayed at a constant level of about 10^3 copies/mL. Further the genes for *pceA*, *tceA*, *vcrA* and *bvcA*, which are encoding for the reductive dehalogenases of *Dehalococcoides* spp. were analysed with qPCR during the experimental time. The reductive dehalogenase genes showed specific patterns: the *pceA* gene copies/mL were mainly increasing during the dechlorination of TCE to DCEs and the *tceA* and *vcrA* gene copies/mL during the dechlorination of DCEs to VC and Ethene. Different *Dehalococcoides* spp. contain different of the dehalogenase genes, e.g. *Dehalococcoides* spp. strain BAV-1 carries the gene for the *bvcA* reductive dehalogenase and can catalyze the dechlorination step from VC to Ethene. It was clearly shown that all nine sediments contained active dechlorinating microorganisms, which were able to dechlorinate PCE at least to cDCE.

In most of the experiments auxiliary substrates (Yeast extract, NaAcetate, NaPyruvate and Hydrogen) were added to provide the electron donors necessary for reductive dechlorination (see Figure IV-5). Therefore, additional tests were set up to simulate field conditions. In these experiments, Yangtze River sediment was used without any addition of external auxiliary substrates. The results of the dechlorination experiments with sediments only amended with PCE and mineral medium or water are shown in Figure IV-6.

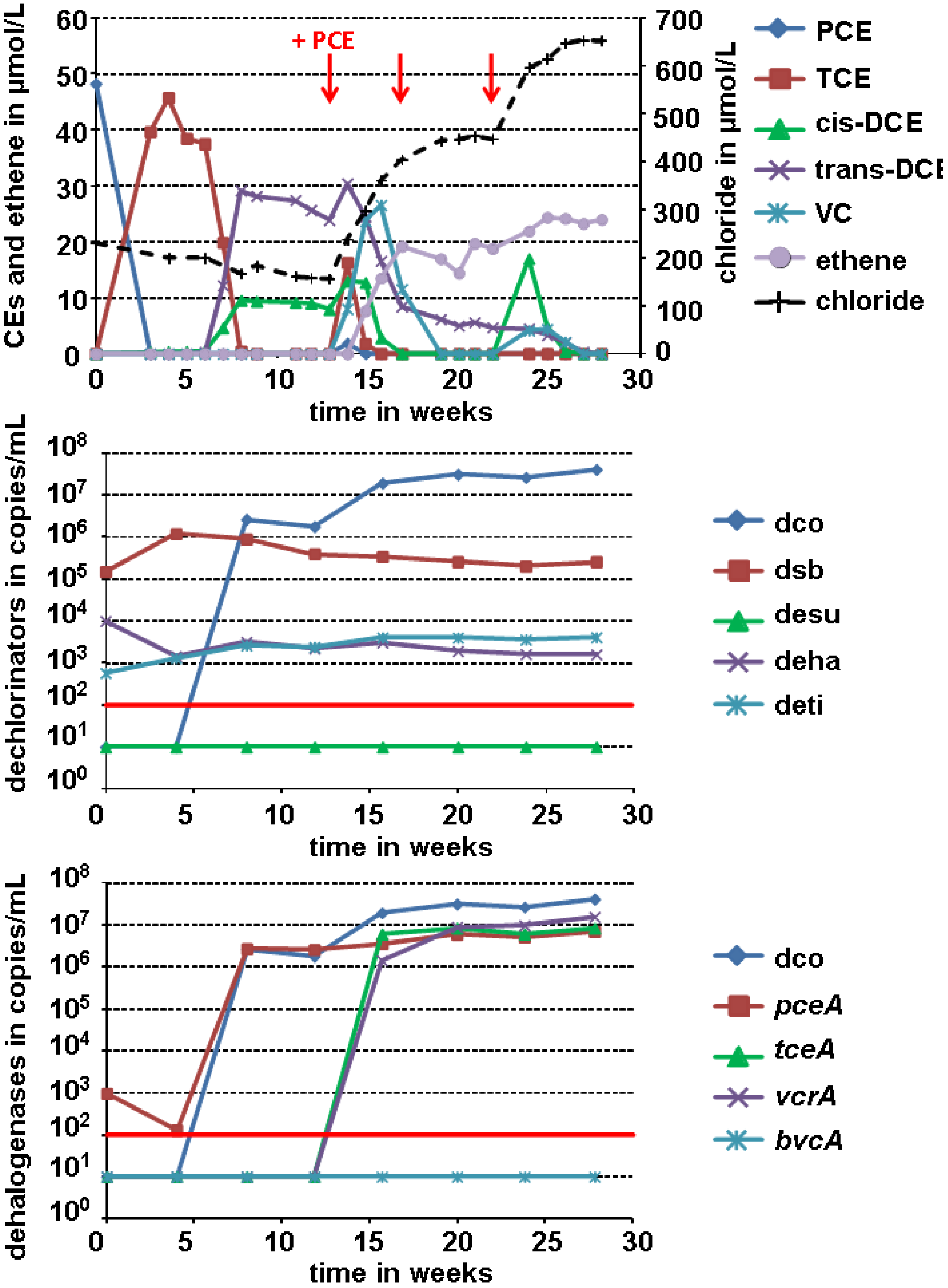


Figure IV-5: Dechlorination of PCE (top), dechlorinating microorganisms (middle), reductive dehalogenase genes (bottom) of the culture XX07

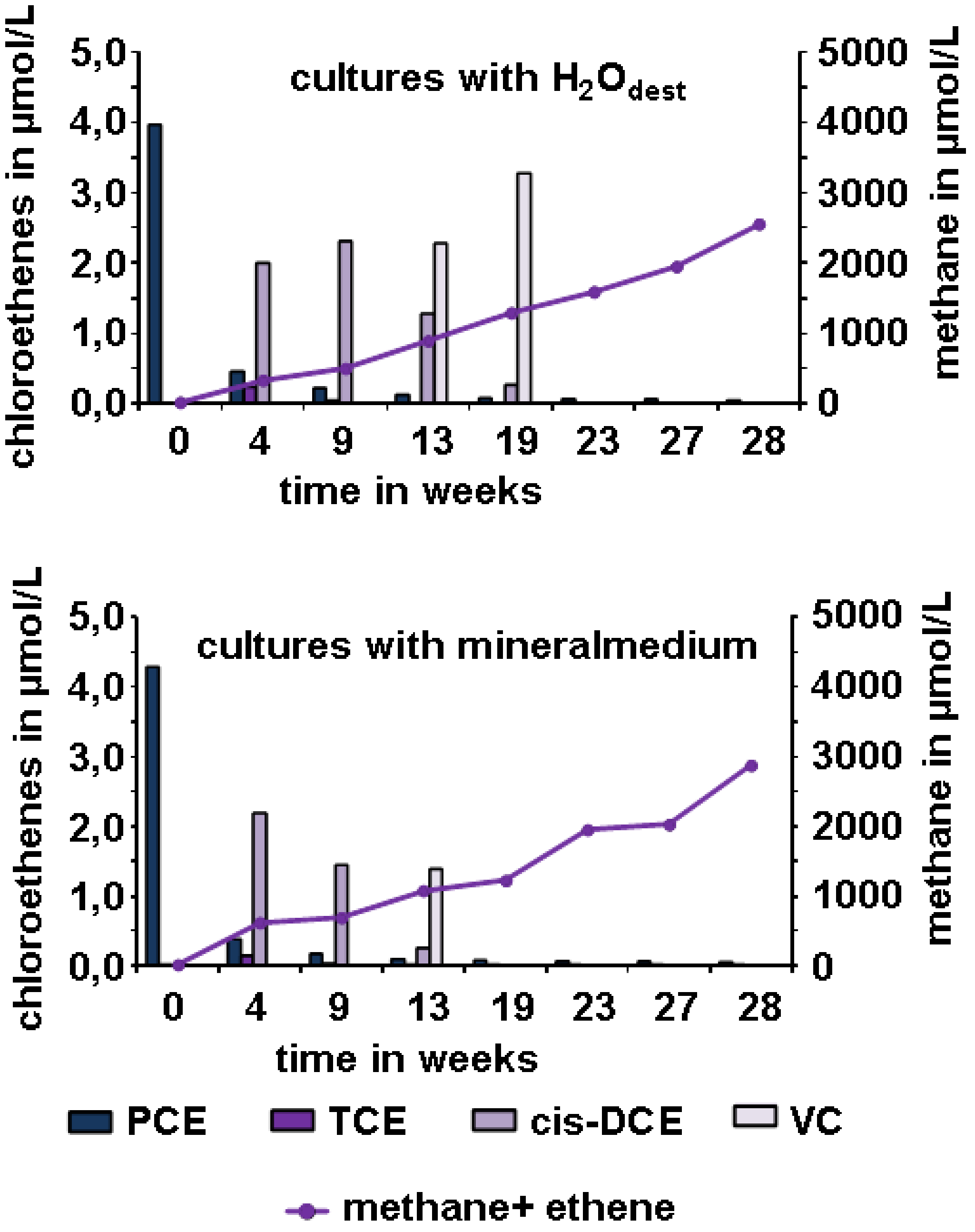


Figure IV-6: PCE dechlorination through batch samples with sediments from sampling location XX01 in year 2012

The sediment XX01 (2012) was able to completely dechlorinate PCE within 28 weeks. Only small differences were found between the experiments with water and mineral medium. Further a high methane production was detected in the cultures. With these experiments it was clearly shown, that the TGR sediments contain viable active dechlorinating microorganisms, which show the ability to dechlorinate PCE without any external addition of mineral salts or auxiliary substrates. Obviously, the organic compounds associated with the sediment (TOC: 1,3%) are used as natural electron donors. Therefore, it is likely that reductive dechlorination occurs also under field conditions.

2.4 Substrate spectrum of the TGR cultures

PCE has been reported as a pollutant in Chinese surface water (Li et al. 2006, Han et al. 2011, Wolf et al. 2013). In particular in river sediments, several other hydrophobic chlorinated pollutants are relevant in China and worldwide, including Hexachlorocyclohexanes (HCHs) (Wang et. al. 2009), Chlorobenzenes (CBs), Chlorophenols (CPs) (Tang et. al. 2007), and Polychlorinated Biphenyls (PCBs) (Jiang et. al 2000, Wang et. al 2009).

Hexachlorocyclohexanes (HCHs)

1,2,3,4,5,6-HCH is a monocyclic chlorinated hydrocarbon. It exists in 8 different isomers, but only the four isomers (α, β, γ, δ) were used in commercial pesticides (Willet et. al. 1998). γ-HCH also known as Lindan has the highest pesticidal activity of the four isomers and it was mainly used as an insecticide. The use of the insecticide (Lindan) caused diffuse contaminations. α-, β- and δ-HCH remained as by-products during the Lindan production and were stored at open-air waste sites. Due to the open storage the by-products (α-, β- and δ-HCH) caused point source contaminations (Lal et al. 2010). The application of HCHs is generally banned nowadays, because of their toxicities, environmental persistence and accumulation in food chains (Quintero et. al. 2005). *Dehalobacter* spp. is one of the microorganisms known to anaerobicaly dechlorinate HCHs. α- and γ-HCH are faster degraded than β- and δ-HCH (Lal et al.. 2010).

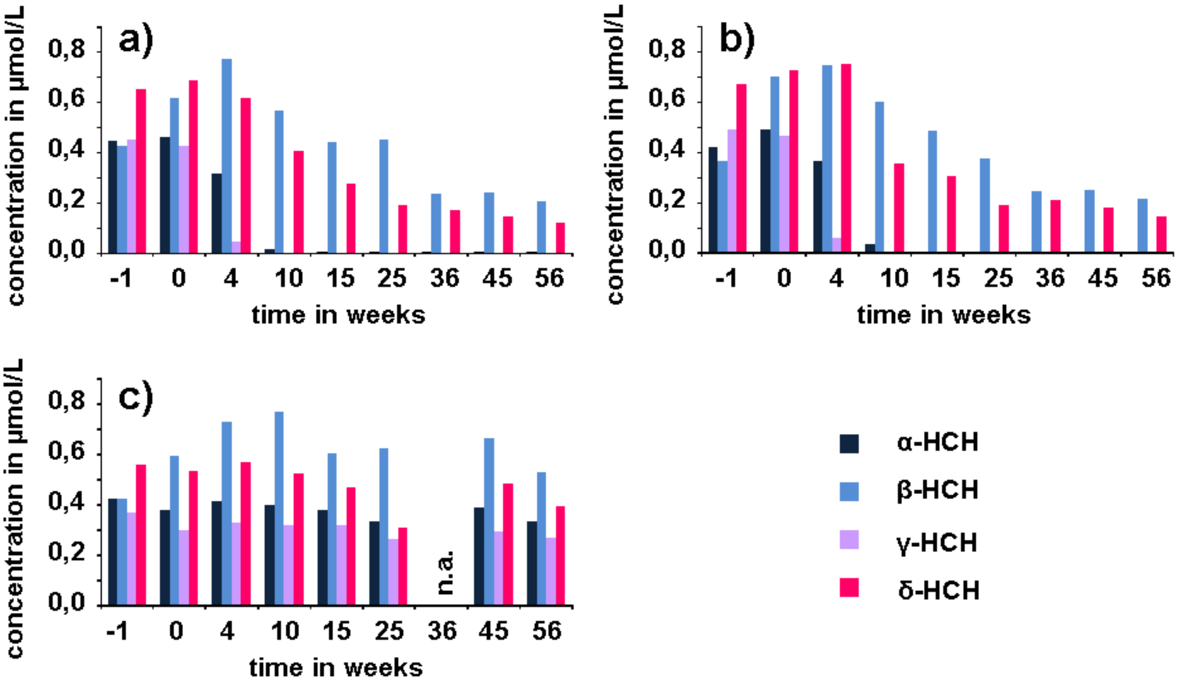


Figure IV-7: Degradation of HCH

For the two Yangze River cultures and the abiotic control, which were amended with the mixture of α-, β-, γ- and δ-HCH, the pattern of the HCHs was followed for 56 weeks (Figure

IV-7). The active cultures (Figure IV-7 a) and b)) showed in the first four weeks a fast decrease in γ-HCH. Further a fast decrease in concentration was found for α-HCH. The concentration of α-HCH in the active cultures was at the beginning 0.47 µmol/L and after 10 weeks 0.03 µmol/L. After 15 weeks both substances were below the detection limit. For the abiotic control no significant decline for α-HCH and γ-HCH was observed. β- and δ-HCH showed a decrease in the active cultures to a value of 0.2 and 0.15 µmol/L. The decrease in the active cultures was more pronounced than in the sterile control.

Pentachlorophenol (PCP)

Chlorophenols consist of a Benzene-ring with an OH-group, which is substituted with one to five chlorine atoms. Depending on the position of the chlorine atoms 19 different CPs are existing: Pentachlorophenol (PCP), 3 Tetrachlorophenols (TeCPs), 6 Trichlorophenols (TCPs), 6 Dichlorophenols (DCPs) and 3 (Mono-)Chlorophenols (CPs) (Adrian et al. 2007, Gao et al.. 2008). There are several sources of CP contamination in the environment. CPs were used as pesticides, herbicides, fungicides, mould inhibitors and as wood preservatives. Other sources of contamination are accidental spills, hazardous waste disposal sites, storage tanks or municipal landfills (Olanarian & Igbinosa 2011). PCP is known to be anaerobically dechlorinated by the strains *Dehalococcoides* spp. and *Desulfomonile* spp. (Mohn & Kennedy 1992, Adrian et al. 2007). For lower chlorinated phenols also *Desulfitobacterium* spp. has shown dechlorinating activity (Gerritse 1996).

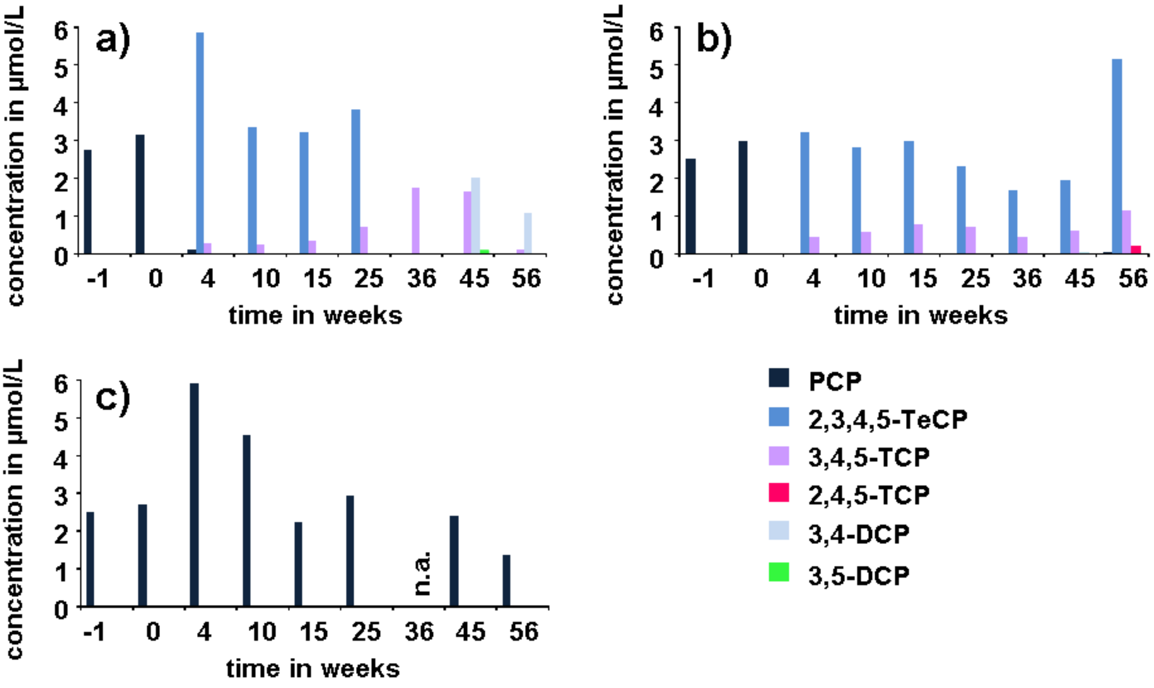


Figure IV-8: Dechlorination of PCP and its dechlorination products

In Figure IV-8 the degradation pattern of the cultures amended with PCP are shown. In the active cultures Figure IV-8 a) and b) a fast dechlorination of the 3 µmol/L PCP to mainly 3 to 5 µmol/L TeCP and small amounts of 0.4 µmol/L TCP could be observed in the first four weeks. For culture a) the dechlorination pathway was as follows; PCP, 2,3,4,5-TeCP, 3,4,5-TCP mainly to 3,4-DCP and minor to 3,5-DCP. In culture b) the dechlorination pathway was PCP, 2,3,4,5-TeCP to mainly 3,4,5-TCP and small amounts of 2,4,5-TCP. In the sterile control no TeCPs and TCPs were formed within 56 weeks.

Hexachlorobenzene (HCB)

Chlorinated benzenes consist of a benzene ring, which is substituted with one to six chlorine atoms. Depending on the position of the chlorine atom 12 different CBs are existing: Hexachlorobenzene (HCB), Pentachlorobenzene (PeCB), 3 Tetrachlorobenzenes (TeCBs), 3 Trichlorobenzenes (TCBs), 3 Dichlorobenzenes (DCBs) and Chlorobenzene (CB) (Field & Sierra-Alvarez 2008a). CBs have various uses in industry, such as additives in oil, lubricants, dye-carriers, dielectric insulation-reagents and as solvents. They are also intermediates in the industrial production of drugs, scents, dye stuff, herbicides, and insecticides (Adrian & Görisch 2002). Due to its use as a solvent and fungicide HCB has been released to the environment (Wu et al. 2002). Anaerobic dechlorination of higher chlorinated benzenes was proofed for *Dehaloccoides* spp. (Field & Sierra-Alvarez 2008a) and for lower chlorinated benzenes for *Dehalobacter* spp. (Nelson 2011).

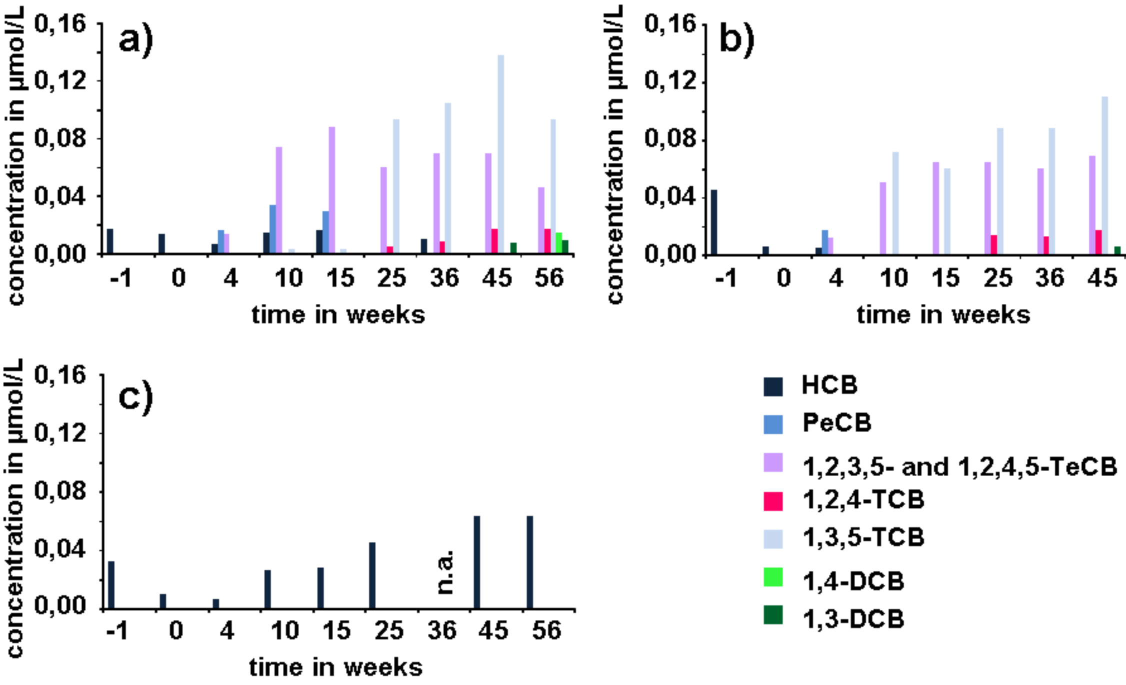


Figure IV-9: Dechlorination of HCB and its dechlorination products

For the Yangtze River cultures spiked with HCB, the dechlorination can be seen in Figure IV-9. The found dechlorination pathway was in both active cultures HCB, PeCB, 1,2,4,5- or 1,2,3,5-TeCB to mainly 1,3,5-TCB and small amounts of 1,2,4-TCB. Following 1,3,5- and 1,2,4-TCB to 1,3- and 1,4-DCB. 1,3,5-TCB showed higher concentrations (0.14µmol/L) compared to the spiked HCB (0.02µmol/L). The reason for the higher concentration of the dechlorination product is the better water solubility of 1,3,5-TCB of 6mg/L, which is 1000 times higher than the water solubility of HCB.

Polychlorinated Biphenyls (PCB)

Polychlorinated Biphenyls are composed of a Biphenyl-core with one to ten chlorine atoms. The different positions and combinations of the chlorine atoms lead to a group of 209 different PCB congeners. PCBs have been extensively used in industry from the 1920s to the 1970s, as heat transfer fluids, hydraulic fluids, solvent extenders, plasticizers, flame retardants, organic diluents and dielectric fluids (Abramowicz 1995). Reductive dehalogenation is very important, because with the reduction of chlorine atoms also the carcinogenic potential of the substances is reduced (Abramowicz 1995). Only few bacterial species have been proofed to have the ability of dechlorinating PCBs. These species are *Dehalococcoides* spp. (Bedard et al. 2007), Bacterium o-17 and DF1, which are both closely related to *Dehalococcoides* spp. and belong to the *Chloroflexi* phylum (Field et al. 2008 b).

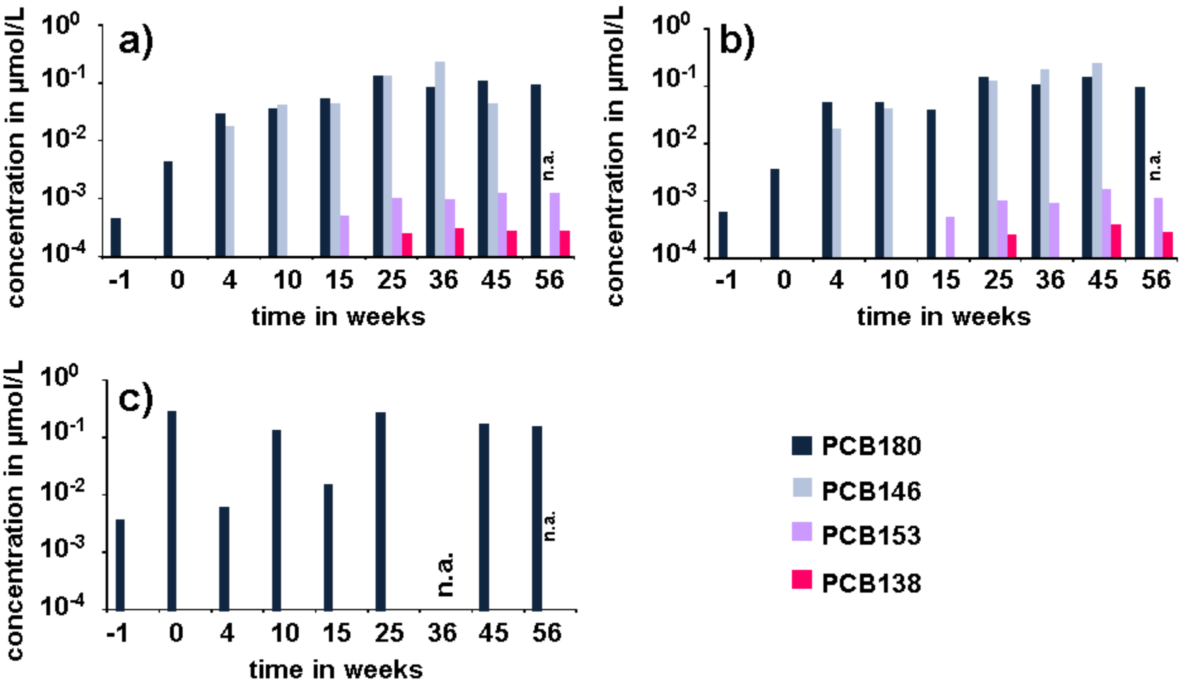


Figure IV-10: Dechlorination of PCB180 and its dechlorination products

The concentration of PCB180 was increasing over the complete experimental time, from starting values of about 5x10^{-3} µmol/L to the highest value of about 1x10^{-1} µmol/L after 45 weeks (see Figure IV-10 a) and b)). In the sterile control (Figure IV-10c) the concentration of PCB180 was also varying during experiment, from values of 4x10^{-3} µmol/L to about 3x10^{-1} µmol/L. In the active cultures a) and b) PCB146, PCB153 and 138, could be detected after 4, 15 and 25 weeks. In the sterile control none of the lower chlorinated PCBs could be detected.

With our findings we were able to demonstrate the capability of the indigenous microbial community of Yangtze River sediments to dechlorinate a wide spectrum of relevant chlorinated pollutants. The results indicate that the degradation processes are likely to occur also under field conditions and contribute to a continuous transformation in Yangtze River sediments.

2.5 Oxygen tolerance of the Yangtze River cultures

Contaminated aquifers or river sediments often are anaerobic but can be exposed to oxygen for short periods due to varying hydrological conditions. Especially in the Yangtze River a shift of sediment associated microorganisms from anaerobic to aerobic regions is feasible due to turbulent water flow. Some microorganisms (e.g. *Dehalococcoides* spp.) are thought to be strictly anaerobic and contact with oxygen is harmful to them. Therefore the Yangtze-culture was tested for its oxygen tolerance. The culture was held for 72h under aerobic conditions, and afterwards the anaerobic dechlorination of PCE was examined. The PCE dechlorination was followed for 13 weeks (see Figure IV-11).

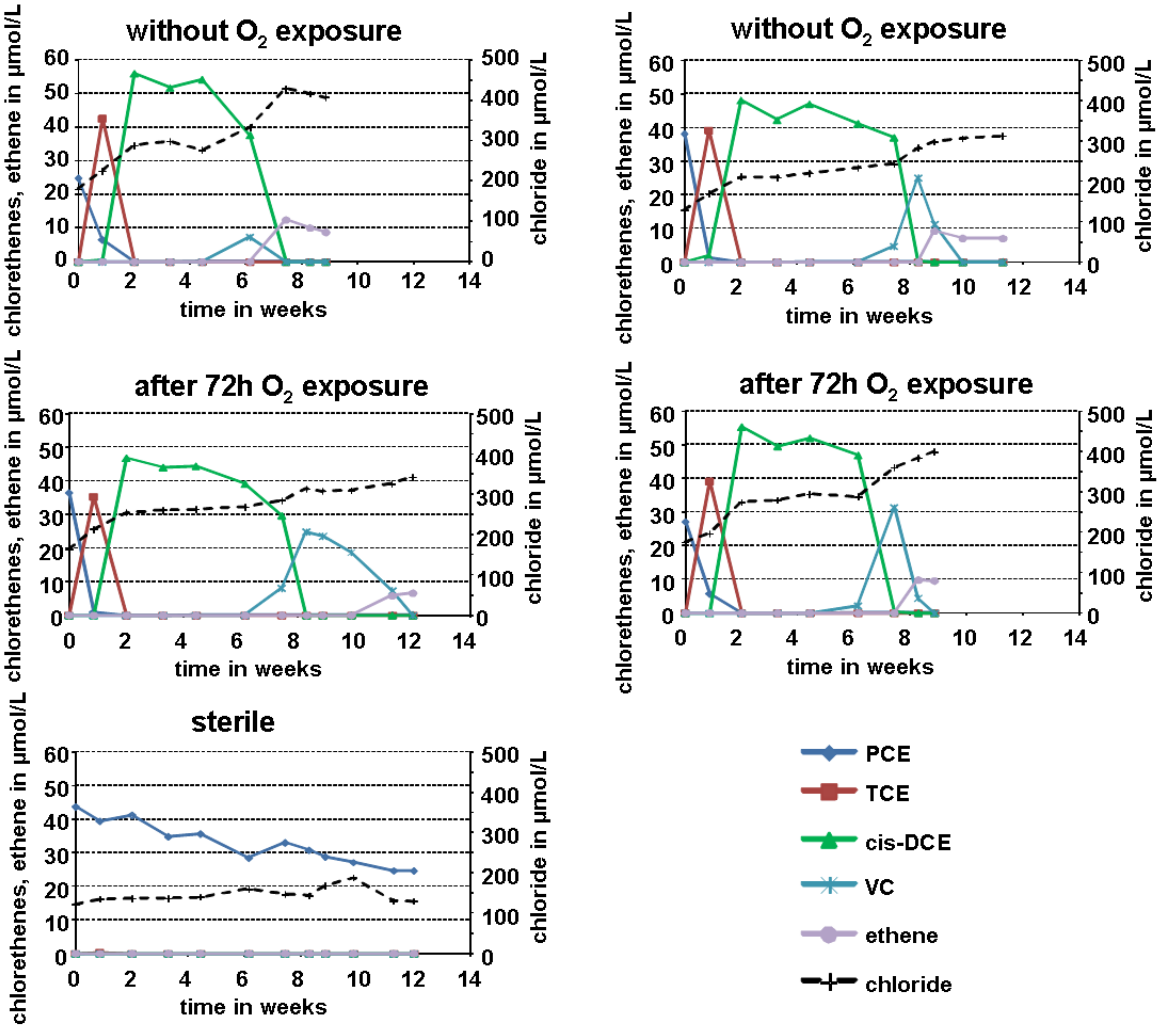


Figure IV-11: Comparison of the echlorination potential of cultures after 72h contact with oxygen and control cultures

Within 11 weeks PCE was dechlorinated to Ethene. All active cultures showed similar dechlorination behaviour, especially no differences between the oxygen amended and the control cultures were found.

The cultures were further analysed with molecular biological techniques. A nested PCR was prepared for *Dehalobacter* spp., *Desulfuromonas* spp. and *Desulfomonile* spp. Quantification of bacterial genes was possible for *Desulfitobacterium* spp. and *Dehalococcoides* spp. and the reductive dehalogenase genes *pceA*, *tceA* and *vcrA* of *Dehalococcoides* spp. (Figure IV-12 and Figure IV-13).

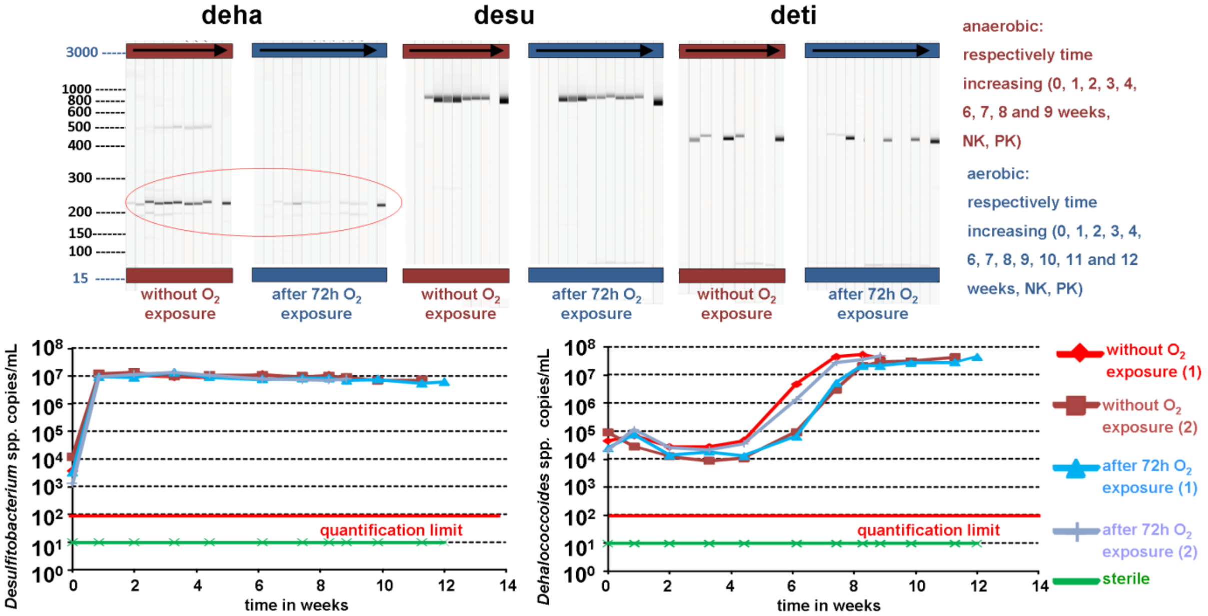


Figure IV-12: Comparison of the dechlorinating microbial community. Similar results were obtained with and without oxygen exposure before conditions were changed to anaerobic. Only Dehalobcter spp. was different and showed oxygen sensitivity.

For *Dehalobacter* spp. an influence of 72h contact with oxygen was detected, because in the control cultures an increase in bacterial genes (positive bands in gelelectrophoresis) could be detected. But in the oxygen amended cultures over the whole experimental time no bands of *Dehalobacter* spp. were within the culture. For all other analysed bacterial genes (*Dehalococcoides* spp., *Desulfitobacterium* spp., *Desulfuromonas* spp. and *Desulfomonile* spp.) no differences between the oxygen amended and the control cultures were found. For *Desulfuromonas* spp. a first detection was after two weeks. *Desulfomonile* spp. bands were detected sometimes during the experiment, but no pattern could be seen. *Dehalococcoides* spp. and *Desulfitobacterium* spp. could be followed by qPCR. The increase in *Desulfitobacterium* spp. copies was within the first week between three and four orders of magnitude and coincided with the dechlorination of PCE to TCE. *Dehalococcoides* spp. gene copies increased after four weeks and correlated with the conversion of cDCE to Ethene.

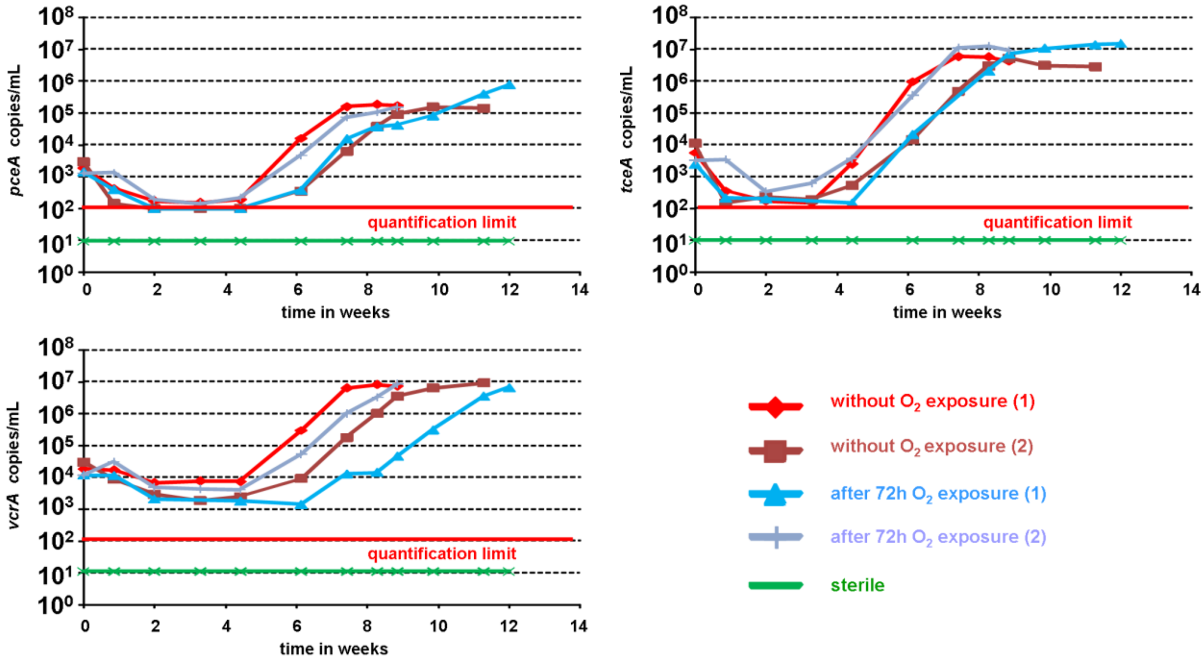


Figure IV-13: Comparison of the reductive dehalogenase genes of Dehalococcoides spp. within the cultures

The cultures were not only tested for the bacterial genes, but also for the reductive dehalogenase genes of *Dehalococcoides* spp. The aim was to test if the oxygen contact had any influence on the different strains of *Dehalococcoides* spp. The course of the *pceA* and *tceA* gene copies/mL was similar to the course of the *Dehalococcoides* spp. copies. Within the first two weeks a decrease of the *pceA* and *tceA* gene copies of about one order of magnitude was detected. The exponential increase started in week four. All cultures showed an increase of about three orders of magnitude to a maximum value of 10^7 copies/mL.

The results clearly showed that the reductively dechlorinating Yangtze community tolerated periods of oxygen contact. After removal of the oxygen and addition of auxiliary substrates, the dechlorinating activity started demonstrating the presence of viable bacteria.

2.6 mRNA expression analysis with the Yangtze cultures

The analysis of reductively dechlorinating microorganisms or of their reductive dehalogenase genes is already a suitable indicator for the potential of reductive dechlorination at a contaminated site. However the detection of genes based on DNA analysis is no proof, that the microorganisms are active. Gene expression, e.g. of the reductive dehalogenase genes, gives evidence for active biodegradation processes. Therefore not DNA extraction is performed, but extraction of messenger RNA (mRNA). mRNA is only formed in viable and active organisms, whereas dead or inactive organisms can still carry intact DNA. Therefore a method was established to detect the activity of the reductive dehalogenase genes *pceA*, *tceA*, *vcrA* and *bvcA* of *Dehalococcoides* spp. To evaluate the expression of the reductive dehalogenase genes six batch cultures were prepared. For the primary substances PCE and cDCE duplicates with active inoculum and single sterile controls were set up for each substance. For all cultures analysis of *Dehalococcoides* spp. and its reductive dehalogenases *pceA*, *tceA*, *vcrA* and *bvcA* was performed with PCR and qPCR. Further the gene expression was evaluated with mRNA extraction and subsequent RT-qPCR. In Figure IV-14 the time course of the PCE or cDCE dechlorination of the active cultures and the sterile controls is depicted, respectively.

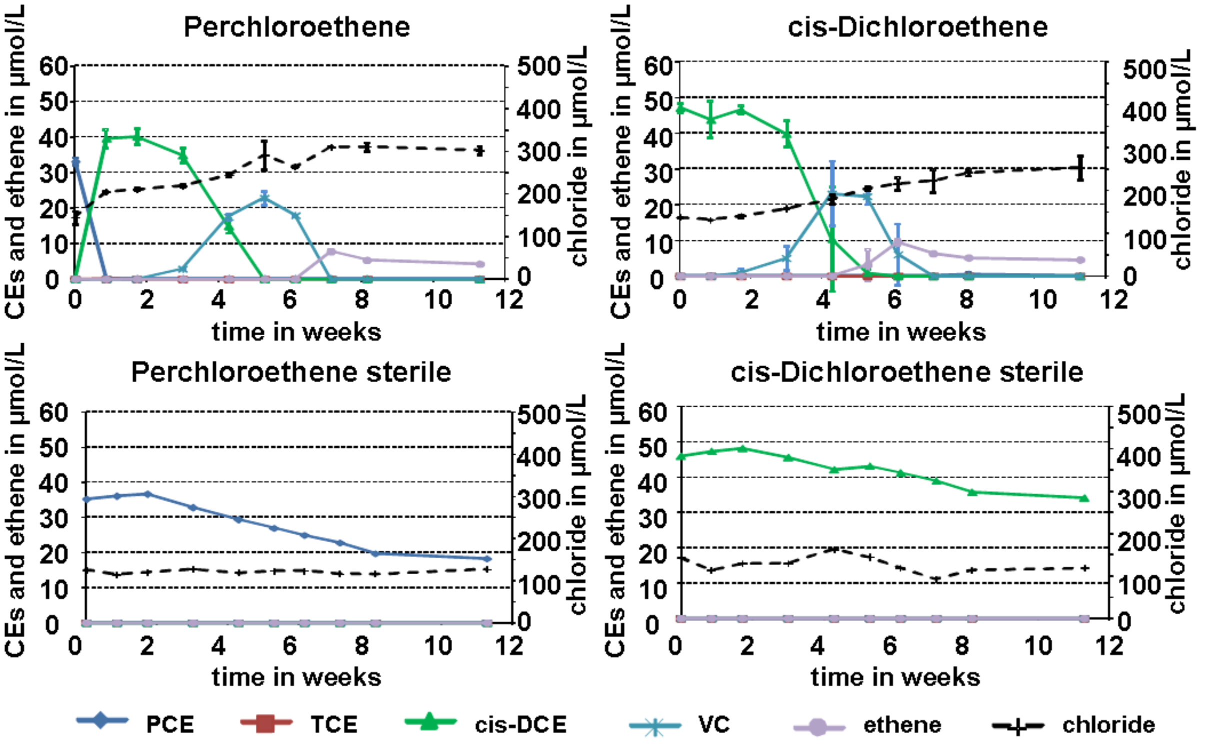


Figure IV-14: Dechlorination pattern of four active cultures in duplicates (top) and two sterile controls amended with PCE or cDCE

All four active cultures were able to completely dechlorinate the primary substance (PCE or cDCE) to the terminal product Ethene. In all active cultures the dechlorination was finished after seven weeks. Also in the sterile controls a decrease of PCE or cDCE was detected, but no increase of Chloride and no dechlorination products were measured.

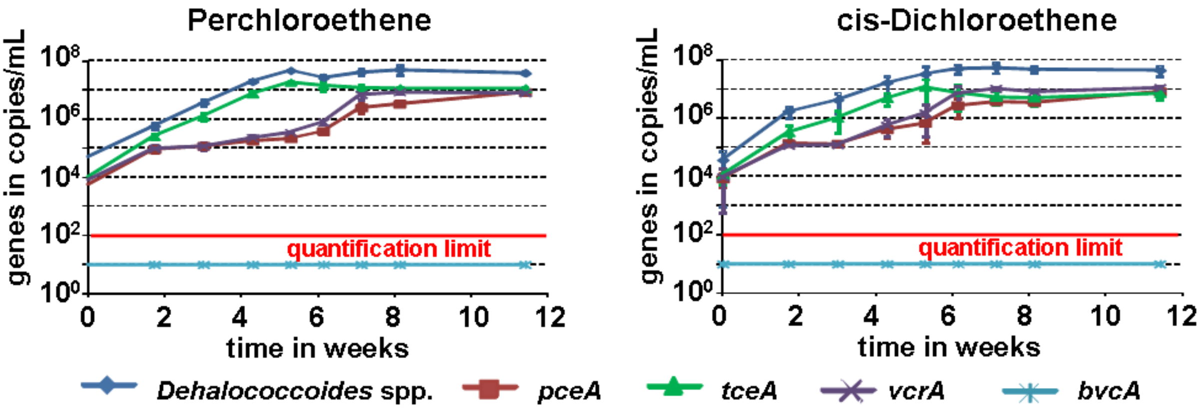


Figure IV-15: DNA analysis of active cultures in duplicates amended with PCE or cDCE

In all active cultures an increase of the reductive dehalogenase gene copies of *pceA*, *tceA* and *vcrA* of *Dehalococcoides* spp. was observed. No *bvcA* genes were detected. The

Dehalococcoides spp. gene copies/mL increased in all active cultures in mean about three orders of magnitude from 4x10^4 to 4x10^7 copies/mL. The course of the increase in *tceA* gene copies was similar to the *Dehalococcoides* spp. genes, but in total numbers the *tceA* gene copies were half an order of magnitude lower, than the *Dehalococcoides* spp. gene copies. The course of the *pceA* and *vcrA* genes was similar, sometimes even identical. After a fast increase from 8x10^3 to 1x10^5 copies/mL of both genes during the first two weeks, the gene copy numbers stayed stable until week three. During the next three weeks a continuous increase of the *pceA* and *vcrA* gene copies was detected, but overall the increase was slower compared to the *tceA* gene. The final concentrations of all three reductive dehalogenase genes were in a similar range of 9x10^6 copies/mL.

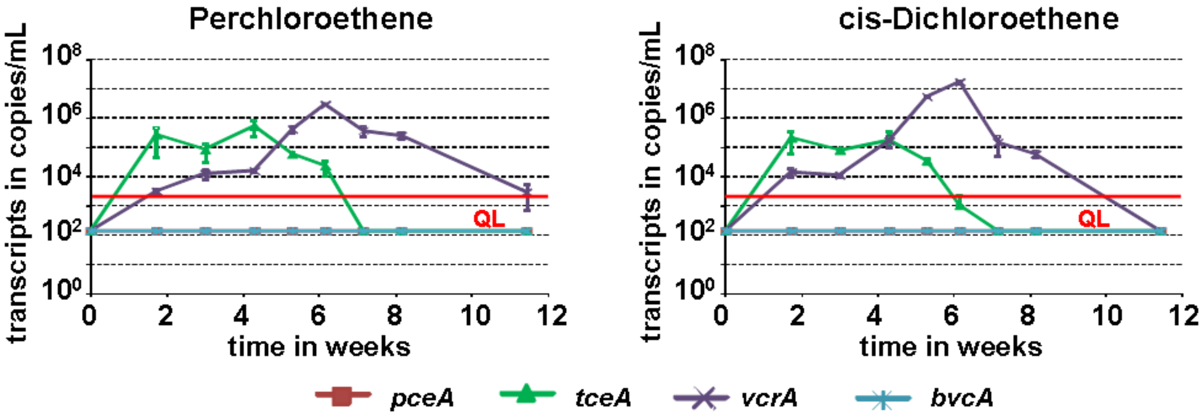


Figure IV-16: mRNA expression results of active cultures in duplicates amended with PCE or cDCE

During the experiment period of eleven weeks an activity of the *tceA* and *vcrA* gene was demonstrated by mRNA detection. The copy numbers for the *pceA* gene transcripts stayed during the whole experiment below the quantification limit of 1.4x10^3 transcript/mL. Between week two and six *tceA* transcripts beyond the quantification limit could be measured, which fluctuated around a value of 1x10^5 transcripts/mL until week five and were afterwards decreasing again.

3 3 Summary and Conclusions

This study focussed on microbial degradation of chlorinated pollutants. All experiments were done with indigenous microorganisms of the Yangtze River. Already in the initial project period, a conceptual model was developed (Figure IV-17). Based on the results obtained in the anaerobic laboratory batch studies with Yangtze River sediments and Yangtze River enrichment cultures the conceptual model was up-dated. The aerobic processes were beyond the scope of this study but are likely to occur considering the available literature (Tiehm & Schmidt, 2011).

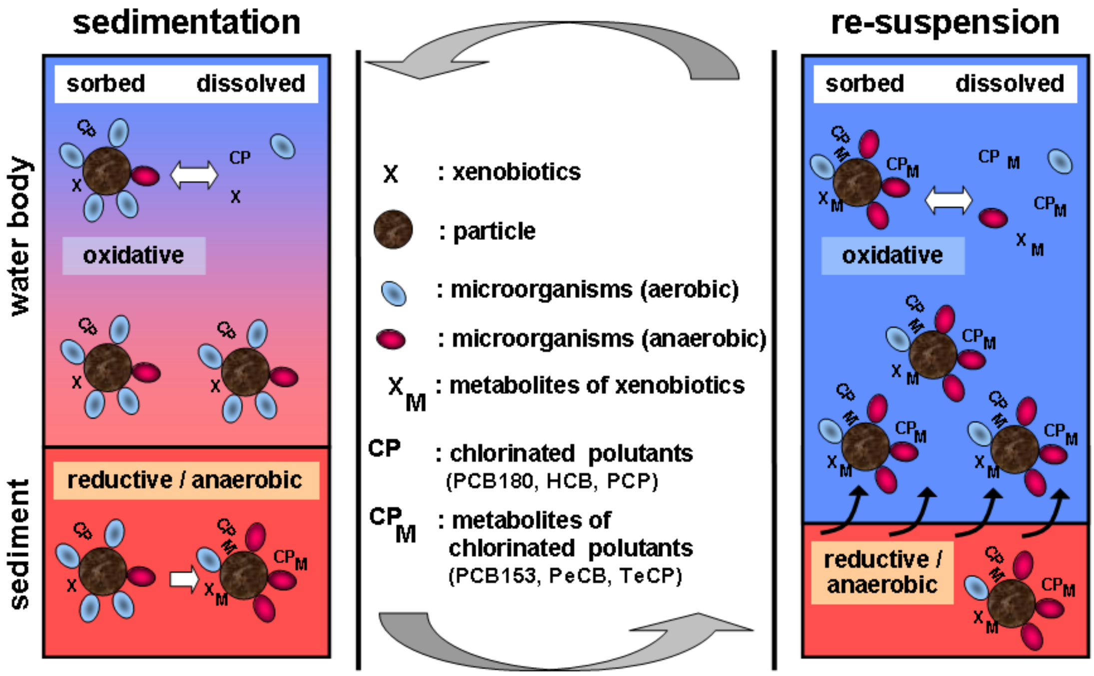


Figure IV-17: Conceptual model of mass transfer and degradation processes, during the filling- and the mixingphases of the Three Gorges Reservoir

The main results of the study are summarized as follows:

Detection of dechlorinating bacteria in Yangtze River samples:

The dechlorinating microorganisms *Dehalococcoides* spp., *Dehalobacter* spp., *Desulfomonile* spp., *Desulfuromonas* spp. and *Desulfitobacterium* spp were detected by PCR analysis in water or sediment samples taken within the TGR. In 85% of the samples at least one of dechlorinating microorganisms was detected, indicating their relevance for pollutant turnover in the Yangtze River. To test the ability of the detected bacteria to degrade chlorinated pollutants batch studies were conducted.

Pollutant degradation in Yangtze River sediments:

In all batch tests incubated with sediments from the TGR catchment area, anaerobic biological dechlorination was demonstrated. *Dehalococcoides* spp. was detected in most of the batch dechlorination tests. However, differences in the biochemical pathways and end-products of reductive dechlorination were observed, most probably due to different halorespiring bacteria community compositions. The culture MP1 repeatedly dechlorinated PCE via TCE to *cis*-DCE. In this culture, *Dehalococcoides* spp. was below the quantification limit during the whole incubation time. In contrast, *Dehalococcoides* spp. was detected with increasing numbers over investigation time in the cultures YCQ1 and XX07. These cultures showed complete dechlorination thus confirming previous reports that bacteria of the *Dehalococcoides* group are the only known microorganism to completely dehalogenate PCE to ethane. Also the culture XX07 showed complete dechlorination to ethene, but the temporarily detected metabolite was *trans*-DCE. For the first time the dechlorination potential of the indigenous microbial community in Yangtze river sediments was demonstrated without any external addition of auxiliary substrates thus simulating field conditions .

Degradation of HCH, PCP, PCB, and chlorinated benzenes:

This part of the study focussed on the degradation of pollutants known to be present in Yangtze River sediments. The culture XX01, which was derived from sediment from the tributary Xiang Xi River at a point close to the Yangtze River, showed with all five highly chlorinated compounds (HCHs, HCB, PCP PCB180 and PCE) dechlorinating activity. In case of all the chlorinated pollutants except PCB, the formation of lesser chlorinated transformation products was demonstrated. In conclusion, the indigenous microbial community was capable to dechlorinate a number of relevant environmental pollutants in the Yangtze River.

Activity after oxygen exposure:

A periodical exposure of sediment associated bacteria to oxygen is likely to occur in the Yangtze TGR, taking into consideration the periodical water level fluctuations and expected spatio-temporal dynamics of the hydrochemical parameters. Therefore, the oxygen sensitivity of the five reductively dechlorinating bacteria *Dehalococcoides* spp., *Desulfuromonas* spp., *Dehalobacter* spp., *Desulfomonile* spp. and *Desulfitobacterium* spp. was tested. For the three dechlorinating bacteria *Desulfitobacterium* spp., *Desulfomonile* spp. and *Desulfuromonas* spp. in none of the experiments influence of the oxygen contact was detected. After oxygen exposure, increasing numbers of *Dehalococcoides* spp. were detected during the anaerobic dechlorination of cDCE to ethene. The results indicate that reductive dechlorination is possible in anaerobic areas even after temporary transfer of the bacteria into aerobic zones.

Demonstration of gene expression (mRNA detection):

In this study, the extraction of high quality mRNA was demonstrated. The gene transcripts (mRNA) found with the RT-qPCR corresponded to the dechlorination of cDCE and VC. As long as cDCE was present in the cultures, gene transcripts of the reductive dehalogenase *tceA* were found. With increasing concentration of VC, also *vcrA* gene transcripts were found in the cultures. After cDCE and VC were depleted, the *tceA* and *vcrA* gene transcripts started to decrease. Thus, the new molecular method enables a direct monitoring of microbial activity by mRNA detection. Therefore, the relevance of different bacteria and genes can be studied. Furthermore, a monitoring of microbial activity in the field might be possible in the future.

With this study, the potential of indigenous microorganisms within the Yangtze River for reduction of chlorinated pollutants was demonstrated. The results indicate that these processes are active in the field and contribute substantially to pollutant elimination in the Yangtze River and the TGR.

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4 Own publications:

Tiehm A., Stoll C., Kranzioch I., **Biodegradation of chlorinated pollutants – New insights and Application of PCR-detection.** Interactions in the Water System-Workshop within the frame of the Sino-German Yangtze-Project. Shanghai, 28.-29.03.2011, Abstract booklet: 6 (oral presentation) (2011)

Kranzioch I., Tiehm A., **PCR detection of reductively dechlorinating bacteria in sediment samples.** The third international Environmental Best Practices Conference, Offenburg, 13.-16.09.2011, book of abstracts: 62 (Poster presentation) (2011)

Kranzioch I., Stoll C., Tiehm A., **Mikrobieller Abbau: Massentransfer im System Schadstoff-Wasser-Sediment.** GIT Labor-Fachzeitschrift 9/2011: 608-611 (2011)

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., Xinag X., Yuan Y. 2011. **The Yangtze-HYDRO Project: a Chinese-German environmental program.** Environmnetal Science and Pollution Research 19:1341–1344. (2012) doi: 10.1007/s11356-011-0645-7

Tiehm A., Kranzioch I., Stoll C., **Monitoring of chlorinated pollutants biodegradation by PCR.** Küppers S., Subklew G., Wilken R.-D. (ed.) Processes in the Yangtze River System – Experiences and Perspectives - , Schriften des Forschungszentrums Jülich, Energy & Environment, Volume 123 (2011) (ISBN 978-3-89336-744-3): 23-24

Kranzioch I., Holbach A., Chen H., Wang L., Zheng B., Norra S., Bi Y., Schramm K.-W., Tiehm A., **PCR-detection of reductively dechlorinating bacteria in Yangtze samples.** Küppers S., Subklew G., Wilken R.-D. (ed.) Processes in the Yangtze River System – Experiences and Perspectives - , Schriften des Forschungszentrums Jülich, Energy & Environment, Volume 123 (2011) (ISBN 978-3-89336-744-3): 57

Kranzioch I., Tiehm A.: **Assessment of pollutant biodegradation at the three gorges dam, China.** International Journal of Water Management “blue facts” 2012: 70-75 (2012)

Kranzioch I., Stoll C., Tiehm A., **Monitoring of PCE degrading bacteria in a Yangtze-sediment enrichment culture.** 11th Urban Environment Symposium, Karlsruhe, 16-19.09.2012, book of abstracts: 55 (Poster presentation) (2012)

Kranzioch I., Holbach A., Chen H., Wang L., Zheng B., Norra S., Bi Y., Schramm K., Tiehm A., **Anaerobic microbial community dynamics in Yangtze sediment samples.** Workshop on processes in the Yangtze River system – 10th Anniversary of Sino-German cooperation, Shanghai, 22-23.09.2012, book of abstracts: 54 (Oral presentation) (2012)

Holbach A., Floehr T., Kranzioch I., Wolf A., **Dilution of pollution? Processes affecting the water quality in the river-style Three Gorges Reservoir.** Environmental Science and Pollution Research 20:7140-7141. (2012) doi: 10.1007/s11356-012-1252-y

Kranzioch I., Stoll C., Holbach A., Chen H., Wang L., Zheng B., Norra S., Bi Y., Schramm K., Tiehm A., **Dechlorination and organohalide-respiring bacteria dynamics in sediment samples of the Yangtze Three Gorges Reservoir.** Environmental Science and Pollution Research 20:7046-7056. (2013) doi: 10.1007/s11356-013-1545-9

References:

Abramowicz D.A., **Aerobic and anaerobic PCB biodegradation in the environment.** Environ mental Health Perspectives 103:97–99. (1995)

Adrian *L., Görisch H.,* **Microbial transformation of chlorinated benzenes under anaerobic conditions.** Research in Microbiology 153:131–137. (2002) doi: 10.1016/S0923-2508(02)01298-6

Adrian L., Hansen S.K., Fung J.M., Görisch H., Zinder S., **Growth of Dehalococcoides Strains with Chlorophenols as Electron Acceptors.** Environmental Science and Technology 41:2318–2323. (2007) doi: 10.1021/es062076m

Aktaş Ö., Schmidt K.R., Mungenast S., Tiehm A., **Effect of chloroethene concentrations and granular activated carbon on reductive dechlorination rates and growth of Dehalococcoides spp.** Bioresource Technology 103:286–292. (2012) doi: 10.1016/j.biortech.2011.09.119

Bedard D.L., Ritalahti K.M., Löffler F.E., **The Dehalococcoides Population in Sediment-Free Mixed Cultures Metabolically Dechlorinates the Commercial Polychlorinated Biphenyl Mixture Aroclor 1260.** Applied Environmental Microbiology 73:2513–2521. (2007) doi: 10.1128/AEM.02909-06

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., **The Yangtze-HYDRO**

Project: a Chinese-German environmental program. Environmental Science and Pollution Research 19:1341–1344. (2012) doi: 10.1007/s11356-011-0645-7

Field J.A., Sierra-Alvarez R., **Microbial degradation of chlorinated benzenes.** Biodegradation 19:463–480. (2008a) doi: 10.1007/s10532-007-9155-1

Field J.A., Sierra-Alvarez R., **Microbial transformation and degradation of polychlorinated biphenyls.** Environmental Pollution 155:1–12. (2008b) doi: 10.1016/j.envpol.2007.10.016

Gao J., Liu L., Liu X., Zhou H., Huang S., Wang Z., **Levels and spatial distribution of chlorophenols - 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol in surface water of China.** Chemosphere 71:1181–1187. (2008) doi: 10.1016/j.chemosphere.2007.10.018

Gerritse J., Renard V., Pedro Gomes T.M., Lawson P.A., Collins M.D., Gottschal J.C., **Desulfitobacterium sp. strain PCE1, an anaerobic bacterium that can grow by reductive dechlorination of tetrachloroethene or ortho-chlorinated phenols.** Archives of Microbiology 165:132–140. (1996) doi: 10.1007/s002030050308

Han F.A., Chen J., Jiang Z.F., **Investigation of VOCs and SVOCs in Surface Water Source in Jiangsu, Zhejiang, Shandong Province, China.** Journal of Environment and Health 28:890–894. (2011)

Holliger C., Schraa G., Stams A.J., Zehnder A.J., **A highly purified enrichment culture couples the reductive dechlorination of tetrachloroethene to growth.** Applied Environmental Microbiology 59: 2991-2997. (1993)

Jiang X., Martens D., Schramm K.W., Kettrup A., Xu S.F., Wang L.S., **Polychlorinated organic compounds (PCOCs) in waters, suspended solids and sediments of the Yangtse River.** Chemosphere 41:901–905. (2000) doi: 10.1016/S0045-6535(99)00435-X

Lal R., Pandey G., Sharma P., Kumari K., Malhotra S., Pandey R., Raina V., Kohler H.P.E., Holliger C., Jackson C., Oakeshott J.G., **Biochemistry of Microbial Degradation of Hexachlorocyclohexane and Prospects for Bioremediation.** Microbiology and Molecular Biology Reviews 74:58–80. (2010) doi: 10.1128/MMBR.00029-09

Li B., Chen H., Cao X., **Chlorinated Hydrocarbons and BTEX in Yangtze River Delta Region Shallow Groundwater, China.** The 34th Congress of International Association of Hydrogeologists. (2006) URL: http://en.cgs.gov.cn/Achievement/The34thCongress/Recovery/18687.htm

Mohn W.W., Kennedy K.J., **Reductive dehalogenation of chlorophenols by Desulfomonile tiedjei DCB-1.** Applied Environmental Microbioliology 58:1367–1370. (1992)

Müller B., Berg M., Yao Z.P., Zhang X.F., Wang D., Pfluger A., **How polluted is the Yangtze river? Water quality downstream from the Three Gorges Dam.** Science of The Total Environment 402:232–247. (2008) doi: 10.1016/j.scitotenv.2008.04.049

Nelson J.L., Fung J.M., Cadillo-Quiroz H., Cheng X., Zinder S.H., **A role for Dehalobacter spp. in the reductive dehalogenation of dichlorobenzenes and monochlorobenzene.** Environmental Science and Technology 45:6806–6813. (2011) doi: 10.1021/es200480k

Olaniran A.O., Igbinosa E.O., **Chlorophenols and other related derivatives of environmental concern: properties, distribution and microbial degradation processes.** Chemosphere 83:1297–1306. (2011) doi: 10.1016/j.chemosphere.2011.04.009

Quintero J.C., Moreira M.T., Feijoo G., Lema J.M., **Anaerobic degradation of hexachlorocyclohexane isomers in liquid and soil slurry systems.** (2005) Chemosphere 61:528–536. doi: 10.1016/j.chemosphere.2005.02.010

Schmidt K.R., Stoll C., Tiehm A., **Evaluation of 16S-PCR detection of Dehalococcoides at two chloroethene-contaminated sites.** Water Science & Technology: Water Supply 6:129. (2006) doi: 10.2166/ws.2006.787

Tang Z.W., Yang Z.F., Shen Z.Y., Niu J.F., **Pentachlorophenol residues in suspended particulate matter and sediments from the Yangtze River catchment of Wuhan, China.** Bulletin of Environmental Contamination and Toxicology 78:158–162. (2007) doi: 10.1007/s00128-007-9017-x

Tiehm A., Schmidt K.R., **Sequential anaerobic/aerobic biodegradation of chloroethenes-aspects of field application.** Current Opinion in Biotechnology 22:415–421. (2011) doi: 10.1016/j.copbio.2011.02.003

Wang J., Bi Y., Pfister G., Henkelmann B., Zhu K., Schramm K.W., **Determination of PAH, PCB, and OCP in water from the Three Gorges Reservoir accumulated by semipermeable membrane devices (SPMD).** Chemosphere 75:1119–1127. (2009) doi: 10.1016/j.chemosphere.2009.01.016

Willett K.L., Ulrich E.M., Hites R.A., **Differential Toxicity and Environmental Fates of Hexachlorocyclohexane Isomers.** Environmental Science and Technology 32:2197–2207. (1998) doi: 10.1021/es9708530

Wolf A., Bergmann A., Wilken R.D., Gao X., Bi Y., Chen H., Schüth C., **Occurrence and distribution of organic trace substances in waters from the Three Gorges Reservoir, China.** Environmental Science and Pollution Research 20:7124–7139. (2013) doi: 10.1007/s11356-013-1929-x

Wu Q., Milliken C.E., Meier G.P., Watts J.E.M., Sowers K.R., May H.D., **Dechlorination of Chlorobenzenes by a Culture Containing Bacterium DF-1, a PCB Dechlorinating**

Microorganism. Environmental Science and Technology 36:3290–3294. (2002) doi: 10.1021/es0158612

Zhang J., **Geochemistry of trace metals from Chinese river/estuary systems: An overview.** Estuarine, Coastal and Shelf Science 41: 631-658. (1995) doi: 10.1006/ecss.1995.0082

V MINIBAT - Spatio-temporal resolved in-situ and on-line monitoring of the dynamics of water body relevant parameters by means of a towed under water multi sensor system & Numerical modeling of pollutant transport dynamics

FKZ: 02WT1131

[1]Institute for Mineralogy and Geochemistry, Karlsruhe Institute for Technology, Germany & [2]Institute for Geotechnical Engineering, University of Stuttgart, Germany

Stefan Norra[1]

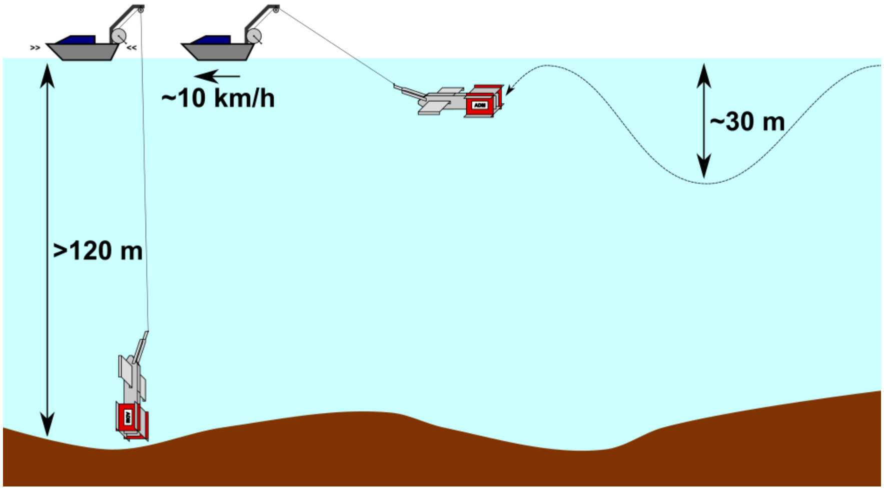
Bernhard Westrich[2]

Andreas Holbach[1]

Wei Hu[1]

Simon Leib[1]

Xiaohui Tang[1]



1 Introduction

Freshwater is an essential resource for human life. More than 45,000 large dams impound the world's Rivers to sustain drinking and irrigation water, energy supply, flood control, infrastructure, and economic benefits (1). With around 22,000 large dams, China hosts almost half of them (1). The Yangtze River, which is shown in Figure V-1, serves as the main drinking water source for its adjacent regions (2). Impacts of dams on ecosystems are widely known, but reliable predictions for new reservoirs remain difficult (3).

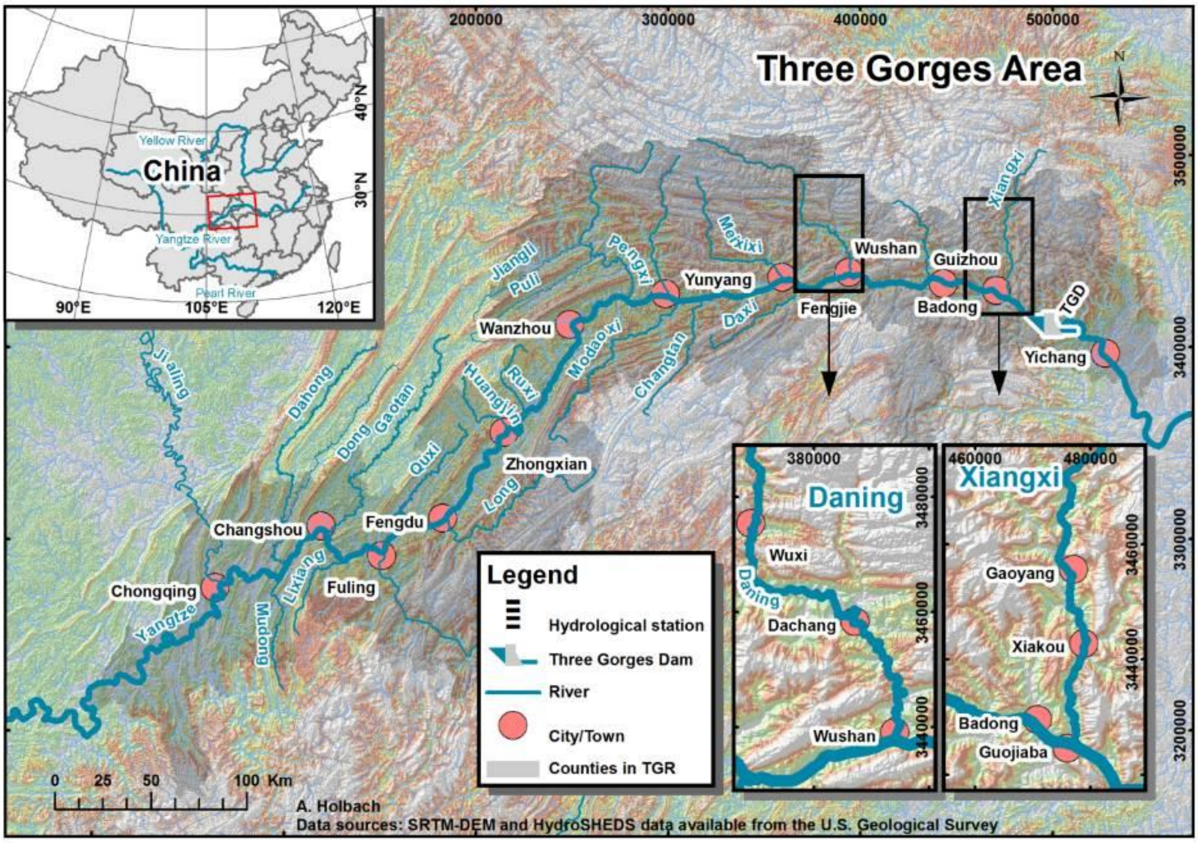


Figure V-1. The Three Gorges Reservoir area within China and our major MINIBAT monitoring sections in the Daning River and Xiangxi River backwaters.

There are 28 large reservoirs (storage capacity: ≥ 20.0 km^3; dam height: ≥ 100 m) in a same order of magnitude as the TGR (e.g., Volta, Kariba, and Manicouagan) (4). But, the only one that can also compete with the TGR (dam height: 181 m; storage capacity: 39.3 km^3; mean residence time $R = 29.6$ days) in terms of mean water residence time R is the Itaipù Reservoir (dam height: 196 m; storage capacity: 29.0 km^3; $R = 33$ days) located on the border between Brazil and Paraguay (5). Furthermore, the specific water level management of the TGR is designed to compensate the seasonal inflow changes between less than 5,000 m^3/s in winter and greater than 70,000 m^3/s in summer (2010-2013) (6). Its seasonal 30 m water level fluctuation between 145 and 175 m above sea level (m.a.s.l.) results in monthly R values within $8 < R \leq 81$ days for the whole TGR. As for hydrodynamic criteria, reservoirs can be classified into three classes: (A) fully mixed, (B) seasonally mixed, and (C) well stratified.

The TGR contains all classes of water bodies ranging from almost fully mixed to seasonally stratified water bodies occurring in backwater section of tributaries during winter (7). Thus the TGR is a dynamic River-reservoir system with extraordinary interaction calling for challenging studies on hydrodynamic driven processes.

1.1 Environmental challenges in the TGR

Since 2003, the impoundment of the Three Gorges Reservoir (TGR) on the Yangtze River in China burdened its tributary backwaters with severe environmental threats (8). Geohazards, for example, earth quakes, soil erosion, and landslides, as consequences of the establishment of TGR, have considerably intensified and remain a recent research field (9)(10). Drastic ecological changes of both, terrestrial and aquatic habitats took place in the same instant and may have caused irreversible losses of biodiversity (11). This is particularly critical because the TGR region is a biodiversity hotspot and characterized by many endemic species (11). The water bodies of the TGR are seriously threatened by eutrophication. Frequent algal blooms, especially in the TGR tributary backwaters, put the main drinking water source and a major food source at stake while their formation processes still remain unsatisfyingly understood (8)(12)(13). Furthermore, some studies reported increasing heavy metal contents in soils and sediments of the TGR area, particularly within the water level fluctuation zone (14)(15). However, a TGR-wide synoptic heavy metal balance is still missing.

On a global scale, eutrophication of freshwater resources and heavy metal accumulation in reservoir sediments are major environmental problems and are closely related to anthropogenic impacts in the corresponding watersheds (16). New reservoirs are extremely susceptible to these threats because their hydrodynamics are artificially and rapidly changed by the impoundment. Eutrophication and heavy metal accumulation in the TGR are thus representative environmental threats of large reservoirs worldwide.

Confluence zones of reservoir tributaries with the Yangtze River main channel are main drivers of pollutant dynamics in the TGR and are thus keys to develop mitigation measures (12). Dealing with large and dynamic reservoir water bodies, like the TGR, mixing of different water bodies is of peculiar importance. Similar to the role of biogeochemistry in estuaries where freshwater and salt water meet (17) the confluence zones where mixing processes are driven by hydrodynamics play a key role for site specific chemical and processes which are responsible for the fate and pathways of dissolved and particulate pollutants and their distribution in the whole water body (18).

Nutrient loads in the main stream of Yangtze River are considerably higher compared to its tributaries and are effectively transported into the tributary by the backwater effect (19). Thus, threats on humans and the ecosystem caused by pollution, changed hydrodynamics, higher nutrient content , and increasing eutrophication and algal bloom events (20)(21) are widely discussed.

1.2 Objectives of this Project

In the frame of the environmental challenges described above and China's discernment to aspire to a sustainable management of the TGR region, the Sino-German environmental research program "Yangtze-Hydro Project" was established and funded from BMBF and MOST since 2010 (23). It aimed to conduct interdisciplinary research on the sustainable utilization and development of the newly created ecosystem in the TGR. The following joint projects are designed to analyze the impact of the impoundment of the Yangtze River on the flow regime and the associated transport and mixing processes of toxic and eutrophic substances relevant to water quality and River ecosystem.

(i) The MINIBAT sub-project aimed to develop and implement effective techniques and strategies to monitor water quality distribution dynamics in 3D-space and time in critical areas throughout the regions affected by the TGR. This methodical approach is meant to contribute to the following relevant aspects of water quality in the TGR:

- Physical and chemical water quality properties under typical hydrological scenarios , extreme events, landslides, and accidents
- Eutrophication and algal blooms
- Sources, transport, degradation, sedimentation and resuspension of pollutants in the TGR water bodies
- Mapping and contamination risk assessment of areas suitable for drinking water production
- Pollution from point sources, flooded industry areas, and flooded cities
- Stratification in the TGR water bodies and effects on water quality and pollutants
- Effects of the Three Gorges Dam on water quality in the middle and lower reaches of the Yangtze River
- Effective monitoring strategies for large-scale reservoirs

(ii) The Three Gorges Dam has drastically changed the hydrodynamics of the Yangtze River and its tributaries and hence, the transport and mixing of dissolved and particulate substances must be simulated by numerical model as to interpret and confirm the data and results of the MINIBAT measurements. The focus of the numerical modeling is on

- Spatial impact of the water level change at the Three Gorges Dam on major tributaries, i.e. Daning River and Xiangxi River
- Mixing of water and pollutants between the Yangtze River and its tributaries
- Distribution and concentration of contaminants, eutrophic substances, in particular algae in the Wushan Lake at significant hydrological scenarios
- Trajectories, residence time and exposition of dissolved and particulate pollutants in different zones of the Wushan Lake

- Backwater effect in the Daning River and penetration of Yangtze water upstream into the Daning River at high Yangtze water level
- Water exchange at: (i) steady state water and discharge conditions, (ii) rising and (iii) falling water level conditions including limits without water exchange
- Optimum location of disposal of a sewage station of water treatment plant to minimize eutrophic impact on Wushan Lake

2 Technical developments and methods

A major part of this project focused on the construction of a new and advanced version of the original MINIBAT in situ and online multisensor probe (22). This new MINIBAT was meant to be applicable under field conditions in the Yangtze River in China, particularly in the TGR. Furthermore, it additionally should be equipped with a new sensor for 'colored dissolved organic matter' (CDOM), as well as with a remote controlled water sampling system. This sampling system needed to be newly designed and integrated into the mechanics and electronics of the MINIBAT.

2.1 Fieldwork and application of the MINIBAT system in the TGR

In the frame of this project, we conducted nine fieldtrips in China; a corresponding timeline is shown in Figure V-2. To get a first overview of the study area's dimensions, conditions and the actual water quality situation we visited three sites along the TGR for water and sediment sampling during our first fieldtrip in April 2011: (1.) the Daning River, a major tributary entering the Yangtze River approximately 120 km upstream of the TGD, (2.) the

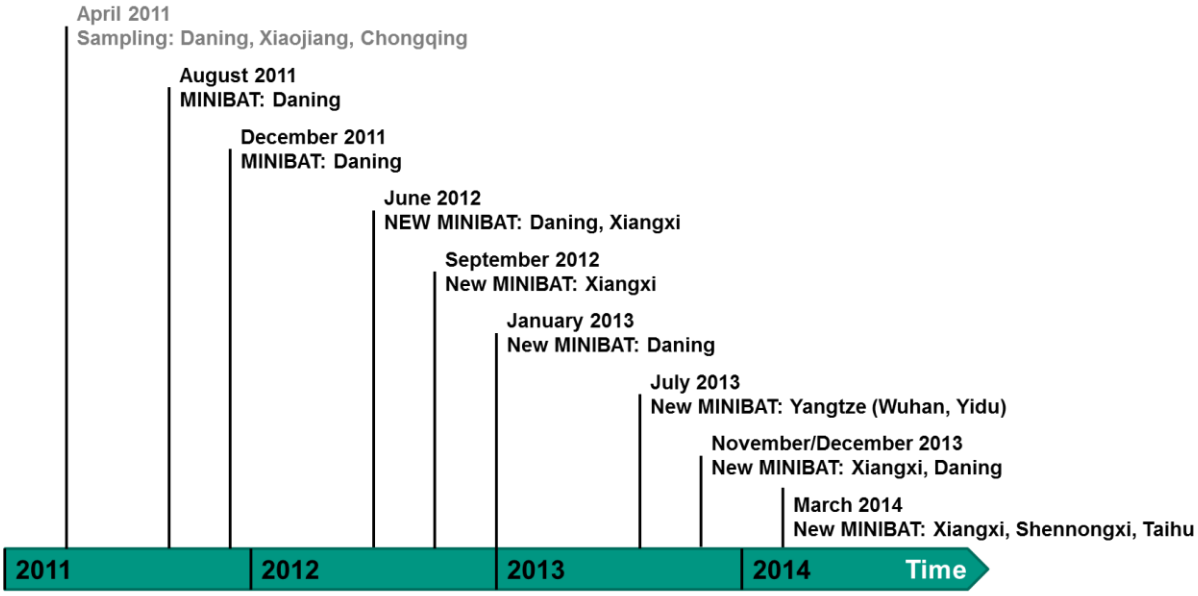


Figure V-2. Timeline of the fieldwork conducted within this sub-project. Note: in April 2011 the fieldwork was done without the MINIBAT. In August and December 2011 we could apply an old MINIBAT system. The newly developed MINIBAT system could be applied from June 2012 on.

Speed boat
Wushan 2011-08

Fishing boat
Xiakou 2012-06

Small speed boat
Wuhan 2013-07

Large vessel
Wuhan 2013-07

Figure V-3. Different types of boats and the corresponding MINIBAT installations throughout the conducted fieldwork. The MINIBAT can be installed and applied very flexibly.

Xiaojiang River another major tributary entering the Yangtze River around 450 km upstream of the TGD, and (3.) the confluence zone of the Jialing River with the Yangtze River around the megacity Chongqing, approximately 600 km upstream of the TGD.

During a one week fieldtrip in August 2011 we successfully applied a MINIBAT system in the TGR for the first time. We decided to focus our investigations on the approximately 40 km long Daning River backwater and its confluence zone with the Yangtze River around Wushan City. In December 2011 we carried out a field trip to the same area again for one week to conduct further MINIBAT measurements, now under different hydrological and climatic conditions. All TGR fieldwork in 2011 was jointly organized with our partners of the 'Chinese Research Academy of Environmental Sciences' (CRAES) in Beijing. Simultaneously, the new and advanced MINIBAT system was constructed and could be successfully tested on Lake Constance in March 2012. This was done in collaboration with the 'Institute of Lake Research' of the 'Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg' (LUBW-ISF) and their research vessel 'Kormoran'. We could perform the first TGR fieldtrip with this new MINIBAT in June 2012. The initial commissioning could be successfully done in the Daning River together with the MINIBAT manufacturer 'ADM-Elektronik' (ADM) and CRAES. Afterwards we moved to the Xiangxi River backwater, another major tributary of the TGR entering the Yangtze River approximately 40 km upstream of the TGD. This second part of the fieldwork was supported by the 'Institute of Hydrobiology' of the 'Chinese Academy of Sciences' (CAS-IHB). Further fieldwork took place in the Xiangxi River backwater in September 2012, and the Daning River in January 2013. Due to custom related issues we needed to export en re-import the MINIBAT from and to China, afterwards. However, we were able to continue our fieldwork in July 2013, where we applied the MINIBAT in the Yangtze River sections around Wuhan and Yidu, both located downstream of the TGD. In November/December 2013 we investigated the water bodies

Figure V-4. MINIBAT long-term monitoring application in the shallow water Lake Taihu.

of the Xiangxi River and the Daning River, once more. Our last fieldtrip took place in March 2014, where we started again in the Xiangxi River backwater. During the runtime of the project we could establish a new collaboration with colleagues from the 'China Three Gorges University' (CTGU) in Yichang, who were willing to support our MINIBAT fieldwork. Thus, we were also able to visit another major TGR tributary, the Shennongxi River backwater, located approximately 75 km upstream of the TGD in March 2014. Furthermore, together with CRAES we arranged MINIBAT fieldwork in the Taihu, a huge and shallow Lake, which is also connected to the Yangtze River and located close to its mouth near Shanghai city.

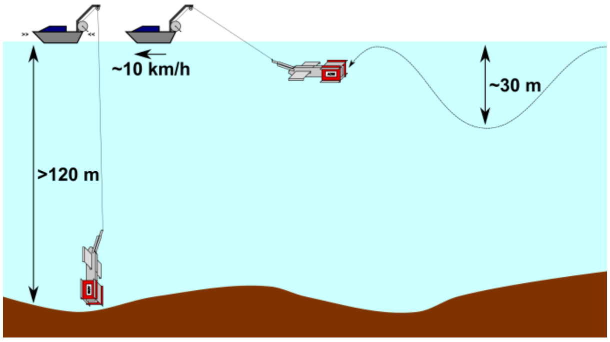


Figure V-5. MINIBAT application modes. Left: MINIBAT depth profiling when the boat does not move. Right: continuous MINIBAT measurements when it is dragged behind the boat.

During all this fieldwork we had to manage different hydrological conditions and arrange available infrastructures. Some impressions of varying MINIBAT installations on the different types of boats are compiled in Figure V-3. Different types of boats and the corresponding MINIBAT installations throughout the conducted fieldwork. The MINIBAT can be installed and applied very flexibly.. Here we have to highlight, that we successfully applied the MINIBAT under all conditions that we found. It is, however, sometimes necessary to adapt the fixation of the winch and the specific monitoring application modes.

The MINIBAT body is meant to be dragged behind a boat (Figure V-5). Two remote controlled wings in the front can make the MINIBAT dive down and up to various depths. Due to the safety of the MINIBAT the cable length could not be extended arbitrarily during our continuous measurements. We had to take into account water depth, boat traffic, and fishnets as factors limiting the cable length to a maximum of approximately 60 m. Under these conditions in the TGR we could reach dive depths of approximately 30 m during continuous measurements. However, the MINIBAT can also simply be used as a depth profiling probe when the carrying boat does not move (Figure V-5). Like this, we are theoretically able to utilize the total cable length of 160 m on the winch. Practically, we performed measurements and took samples from more than 120 m depth in the TGR. In Lake Taihu with very shallow water depths mainly below 2 m we were also able to drag the MINIBAT through the water. To perform depth profiling at one site in this Lake we had to implement minor modifications. The length of almost 1 m of the whole MINIBAT body itself prevents from reasonable depth profiling in this shallow water when the MINIBAT is in its typical vertical position. Thus, we adapted the position of the MINIBAT drawbar. We fixed the drawbar in backward direction to keep the MINIBAT in a horizontal position while hanging at the winch (Figure V-4). Like this it was possible to perform long-term MINIBAT depth profiling measurements with high vertical resolution.

2.2 Development and implementation of a sampling system for the MINIBAT

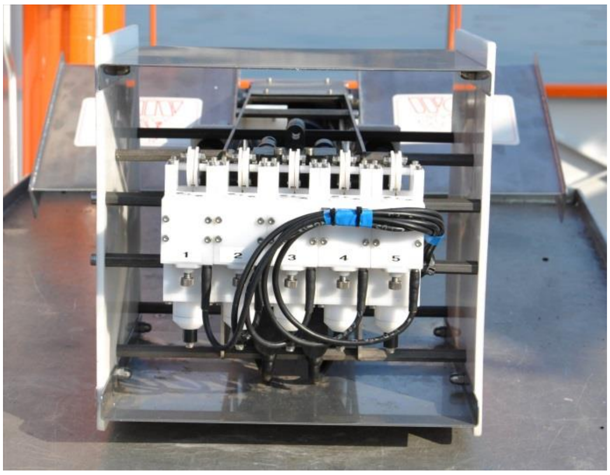


Figure V-6. The newly designed sampling system installed in the back of the MINIBAT. Five samplers can collect 50 mL of water each. The release mechanism is triggered by remote control from the boat.

The company ADM designed a rack of five water samplers with approximately 50 mL sample volume each, to be placed in the back of the MINIBAT (Figure V-6). The parts were produced from POM by the geo-workshop of KIT; ADM assembled the parts, developed the electronics, and added the mounting position on the MINIBAT corpus. The pistons of the samplers can now suck water into a tube which is sealed by O-rings on both ends in closed position. This mechanism is simply driven by strained rubber bands. Together with the LUBW-ISF, we tested the first prototype of this sampling system on Lake Constance in March 2012. The release mechanism worked with an electromagnet. However, we detected that the emitted electromagnetic fields during the release process caused strong signal deflections of the electrochemical sensors for O_2-sat, pH, and H_2S. Consequently, it was necessary to rework the release mechanism and the electromagnets were replaced by a small electric motor to trigger the release of the samplers. This adaptation eliminated those disturbing signal deflections.

In July 2013, we faced another challenge with the high sediment loads of the Yangtze River in the sections downstream of the TGD. The suspended particles here contained considerable fractions of sand, thus, significantly differing from the mainly silty and clayey suspended particles in the TGR water bodies. The pistons of the water samplers got stuck in the tube. Thus, ADM increased the mechanical backlash between the pistons and the tubes of the samplers to facilitate their applicability in waters with sandy suspended sediment loads.

2.3 Adaptations on the MINIBAT

The strong motor that moves the wings in the front of the MINIBAT caused similar problems as the electromagnet sampler release mechanism described above. Anytime the motor was started the electrochemical sensors for O_2-sat, pH, and H_2S exhibited strong signal deflections. Hence, ADM modified the steering electronics of the motor. The abrupt motor start-up with full voltage was modified accordingly; the start-up of the motor was set to happen smoothly by an increasing voltage function. Herewith, the intensities of emitted changes of electromagnetic fields could be considerably reduced and we detected less impact on the affected sensors. However, signal deflections can still be observed and further adaptations, like electromagnetic shielding of the motor, should be considered for further technical improvements of the MINIBAT.

In case of strong turbulences in the monitored water bodies, the MINIBAT sometimes rolls over when it is dragged behind a boat. This is problematic and especially dangerous in shallow waters, as the steering of the wings suddenly works the other way round. We could improve and stabilize the diving behavior of the MINIBAT by increasing the angle of the drawbar in the front. This deepened the mass center of the dragged MINIBAT and considerably reduced the rollover frequency of the MINIBAT.

2.4 Geostatistical evaluation of water quality data

2.4.1 3D Kriging estimation of water quality distributions

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2D and 3D geostatistical kriging estimation of water quality data was already used for various studies.(24)(25)(26) However, several studies carried out with a MINIBAT or similar instruments lack a detailed description about which method was used for spatial interpolation of the data.(27)(28) Others apply inverse distance weighted (IDW) approaches without considering the unique properties and spatial dependency of each dataset and variable.(29) Standard 3D kriging methods as also used by Haas 2008(29) do not significantly improve interpolated data obtained from MINIBAT measurements compared to IDW technique. The special spatial distribution structure of MINIBAT measurement points needs to be taken into account for the directional variogram calculation to improve the quality of kriging results and to benefit from the uncertainty estimation received from the kriging procedure. Therefore we developed effective methods. The 3D geostatistical software package isatis (Geovariances) was used to evaluate and interpolate the measured data. For each parameter, directional variogram models were fit to experimental anisotropic variograms in both horizontal and vertical directions. To calculate the vertical experimental variogram, a migration procedure of the horizontally widely distributed data points into the nearest node in a regular gridfile (500×500×0.25 m) was performed in isatis. The resulting gridfile reduces the distance between two sampling points to only its vertical component. The raw data points in their sinusoidal spatial structure would otherwise lead to variograms mainly derived from horizontal distances absolutely not representing variances related to the vertical distance component. Cross-validation was performed to test the applicability of the defined variogram models. These were then used for a 3D kriging procedure with a search neighborhood (500×500×5 m) into grid files (30×30×0.5 m) representing the volumes of the water bodies. Kriging estimation was only performed in between the data points. No extrapolation was intended. Referring to Journel and Rossi (1989)(30) in this case, the ordinary kriging approach can be used to achieve reasonable kriging results, even in the presence of a global trend component. Only the experimental variogram tends to predict too high estimation errors in presence of a global trend.(31) This effect was minimized by manually excluding data points from high gradient areas from the experimental variogram calculation.

2.4.2 Spatiotemporal kriging estimation of water quality distributions

Water bodies are dynamical systems changing in time. A challenge for water quality investigations is to include the factor time into spatially resolved analyses. Therefore, we adapted a geostatistical method for spatiotemporal kriging estimation of water quality distributions.

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Time can be mathematically considered as an additional dimension in a spatiotemporal coordinate system.(33) The specific distribution of an environmental variable in space and time can then be treated as one realization of a spatiotemporal random function $Z(u,t)$ with $u \in \text{space}$ and $t \in \text{time}$. In our study, we consider the recorded MINIBAT values of each water quality parameter i as realizations of a spatiotemporal random variable $z_i(u,t)$ as a subset of $Z_i(u,t)$ with individual probability distributions.(33) Kriging is a tool to optimally estimate the realization of the corresponding spatiotemporal random function $Z_i(u,t)$ based on a (semi)variogram model that is derived from experimental (semi)variograms of the measured data $z_i(u,t)$. Even in the presence of global trends in the environment (e.g., thermal stratification in Lakes), ordinary kriging with a local neighborhood delivers reasonable estimation results with similar quality compared to the application of a trend model in the universal kriging approach, as long as no extrapolation beyond the sampling domain is intended.(34) We only used kriging to estimate data points within a convex hull around the acquired data points. Consequently, we could neglect probable trend components within our data. Again, we used the software isatis (Geovariances) to perform geostatistical data evaluation. Our recorded data points are characterized by three spatial coordinates: We projected the recorded GPS coordinates (WGS-84) to UTM zone 49 Easting and Northing values during import to isatis; Elevation above sea level e_s was calculated for each data point as $e_s = l_w - d_{bw}$ (l_w is the daily TGR water level(6); d_{bw} is the depth of each data point below l_w). The time of each data record td is thus a fourth component characterizing the data set in its spatiotemporal domain. Consequently, we could only perform spatiotemporal kriging after reasonably reducing the three-dimensional (3D) spatial coordinate system into a two-dimensional system. Because of the narrow and long channel-like shape of the Xiangxi River backwater, we could replace the Easting and Northing values by a linear horizontal distance component d_h. Therefore, we cumulated horizontal distance increments along the center of the water body starting at its confluence with the Yangtze River main channel. The resulting d_h values were projected onto our recorded MINIBAT data points. The final 3D spatiotemporal coordinate system consists of $(d_h|e_s|t_d)$ as its three principle directions. From our recorded data sets, we drew experimental (semi)variograms along these three main directions and manually fit regional anisotropic variogram models. A moving local neighborhood was used for the subsequent cross-validation and ordinary kriging calculations performed in isatis. We also checked the calculated kriging standard deviations against the absolute ranges of estimated water quality parameter values.

2.5 Numerical modelling of hydrodynamics and water quality

2.5.1 1D model HEC-RAS

To get an overview over the change of water level and discharge and its direction a 1D model was used as an approach to confine the domain influenced by the backwater effect depending on the boundary conditions at the Yangtze, i.e. discharge and water level elevation and the discharge of the Daning River as upstream inflow. Satellite data as well as data of the MINIBAT measuring campaigns were used, analyzed and compiled to a unified digital elevation data set. This dataset was used as input data for the 1D HEC-RAS model to describe the flow velocity in the water body between two neighbouring cross sections which afterwards have been used for the AQUATOX model (35) and the WASP model as reported here.

The backwater influence on the Daning River due to the impoundment of the Three Gorges Reservoir is up to 50 km from the confluence of the Daning River to the upstream of the Dachang Lake. The modelling domain of the lower Daning River is from the Dachang Lake to the Wushan Lake with the confluence to the Yangtze River (Figure V-22). The length of the River channel is about 43 km. For the upstream boundary of the model domain the discharge data from the Wuxi hydrological station is used. The upstream and downstream boundaries for the Yangtze River are set as the discharge and water level at the Wushan hydrological station accordingly. Figure 1 shows the modelling domain of the Daning River on top of the satellite image with high water level close to 175 m.a.s.l..

It is important to mention that the 1D modelling clearly shows the fluctuation of the water level, the flow direction and the excursion of the water bodies over the seasons whereas the 2D model provides the information about the pathways of pollutants, their spatial concentration and residence time.

2.5.2 2D model TELEMAC

In the 2D modelling a complete mixing over the water depth is assumed and hence, density driven stratification caused by seasonal temperature difference of the Yangtze and its tributaries are neglected. Although this assumption does not describe the flow velocities and the concentration field in a quantitative manner it allows to show the dominating large scale flow pattern with recirculating zones and dead water bodies and hence, the pathway and relative residence time of substances in different water zones in order to underline and interpret the field measurements of the MINIBAT.

As for the modelling of the Wushan Lake and the Dachang Lake the computational domain of the 2D Model TELEMAC covers the 3 km long section from the upstream inflow of the Daning River to the downstream area of confluence with the Yangtze River and the adjacent 5.4 km section of the Yangtze River itself. The bathymetry data are obtained from the SRTM satellite digital elevation model (DEM) and MINIBAT water depth echo recorder. The computing mesh generated for the model domain is shown in Figure V-25 in 3D view.

Since the interaction of the Yangtze and its tributaries is highly dynamic and important for temporal water quality assessment the water exchange mechanisms must be identified and quantified by 2-D tracer transport modelling resulting in a ranking as follows:

(i) Turbulent water exchange rate at interface, steady flow conditions $Q_{TU} = \varepsilon UA$ in m³/s with a global exchange parameter ε between 10^{-3} and 10^{-4} Q_{Tu} is about 50-150 m³/s
(ii) Advective in-/outflow due to water level change, $Q_{Ya,\ Wu} = UA$ m^3/s with mean in-/outflow velocity U over the interface area A or Daning River inflow Q_{Da}
(iii) Exchange due to density flow currents controlled by densimetric Froude Number Fr_d defined as $Fr_d = U/(\Delta\rho/\rho * g * h)^{1/2}$ with flow velocity U, relative density difference $\Delta\rho/\rho$ and thickness h of denser/or lighter water layer

The model shows that the Yangtze River is most of time of a year dominant, the higher the flow velocity and water level of the Yangtze the higher the mixing intensity and spatial extension of the recirculating zone. At the same time the residence time in the Wushan Lake is decreasing, and further reduced by some inflow of Yangtze $+Q_{Ya}$ and/or Daning River Q_{Da}. The density current effect is considered as small compared to the other effects. However, the Wushan Lake water quality is influenced by the Daning River discharges up to about 500 m³/s.

2.5.3 Water Quality Analysis Simulation Program (WASP)

The Model WASP (Water Quality Analysis Simulation Program) from EPA (US Environmental Protection Agency) is an open-source software and contains different model types, here the eutrophication option was chosen to start the investigation on algae. The equations solved by WASP are based on the key principle of the conservation of mass. WASP traces each water quality constituent from the point of spatial and temporal input to its final point of export, conserving mass in space and time. The input data consists of model segmentation, advective and dispersive transport, boundary concentrations, point and diffuse source waste loads, kinetic parameters, constants, time functions, and initial concentrations. The user defines the time steps of model processing, which is here defined as an interval of 14 minutes. WASP saves the values of all display variables for subsequent retrieval by the postprocessor program to produce the result graphs and tables of variables (54).

The area of the Wushan Lake is divided into segments, whose sizes are determined by the 2D mesh on the surface, where the width and length are geometrically designed. One simple mesh with 15 segments and a mesh with higher resolved mesh of 76 segments were created. The depth of the segments is defined to 20 m, because keeping the algae in perspective, it is sufficient to have at least the euphotic depth within the segment, which means the depth from the surface down to the level of 1 % photosynthetically active solar radiation (wavelength 400-700 nm) left.

As a first step, the time period of a field trip from 25.11.2013 to 07.12.2013 was chosen as temporal period. For the Yangtze estuary, it was shown that highest algal cell concentration peak appears in June to September (56). Hence, for the second model time period, MINIBAT measurement data of water quality parameters from former summer field trips are used as input.

The water quality data, which were measured by the MINIBAT at fieldtrips in winter 2013 and the summers of 2011-2013 were used in the model. For each segment, a mean value of the different parameters like nutrient concentrations, temperature, pH and oxygen was calculated in the geographic information system ArcGIS 10.0. Also the hydrological data from the TELEMAC model served to determine the flow direction and velocity in all segments. Other input values were cited out of literature or calculated, e. g. the solar energy input of solar irradiation

3 Scientific results

3.1 Water mass interaction and algal bloom formation in the Wushan Lake

3.1.1 Mixing processes in the Daning River backwater observed in April 2011

From the first field investigation, where we only took water samples, we could already get insights into mixing processes and their impacts on pollutant transport. In Figure V-7 we displayed the depth resolved dissolved phosphorus ($P_{diss.}$) fraction of water samples from the Daning River and its confluence zone with the Yangtze River across the Wushan Lake. The $P_{diss.}$ distribution is clearly divided into 2 major groups of water masses with 2 transition samples (*,**). The water masses originating from the Daning River exhibit a clear depth stratification of $P_{diss.}$ abundance with increasing trend towards higher water depths. On the other hand the water masses originating from the Yangtze River exhibit a homogeneous distribution of $P_{diss.}$ across the whole water column. Most interesting is, however, that we can find samples, geographically taken from the Daning River, that obviously belong to the Yangtze River group. This is highlighted in Figure V-7 by the grey line that connects samples of the depth profile right behind the entrance of the Daning River. All but one (* in Figure

V-7) of the Wushan Lake samples belong into the Yangtze River group. This surface transition sample likely represents the mixing process of both water masses. The second transition sample (** in Figure V-7) in the middle layer was taken upstream of the confluence zone. It is thus unlikely that mixing with Daning River water was responsible here. However, there are several small creeks entering the Yangtze River main channel there. Most likely one of these caused the dilution of $P_{diss.}$ in this specific sample.

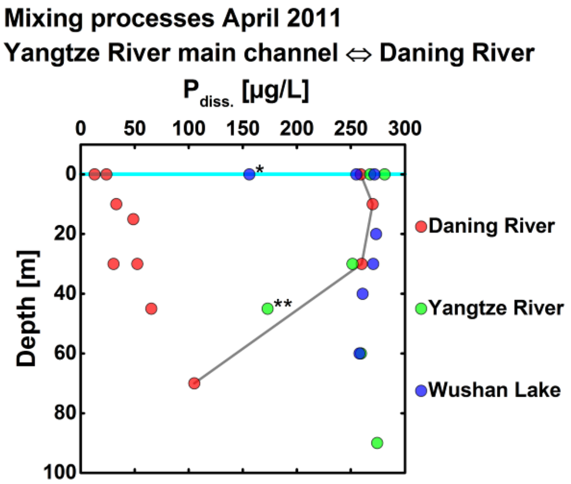

Figure V-7. Dissolved Phosphorus in water samples from April 2011. Samples derived from the Daning River, Yangtze River, and from the Wushan Lake and are plotted against sampling depth. Marked samples are explicitly mentioned in the text.

This mixing effect is also present for other anthropogenic pollutant elements. In Figure V-8 we displayed the dissolved concentrations of several pollutant elements against the corresponding P_{diss} concentrations and can see a clear positive relationship.

This example shows that the water quality and chemistry of the Wushan Lake and parts of the Daning River backwater are dominated by the Yangtze River main channel. Generally, pollutant loads in the Yangtze River are considerably higher in the Yangtze River main channel. These pollutant loads can then be transported upstream into the tributary backwaters with ecological consequences of unknown extent.

3.1.2 *Algal bloom formation and water mass mixing in August 2011*

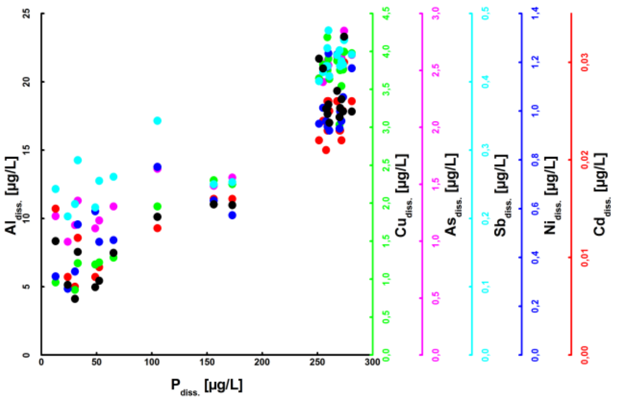

Figure V-8. Dissolved Phosphorus against dissolved Al, Cu, As, Sb, Ni, and Cu in water samples from April 2011. Samples derived from the Daning River, Yangtze River, and from the Wushan Lake.

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Increasing eutrophication and algal bloom events in the Yangtze River Three Gorges Reservoir, China, are widely discussed with regard to changed hydrodynamics and nutrient transport and distribution processes. A profound understanding of the processes leading to the formation of algal blooms, especially harmful algal blooms, is necessary but is neither achieved internationally (36) nor for the TGR (37). Vertical Mixing dynamics (8), density current-driven nutrient inputs into tributary backwaters (38)(19), temperature and thermal stratification (37), as well as light attenuation by suspended particles (39) are all considered being regulatory factors for the formation of algal blooms in TGR. Insights into water exchange and interaction processes between water masses related to large-scale water level fluctuations in the reservoir are crucial to understand water quality and eutrophication dynamics. The importance of "Effects of inflow on harmful algal blooms" (36) was highlighted by a same-titled special issue in the Journal of Plankton Research. Therefore, confluence zones of tributaries with the Yangtze River main stream are dedicated key interfaces. Each algal bloom formation is an individual event, and its driving forces depend on the prevailing specific ecological conditions. It is, thus, important and necessary to study the processes leading to algal blooms in a very high spatial and temporal resolution to figure out the driving forces and ecological interactions leading to single algal bloom events. The synthesis of such datasets will then significantly contribute to a better generalized understanding of algal bloom formation.

The dataset described in this study was recorded in situ and online with a MINIBAT from 23 to 29 August 2011 after heavy precipitation and a subsequent discharge peak and water level increase in TGR. Geostatistical evaluation of the water quality data was performed (chapter 2.4.1), and results were compared to phosphorus contents of selected water samples. The precipitation event triggered the inflow of huge water masses from the Yangtze River into the lower section of the Daning River, the so-called Wushan Lake. The observed results reveal very detailed insights into the related water mass interactions and water quality dynamics in the confluence zone of the Daning River and the Yangtze River. The corresponding developments and distributions of several water quality parameters were directly related to the development of an algal bloom within the Wushan Lake water body (Figure V-9). The strongly rising water level throughout the measurement period caused Yangtze River water masses to flow upstream into the tributary and to supply their higher nutrient and particulate loads into the tributary water body. Rapid algal growth and sedimentation occurred immediately when hydrodynamic conditions in the confluence zone became more serene again. Consequently, water from the Yangtze River main stream can play a key role in providing nutrients to the algal bloom stricken water bodies of its tributaries.

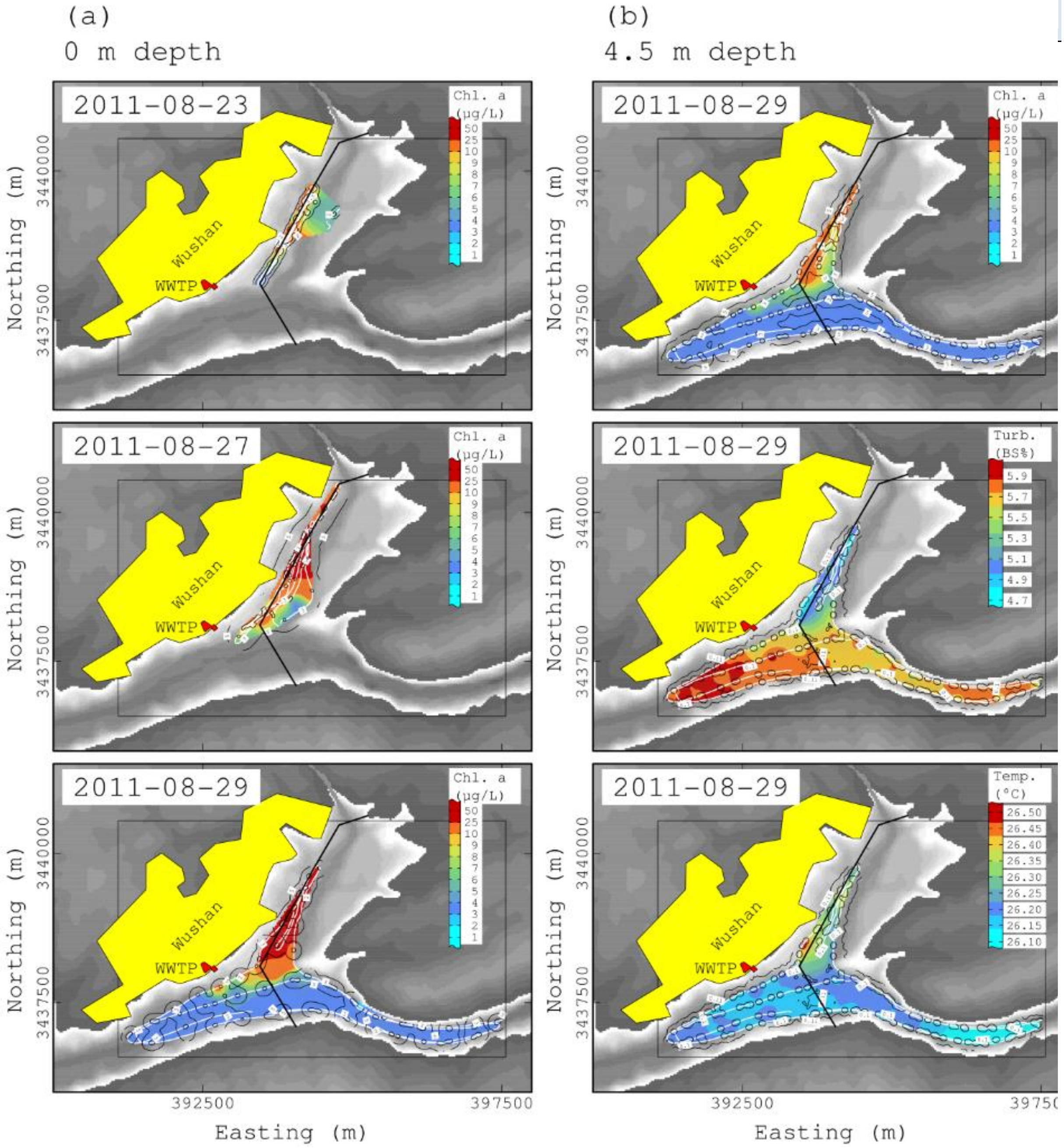

Figure V-9. Kriging estimations for: (a) Chlorophyll α (Chl α) concentration from 23 to 29 August 2011 at the water surface. (b) Chl α, Turb., and Temp. at 4.5 m water depth on 29 August 2011. Kriging standard deviations are shown as isolines. Chl α legend does not have a linear scale to emphasize differences in lower concentration ranges. Reprinted with kind permission from Springer Science+Business Media (12), copyright 2012 Springer-Verlag Berlin Heidelberg.

3.2 Urban pollutant plumes in the Three Gorges Reservoir

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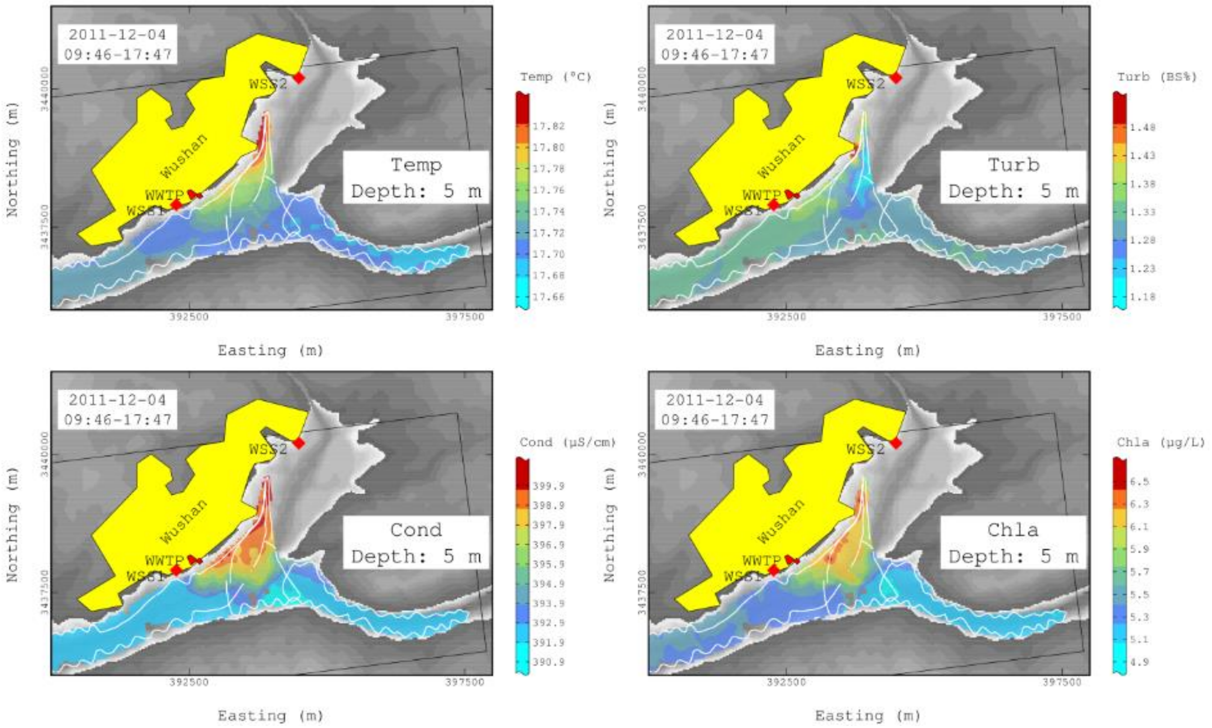

Figure V-10. Distribution of Temp, Turb, Cond (normalized to 25°C), and Chl α at 5 m depth in the water bodies around Wushan City on 4 December 2012. White lines mark MINIBAT measurement cruises. Waste Water Treatment Plant (WWTP) and sampled discharge locations (WSS) are marked in red. Reprinted with kind permission from Springer Science+Business Media (40), copyright 2013 Springer Science+Business Media Dordrecht.

The Three Gorges Reservoir (TGR) in the Yangtze River was among other reasons meant to improve and strengthen socio-economic development of the involved regions. Considerable economic growth and urbanization now pose additional threats to the water quality of the TGR due to urban pollutant inflows. The changed hydrological conditions in the TGR considerably have altered pollutant transport dynamics now causing higher susceptibility of the backwater areas to eutrophication and algal blooms. The Yangtze River is also widely used as a source for drinking water production. The assessment of the urban impact on the water quality in the TGR is, thus, crucial for sustainable future development planning.

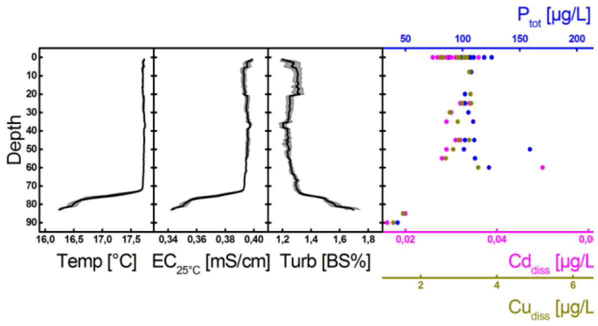

Figure V-11. Left: Depth profiles of Temp, Cond (normalized to 25°C), and Turbidity in front of Wushan measured with the MINIBAT on 04 December 2011. Right: Pollutant distribution across the water column around Wushan, based on ICP-MS analyses of water samples from 4 December, 2011.

Therefore, we performed MINIBAT measurements around the cities of Wushan (Figure V-10) and Dachang (Figure V-12) on the Daning River in the backwater reaches of the TGR in December 2012. Hydrological conditions were stable at constant water level between 174 – 175 m.a.s.l. and low discharge conditions in the TGR during the sampling period. 3D distribution patterns of the parameters temperature, conductivity, and turbidity in the water bodies were modelled using geostatistics. Selected water samples from different depths were analyzed for dissolved and particulate constituents using ICP-MS.

Water quality distribution patterns were geostatistically estimated (chapter 2.4.1) from the in situ and online MINIBAT measurements on 4th and 6th December 2011. Both datasets revealed plumes of higher temperature, conductivity, and turbidity around the urban areas of Wushan City and Dachang City (Figure V-11, Figure V-12, Figure V-13). The plumes were only present in the epilimnion of both water bodies. Around Wushan City the epilimnion included the upper 70 m water column (Figure V-11) around Dachang City only 20 m. Pollutant concentrations (P_{tot}, Cd_{diss}, Cu_{diss}) in the water bodies revealed a similar pattern with higher concentrations in the epilimnion around both urban areas (Figure V-11).

We performed three measurement cruises passing Dachang City in the morning, around noontime, and in the afternoon (Figure V-13). Initially, the highest Turbidity was found north-west of Dachang City in similar areas as the highest Chl α-concentrations. Subsequently, increasing Turbidity was found all along the urban area shoreline. However, in contrast to the results from the Wushan Lake, electrical conductivity and temperature in the Dachang Lake are disconnected to Chl α-concentrations indicating that optimal growth conditions for algae can be disconnected to pollution sources.

Urban pollutant impacts on the water quality in TGR are definitely present and we could successfully monitor them with the applied MINIBAT techniques. Pollutants in the selected water samples were obviously related to water quality parameter distributions. Consequently, the detection of urban point source pollution is also possible.

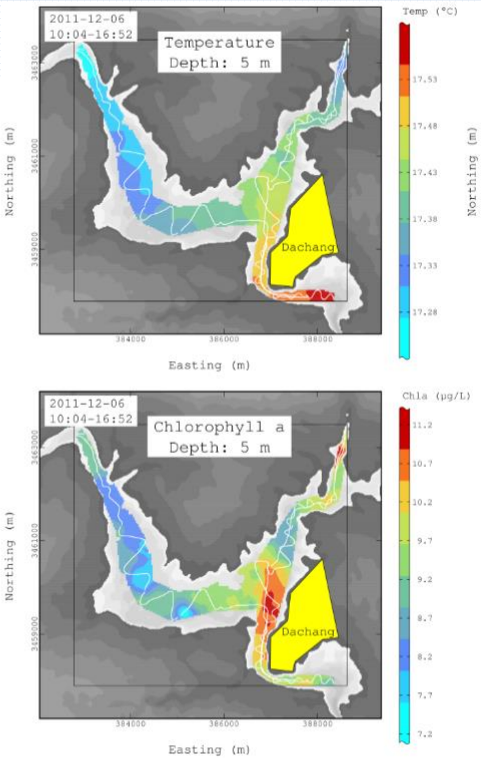

Figure V-12. Distribution of Temp, Cond (normalized to 25°C), and Chl α at 5 m depth in the water bodies around Dachang City on 6 December, 2011. White lines mark MINIBAT measurement cruises. Reprinted with kind permission from Springer Science+Business Media (40), copyright 2013 Springer Science+Business Media Dordrecht. Turbidity values showed a very significant increase around Dachang City during the course of the day (Figure V-13).

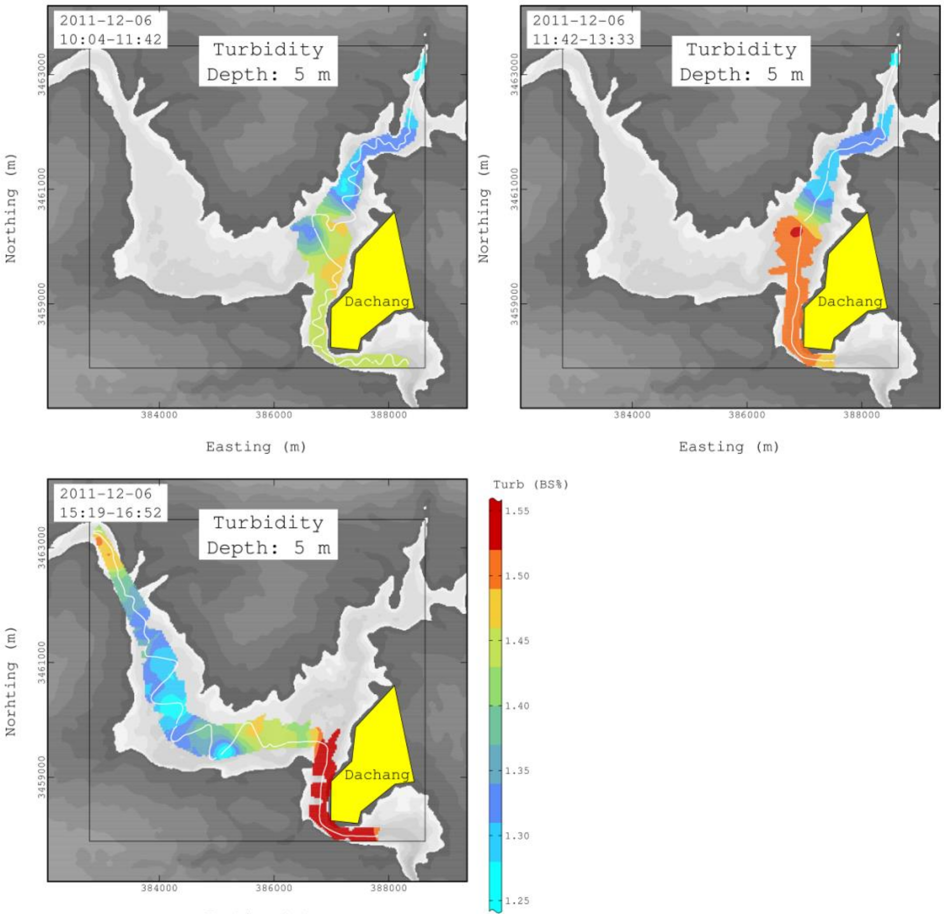

Figure V-13. Distribution of Turb at 5 m depth in the water bodies around Dachang City during 3 MINIBAT measurement cruises on 6 December, 2012. White lines mark MINIBAT measurement cruises. Reprinted with kind permission from Springer Science+Business Media (40), copyright 2013 Springer Science+Business Media Dordrecht.

3.3 Density current amplification of pollutant transport into TGR tributaries

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The impoundment of the Three Gorges Reservoir (TGR) on the Yangtze River in China burdened its tributary backwaters with severe environmental problems (chapter 1.1). Confluence zones of reservoir tributaries with the Yangtze River main channel are main drivers of pollutant dynamics in the TGR and are thus keys to develop mitigation measures. Such a confluence zone was formed within the former Xiangxi River valley (Figure V-1) one of around 40 major tributaries of the TGR entering the Yangtze River main channel approximately 40 km upstream of the Three Gorges Dam (TGD). At its maximum water level of 175 m a.s.l., the TGR backwater reaches more than 35 km upstream into this narrow and channel-like valley (Figure V-1). Similar to most TGR tributaries, the Xiangxi River backwater is seriously affected by algal blooms as well as land use and land cover changes.

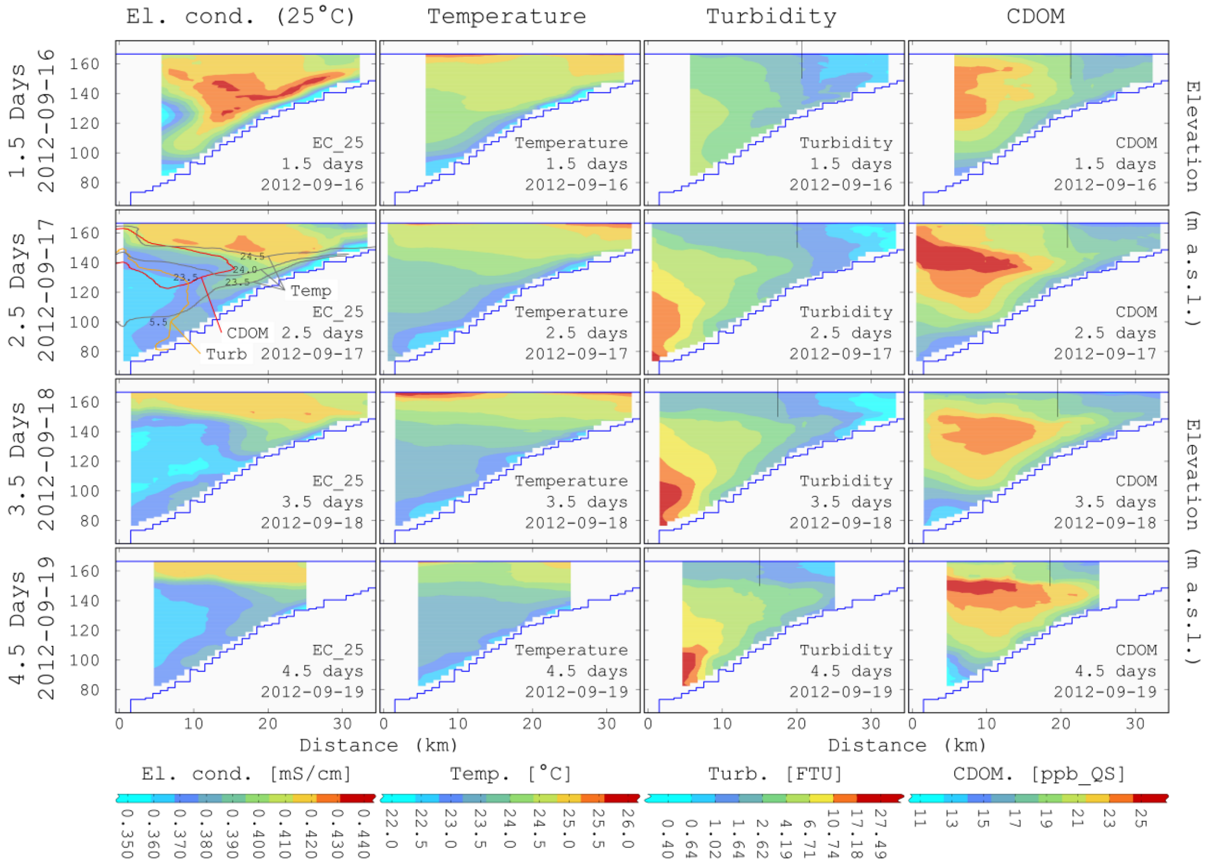


Figure V-14. Dynamic water quality distribution along a longitudinal section of the Xiangxi River backwater. Four extracted time steps of the spatio-temporal interpolated water quality distribution for four out of seven analyzed water quality parameters. Selected isolines of Temp, CDOM, and Turb are added to EC_{25} after 2.5 days. Vertical lines in the CDOM and Turb columns indicate downstream moving water masses at the surface of the midstream Xiangxi River backwater. Reprinted with permission from ACS Publications (32), copyright 2014 American Chemical Society.

In this study, we aimed to capture the effects of hydrodynamic interactions between the Xiangxi River backwater and the Yangtze River main channel on the corresponding water quality distribution patterns. Therefore, we developed a method to integrate (1.) in situ and online measurements with a MINIBAT multisensor probe with (2.) a spatiotemporal geostatistical data evaluation (chapter 2.4.2) and (3.) element content analysis in the dissolved and particulate phases of selected water samples. This method can be utilized for analyses of complex water body interactions even in very remote areas with reasonable amount of staff and material.

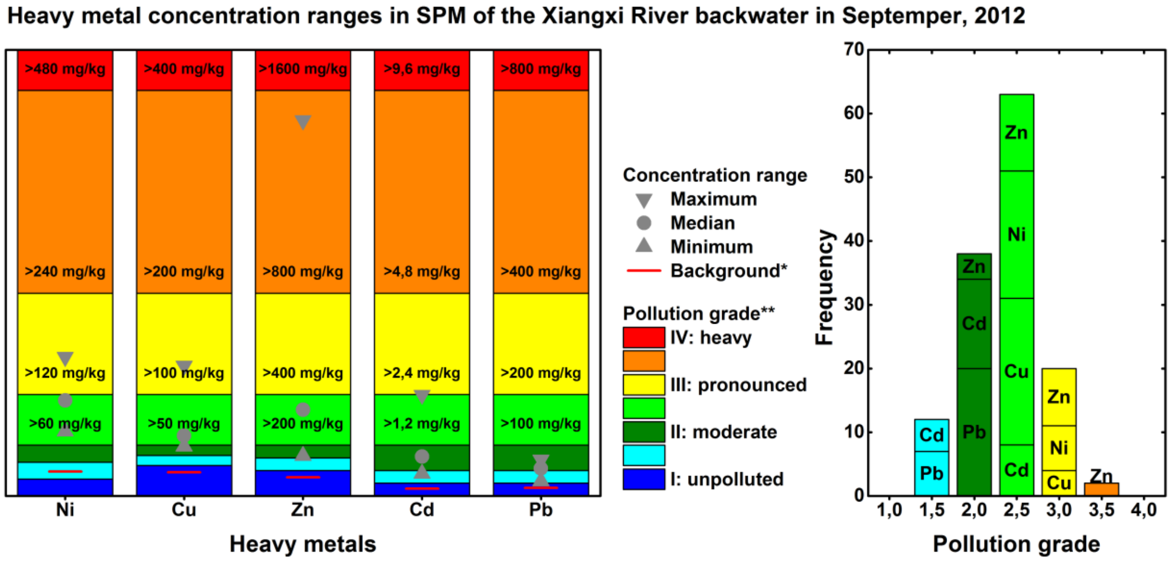


Figure V-15. Heavy metal concentration ranges in SPM of the Xiangxi River backwater in September 2012 in comparison with *local background concentrations (41) and **pollution grade thresholds of SPM in Germany (42). Note: heavy metal concentrations of all analyzed samples exceed local background values. Pollution grade mainly ranges between moderate (2.0) and pronounced (3.0) pollution. Reprinted with permission from ACS Publications (32), copyright 2014 American Chemical Society.

Our results show the movements of density currents throughout the Xiangxi River backwater of the TGR (Figure V-14). Turbidity was linearly and significantly correlated with concentrations of suspended particulate matter (SPM) in the selected water samples. A huge interflow density current from the Yangtze River main channel transported its SPM to the upstream reaches of the tributary backwater. The SPM was considerably polluted with heavy metals (Figure V-15). Water from the upstream backwater moved in opposite direction and carried less but pollutant-enriched suspended sediments. When compiling all the information from our data, we could derive a simplified density pump and pollutant transport flow model for the hydrological situation in the Xiangxi River backwater in September 2012 (Figure V-15).

Generally, the Yangtze River main channel in TGR carries much higher concentrations of nutrients and/or heavy metals than its tributaries (12), (19). On the long term and on the reservoir scale, such a density pump effect could thus supply nutrients and polluted SPM to the upstream tributary backwaters. There, they could further aggravate eutrophication problems and support pollutant accumulation in sediments, food webs, and in the agriculturally used flood plains of TGR water level fluctuation zone.

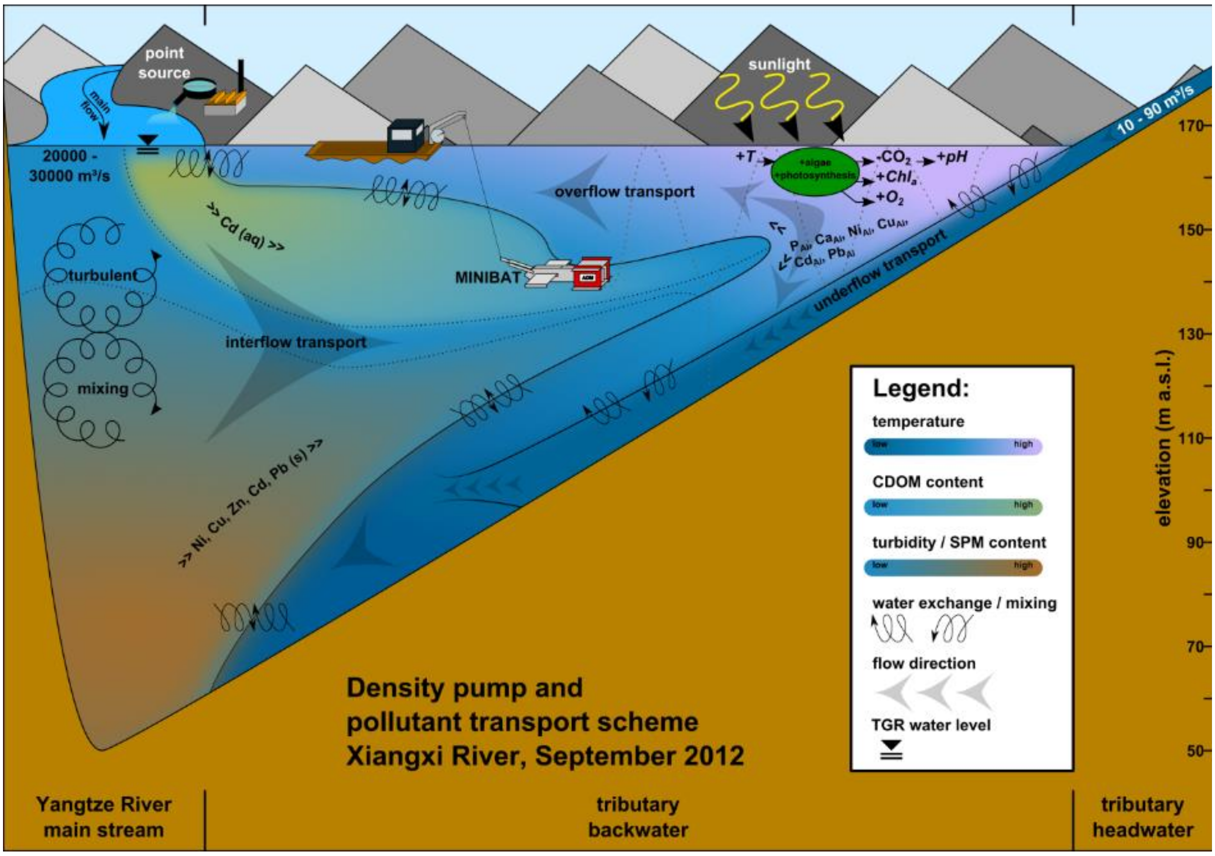


Figure V-16. Simplified density pump and pollutant transport scheme of the Xiangxi River backwater in September 2012. Model flow pattern derived from a compilation of the dynamic distribution of all seven analyzed MINIBAT water quality parameters. Note: turb plume has high total heavy metal concentrations; CDOM plume carries higher concentrations of dissolved Cd; enrichment of P_{Al}, Ca_{Al}, Ni_{Al}, Cu_{Al}, Cd_{Al}, and Pb_{Al} in SPM is related to algae and photosynthesis and distributed accordingly along the surface and the bottom of the upstream tributary backwater. Reprinted with permission from ACS Publications (32), copyright 2014 American Chemical Society.

The seasonal and spatial representativeness and significance of the density pump effect on the absolute water mass/pollutant exchanges between the Yangtze River main channel and its tributaries in TGR need to be further evaluated in the future. Particularly, because the seasonal discharge pattern of the Yangtze River and TGD water level management cause completely different but seasonally typical hydrodynamic conditions in TGR. For the Xiangxi River backwater, it was already demonstrated that intruding density currents from the Yangtze River main channel occurred with a seasonal shift from underflows in winter and spring to interflows in summer and to overflows in autumn (43). Thus, an upstream transport into this tributary bay seems to be always present, but is so far not quantified for pollutants. It is also crucial to evaluate the further fates and pathways of these pollutants in waters and sediments of TGR, and the Yangtze River with adequate techniques; they will move or accumulate either upstream or downstream, but they will stay somewhere and this we should know. Not least because throughout its catchment the Yangtze River and its floodplains serve as a major source of water, food and agricultural cropland for whole China (44), as well as habitat for an invaluable biodiversity (11).

3.4 Water quality in the Yangtze River downstream of the Three Gorges Dam

Table V-1: Pollutant content of the East Lake in contrast to the main stream and drinking water standards (51), (52), (53).

[µg/L]	Cu	Zn	Cd	Pb	As	Sb
Mean value of transects in Wuhan	2.46	5.41	0.04	0.44	3.74	1.17
East Lake mean value (9 samples)	4.51	21.5	0.46	3.60	4.88	4.20
EU	-	-	5.00	10.00	10.00	5.00
WHO	2000	-	3.00	-	10.0	20.0
CHINA	1000	-	10.0	-	10.0	10.0

The water quality in the middle reaches and its dependency on effects of the TGD were investigated during the field trip in summer 2013. Numerous water samples were taken and analyzed for anions and cations with IC, and ICP-MS. Alkalinity as well as contents of NH_4^+ were tested directly in the field with Merck chemical tests. Stable oxygen and hydrogen isotopes were measured by the company Hydroisotop and the suspended sediment contents were measured from weighed filters. Water quality parameters were measured in situ and on-line with the MINIBAT. Depth and cross profiles as well as comparisons with results from other studies were used to assess the present day condition and the changes over time. The Yangtze River water is strongly influenced by its geogenic background. A stable high content of HCO_3^-, Mg^{2+}, and Ca^{2+} over the last 50 years is proven and besides provides a good buffer system - 146 -(47). In contrast, an increase of anthropogenic elements (Na^+, SO_4^{2-}, Cl^-) is recorded during this period (47). Besides waste water inlets, major sources of pollutants are the entries of urban pollutants into the stream water especially during heavy rain events. Therefore, the mixing process which takes place intensely and fast is very important for the water quality. Apart from the mixing process, the water volume ensures a dilution of pollutants and causes a drop of their concentration under a critical limit, leading to low heavy metal concentrations according to drinking water standards (Table V-1). According to Chinese standards all water samples taken in Yidu and Yichang (downstream of TGD) top the limit value of 10 mg/L of nitrate slightly and in one case, meaning a waste water sample, heavily. It was not possible to measure the phosphate concentration, because the detection limit at the analysis instruments were not surpassed. The dam building in the upper reaches disturbed and changed the sediment balance. Downstream the TGD the sediment concentration (Table V-2) has decreased to a great

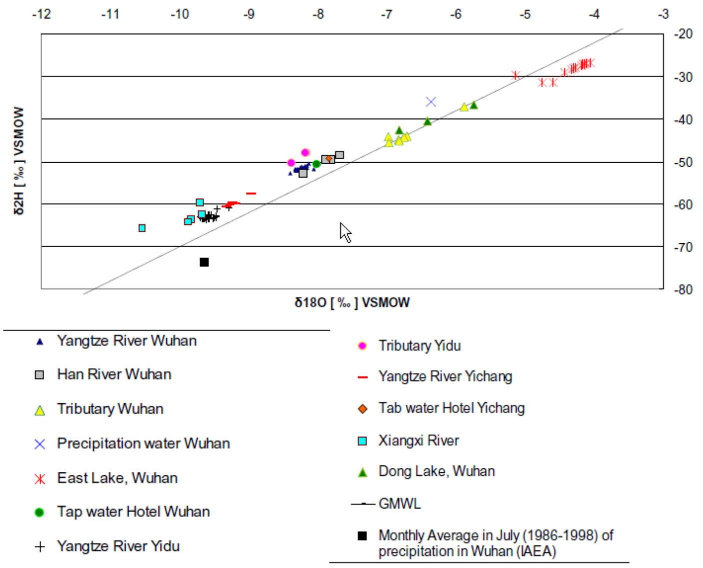


Figure V-17: Stable isotope composition of water samples from the Yangtze River downstream of TGD in July 2013, clustered according to their origin.

extend which leads to erosion of the Riverbed and also to erosion of the connected Lake-River systems (47)(48) that actually should act as sinks (49)(50).

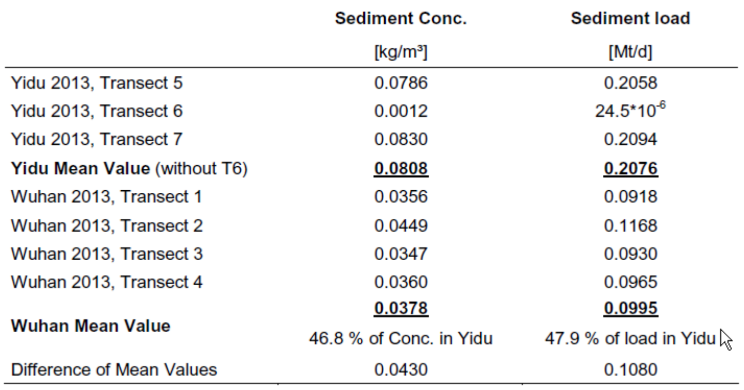
On the contrary, Lakes around Wuhan city do not act as a sink for sediments but as a sink for pollutants since they are the destination for urban inlets. The isotopic illustrates the differences of water types caused through their different origin. Here, the water bodies from the regions of Wuhan show higher δ values as those from the more upstream Yangtze regions at Yichang or Xiangxi. Finally the δ values of the Yangtze at Wuhan reflect the specific mixing processes and the evaporation influences on the water bodies of the East Lake in Wuhan with the heaviest δ values indicating its sink properties.

Comparing lake water quality with the quality of the Yangtze River and with respect to heavy metals and metalloids, it is shown that the Lake water is facing higher concentrations as the River water. This can probably be credited to the accumulation processes (47)(54) that lead to a constantly increasing content of anthropogenic elements. This suggestion is supported by the heaviest isotopic composition of the East Lake water body found in Wuhan due to evaporation processes. In contrast to the Lake water, the stream water quality is in a good condition, mainly due to dilution and mixing effects. In this case, the influence of the dam can be a problem, since the equilibrium is disturbed and regions, that used to act as sinks can change to erosional regions. This could cause the remobilization of pollutants from the sediments, and lead to higher concentrations of pollutants in the stream. Analyses of chemical sediment compositions from the sampled filters will follow until the end of the project and added to the picture.

Interpretation of the isotopic composition on a spatial scale:

The proportions of heavy ^{18}O and ^{2}H isotopes were kindly analysed by the company HYDROISOTOP in Schweitenkirchen, Germany. ^{18}O and ^{2}H of all samples become lower along the course of the River towards North-West (Figure V-18). This mirrors mainly the continentality, so the River greater the distance to the coast, the lighter is the isotopic composition. By investigating isotope ratios along the Yangtze River course without tributaries this process becomes clearer. In the Wushan Mountains the isotope composition has a lower portion on heavy isotopes than water further downstream.

Table V-2: Comparison of mean sediment concentration and mean sediment load of water samples from the Yangtze River downstream of TGD in July 2013.



	Sediment Conc. [kg/m³]	Sediment load [Mt/d]
Yidu 2013, Transect 5	0.0786	0.2058
Yidu 2013, Transect 6	0.0012	$24.5*10^{-6}$
Yidu 2013, Transect 7	0.0830	0.2094
Yidu Mean Value (without T6)	**0.0808**	**0.2076**
Wuhan 2013, Transect 1	0.0356	0.0918
Wuhan 2013, Transect 2	0.0449	0.1168
Wuhan 2013, Transect 3	0.0347	0.0930
Wuhan 2013, Transect 4	0.0360	0.0965
Wuhan Mean Value	**0.0378** 46.8 % of Conc. in Yidu	**0.0995** 47.9 % of load in Yidu
Difference of Mean Values	0.0430	0.1080

Especially interesting are confluence zones where waters from different origin mix. In Figure V-18 the confluence zone in Yidu is depicted. Obviously the isotopic composition of the tributary is characterized by a heavier composition than in the main stream. This implies that the drainage basin of this tributary features a lower level of continentality.

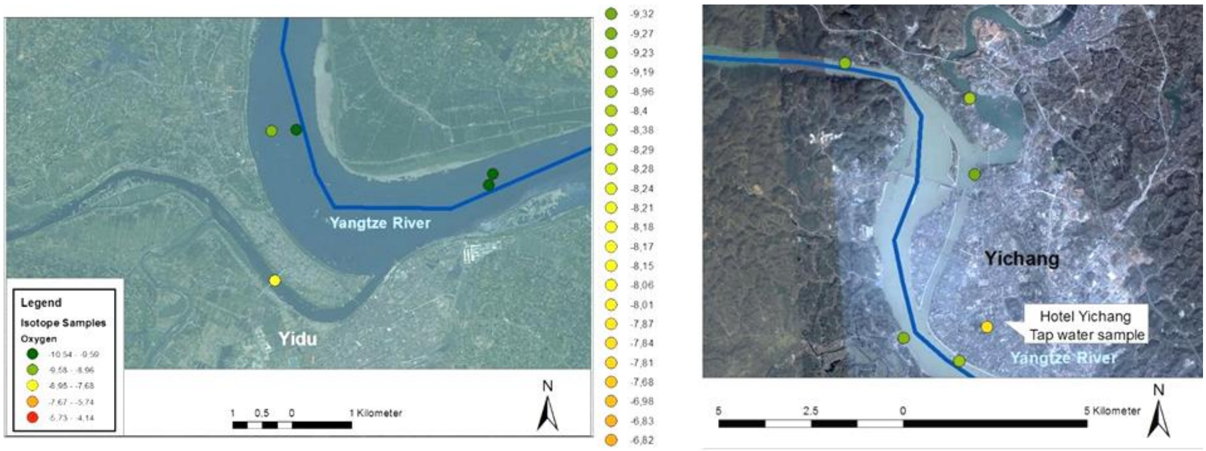


Figure V-18: d^{18}O isotopic composition of water bodies in (left) Yidu and (right) Yichang.

When choosing a more fine-grained classification of the isotope values, more insights are possible. In Figure V-18 a tap water sample from the hotel is illustrated in contrast to stream water samples. The comparison clearly indicates that the tap water used in the hotel does not originate from the main stream of the Yangtze River in Yichang. Again, the tributary exhibits a heavier isotope composition than the main stream.

In contrast to Yichang, the tap water in Wuhan seems to originate from the Yangtze River; at least it is possible seeing the isotope composition; providing a potential method to identify the sources of drinking waters, especially for cases of pollution incidences (see Figure V-19).

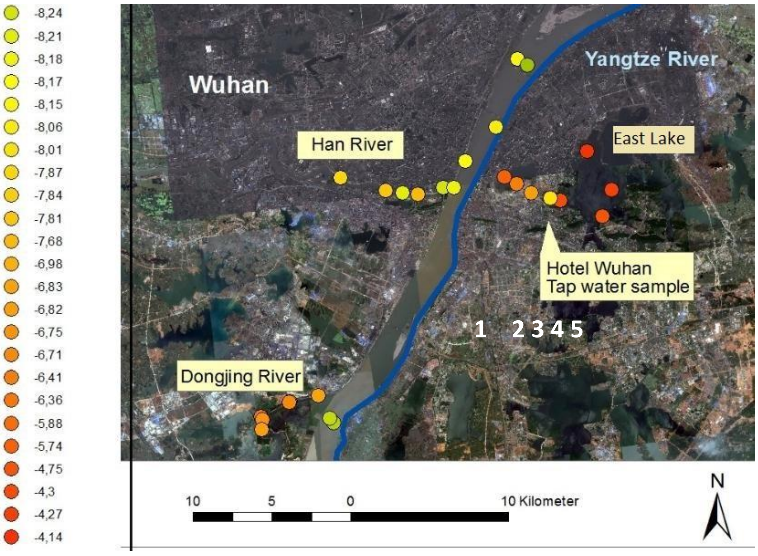


Figure V-19: d^{18}O of various water bodies in Wuhan.

As was the case in Yidu, also in Wuhan both tributaries, the Han River and the Dongjing River show heavier isotope composition than the main stream. Lowest isotopic compositions occur upstream of the Donjing River, downstream the Han River also the Yangtze water have higher δ^{18}O values, indicating the mixing with the tributaries. Another interesting aspect of this plot is the isotopic composition of the Han River. There are five samples, some of them are heavier than the others. The values of the samples which were taken on the 4th of July with the boat and the δ^{18}O values are 8.21 and 8.24. The values of samples from the 7th of July and feature δ^{18}O values are 7.87, 7.81 and 7.68. Between the 4th and the 7th of July there was a lot of rainfall in Wuhan. The rainfall in this period has a distinct heavier isotope composition than the main stream of the Yangtze River, which effects the isotopic composition since the samples, measured after the rainfall clearly are heavier. The differing oxygen values in the Han River indicate that rainfall (especially heavy rain) has an immediate impact on the isotope composition in Rivers. Furthermore, the heaviest signals were detected for the East Lake indicating evaporation processes. Thus, for further investigations of water resources in the Yangtze River system, isotopic considerations of O and H should be involved for the analyses of water body mixing processes, residence times and source identifications.

3.5 *Numerical modelling of water flow patterns in selected areas of the TGR*

3.5.1 *Modelling and interpretation of physico-chemical processes*

a) Daning River tributary

As an initial survey, the correlation between the water level in the Yangtze River and the outflow of in the Daning River was ascertained with the intention to define scenarios that are relevant for sediment and water quality investigations. Unfortunately, official data of discharge and/or water level exist only of water level monitoring stations far away and consist just of daily mean values since 2010. Nevertheless, significant hydrological scenarios (predefined water level in the Yangtze and tributary Daning River) were set and numerical calculations were conducted to describe the large-scale transport processes in the Dachang Lake and Wushan Lake. The results contain basic information on transport pathways, concentration fields, areas of potential sedimentation, retention times and mass exchange of dissolved and particulate matter between both the water bodies of Yangtze and Wushan Lake. The calculation results are very important for the related projects (degradation and transformation processes) and

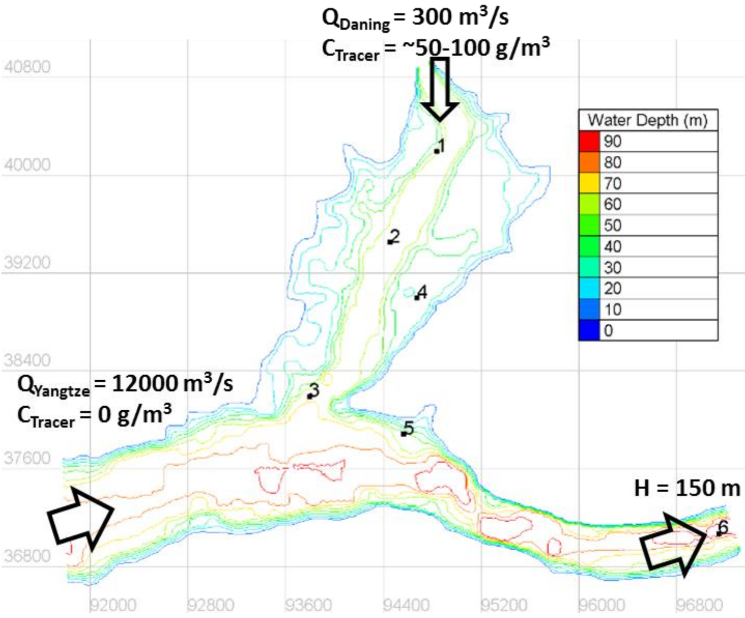


Figure V-20. Layout of Wushan Lake and Yangtze River for numerical modelling: Hydraulic boundary conditions and bathymetric isolines of the Wushan Lake. Pollutant input in the cross section at the entrance of the Daning River to the Wushan Lake.

finally for the draft of a concept for a catchment-oriented management of sediments and water quality under the changed hydrological-hydraulic boundary conditions.

b) Dachang Lake

The transport processes of the Daning River beginning at the Dachang Lake and ending at the confluence in the Yangtze are investigated with the focus on the catchment area of the Daning River. The Dachang Lake is much more shallow than the Wushan Lake, but also has a vertical thermal stratification (measurement data von MINIBAT 08-2011 and 12-2011). In August, a continuous decrease of temperature in the upper 10 m of the water column was identified, but no clear thermocline. In December by contrast, there was an obvious thermocline at a depth of 20 m (total depth of 40m). In this situation, it can be seen that the influence of the backflow of the Yangtze reaches far upstream (circa 40 km) and causes amplitudes of water level up to 30 m. As for the seasonal, effects on the dilution of disposed substances the impact is different depending on the location and strength of source, e.g. Daning River, urban drainage system, and industrial input.

In particular, the influence of the areas within the intertidal zone and the released and mostly diluted substances on water quality have to be considered. Deposition of particulate matter is difficult to estimate, because of a lack of sediment-specific data. However, it can be assumed that resuspension of deposited sediments and particulate matter, respectively can be neglected because of a too low non-erosive shear flow velocities near the bottom Lake.

The calculation results will be analysed and visually presented to show e.g. the mean retention time of a substance in a given water zone. Furthermore, it can be shown which percentage of the near bank areas are inundated on how many days in the year and hence, have no atmospheric interaction. Based on this, the materials cycle on aerobic conditions can be estimated and the concerning parameters can be integrated in the model.

The uncertainties associated with the sediment properties (lack of fall velocities and sedimentation/erosion criteria) and the kinetic parameters for the transformation processes should be chosen in a realistic approximation also like the residual data gaps of the suspended matter in the Daning River.

c) River section between Dachang Lake and Wushan Lake

Even this 30 km long section is strongly influenced by the Yangtze River due to backwater effect with corresponding water level fluctuations which in extreme situation are associated with transport of Yangtze water upstream towards the Dachang Lake. However, the water quality of the Dachang Lake will be hardly affected by the Yangtze River because of the lesser transport distance of mass as compared to the backwater length. Since the flow velocity in the gorge-like narrow River section is significantly higher sedimentation processes are not expected unlike the situation in the Wushan Lake. For similar reason the impact of the “intertidal areas” on water quality processes will not play a significant role.

d) Wushan Lake

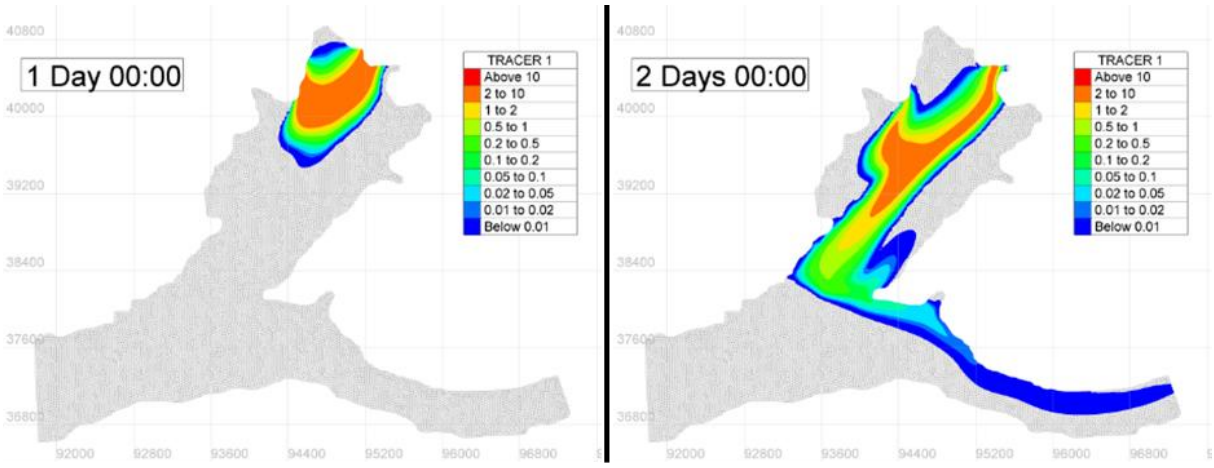


Figure V-21: Development of the concentration field in the Wushan Lake at 24 and 48 hours after a one and a half hours input through Daning River indicating the pathway, counter clockwise recirculation, mixing and transfer to the Yangtze River.

Because of the great depth of the Wushan Lake between 60 and 90 m density-driven stratifications are to be expected and therefore, a realistic approach to numerical modelling has to account for density currents as one of the above mentioned exchange mechanisms. As a first approach dispersion and mixing processes are assumed to take place in the epilimnion of which the thickness is estimated between 50 m (08-2011) and 70m (12-2011) based on seasonal MINIBAT data. However, highly diagnostic results of transport paths and deposition zones can be prepared. There is a strong dynamic influence of the Yangtze on the Wushan Lake concerning the transport, mixing and residence time of substances originating from the Daning River and all sources along the western banks and shore line. After certain mixing with the Yangtze River, the disposed substances may circulate in a well confined zone of the Lake and – depending on Yangtze River water level and discharge and, inflow of Daning River – finally when reaching the Yangtze River get washed out of the Lake after weeks or months as illustrated in Figure V-21 and Figure V-23.

The influence of the Yangtze River on the hydrodynamic processes in the Wushan Lake such as dilution, residence time, water exchange depends on the water level of the Yangtze River, whether it is rising or falling and, the flow velocity of the Yangtze River and, of course on the Daning River discharge as depending on the hydrological conditions of the catchment. The latter is a counteracting force preventing the Yangtze water to be pushed further upstream.

e) Yangtze

The Yangtze controls the hydrodynamic interaction primarily due to the seasonal variation of the water level for flood management. Flow pattern and internal mixing are controlled by turbulent exchange and/or advective in and outflow at the huge contact area at the confluence zone. Obviously, the influence on the Wushan Lake is maximal at high Yangtze River water level and low Daning River flow. Model results indicate that after change of water level and discharge transient processes can take some days up to a month to reach steady state flow and pollutant concentration in the Wushan Lake.

3.5.2 *General influence of the Yangtze River on hydrodynamics of tributaries for the example of the Daning River*

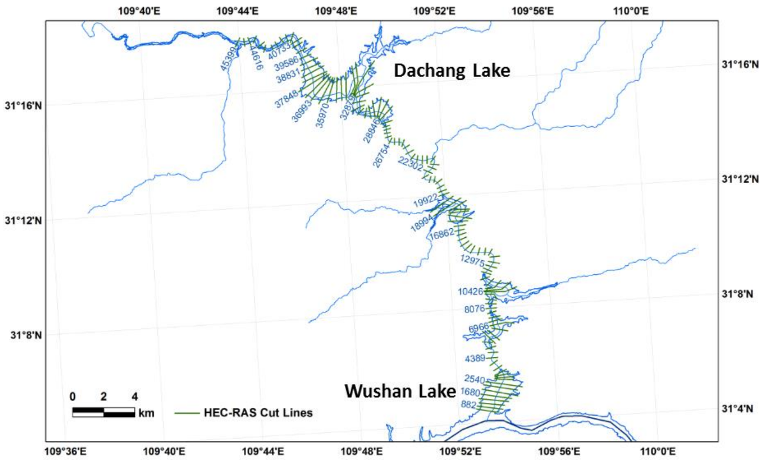


Figure V-22: Elaboration of the synthetical dataset of the bathymetric data and terrain data DEM of the Yangtze (below) until the Dachang Lake (above) for the 1D hydraulical modelling as an input for Aquatox and the 2D-transport modelling Telemac.

Former investigations have shown, that the numerical simulations with the 2D-model is appropriate to analyse the dynamics of the large-scale spatial-temporal conditions of transport. The 1D model approach has been used as a pre-study to show the extension of the hydraulic backwater effect on Yangtzes tributaries and to prepare the model domain for the more complex 2D transport modelling. It could be shown by the 1-D model that the backwater effect into the Daning River tributary reaches beyond the Dachang Lake, but tracer transport modelling show that the Yangtze water will not reach the Dachang Lake.

Due to the lack of bathymetric data, the depth measurements of the MINIBAT were used to get cross section data for Wushan Lake, Dachang Lake, and also for the narrow and 30 km long connecting River section between both Lakes (Figure V-22). The dataset that was synthetically created from River data and terrain data enables now the calculation of the whole interesting area from the Yangtze until far upstream in the Daning River. Some hydrological scenarios with typical discharge and water level conditions that are relevant for water quality were selected for the Yangtze and Daning River tributary. Transport, dispersion and mixing of dissolved or particulate suspended matter are illustrated as concentration fields changing with time. The model results indicate that the interaction between Yangtze and Wushan Lake is characterized by the strong entrainment of the Yangtze. Neglecting density currents and Daning River inflow and, assuming a constant water level of the Yangtze strong turbulent mixing at the interaction zone causes an exchange of water of about 50 m^3/sec, which can be considered as an estimated minimum rate of Yangtze water penetrating into the Wushan Lake. However, due to the varying Daning River inflow and Yangtze River conditions the water of the Wushan Lake is always mixture showing spatial and temporal concentration variation accordingly. The Daning River has a relatively small influence on the conditions in the Wushan Lake except at extreme flood events. In any case, pollutant concentration and residence time, in the Wushan Lake very much depend on the location, e.g. water exchange at the western bank is weak compared to the central part of the Lake 1D-calculations could show that the backflow into the Daning River tributary reaches beyond the Dachang Lake, but the water of the Yangtze River doesn’t arrive at Dachang Lake (Figure V-22).The calculation of dispersion of sewage outflow from Wushan city allows a helpful interpretation of the geostatistically analysed Chl α data of the MINIBAT and, thus confirms the high eutrophication burden of the nearshore water body with nearly all outflow conditions in the Yangtze. Another investigation area is the confluence zone of the Xiangxi River and the Yangtze. In this case, the measurement data of the Xiangxi River and the numerical calculations were constructed regarding the mixing processes with the tributaries in a reasonable and plausible way.

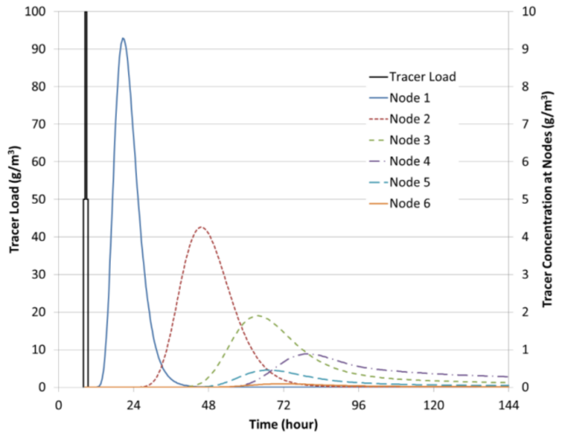


Figure V-23: Short term (90 min) tracer (conservative pollutant) input from Daning River and pollutant concentration in time at different locations in the Wushan Lake. The tracer concentration time lines are plotted for selected nodes of the computing mesh as indicated in Figure V-20.

3.5.3 Modeling the backwater influence on the Daning River and the Wushan Lake (2013)

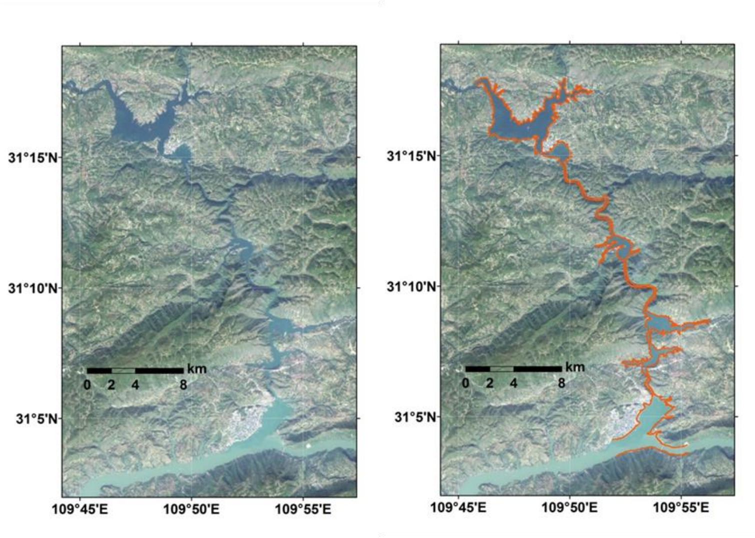


Figure V-24: 2D modeling boundary (orange line) for the lower Daning River at high water level (Satellite image source: Tianditu 2013).

The backwater influence on the Daning River due to the impoundment of the Three Gorges Reservoir is up to 50 km from the confluence of the Daning River to the upstream of the Dachang Lake. The modeling domain of the lower Daning River is from the Dachang Lake to the Wushan Lake with the confluence to the Yangtze River (Figure V-24). The length of the River channel is about 43 kilometers. For the upstream boundary of the model domain the discharge data from the Wuxi hydrological station is used. The upstream and downstream boundaries for the Yangtze River are set as discharge and water level at the Wushan hydrological station accordingly. Figure V-24 shows the modeling domain on top of the satellite image with high water level close to 175 m.a.s.l..

The two dimensional hydrodynamic model TELEMAC 2D was used to simulate the flow field and transport of dissolved substances in the 43 km lower Daning River section and adjacent

5.4 km Yangtze River. The bathymetry data are obtained from the SRTM satellite digital elevation model (DEM) and MINIBAT water depth echo-sounding recorder.

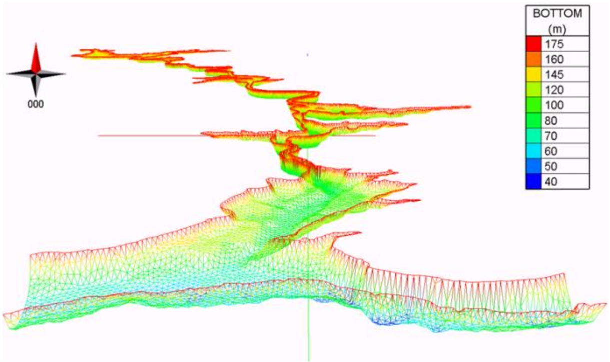


Figure V-25: 2D modelling computing mesh for the lower Daning River in 3D view

Typical hydrological scenarios have been applied for the TELEMAC 2D model including high water level close to 175 m.a.s.l., low water level close to 150 m.a.s.l. and water level rising and falling periods. Figure V-27 shows the influence of the Daning River discharge on the circulation pattern in the Wushan Lake for a constant discharge of 12000 m3/s in the Yangtze. The annual mean discharge of the Daning River is 136 m^3/s. After the impoundment, most of the time there is a dominating counter-clockwise circulating flow field in the Wushan Lake due to strong turbulent entrainment force exerted by the Yangtze main stream. At lower water level, e.g. 150 m a.s.l., the extension of the circulation flow field in the Wushan Lake is reduced. The circulation flow pattern in the Wushan Lake become weaker when the Daning River discharge increases to 500 m^3/s, and it disappears almost completely for discharge higher than about 1,000 m^3/s (Figure V-27), meaning that there is no more mixing with the Yangtze water.

The old Dachang Town in brown color is partially submerged at low water level period in left Figure V-26 and totally submerged at high water level in right Figure V-26. The Dachang Lake area was selected to establish one national wetland park from 2011. It is important to study the flow field, nutrient transport, and mixing in this area and their impact on algae bloom.

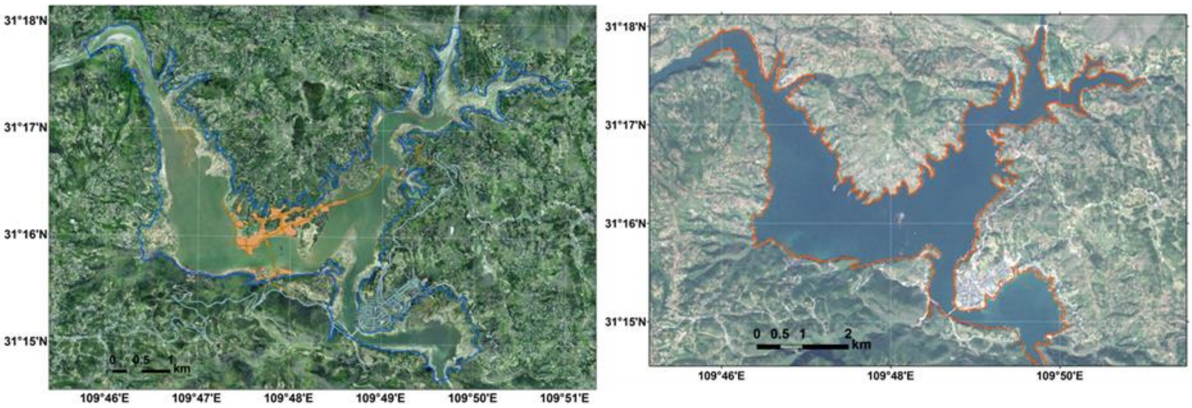


Figure V-26: Left: Partially inundated old Dachang Town (brown color) in the Dachang Lake at low water level. Right: 2D modelling boundary (orange dots) for the Dachang Lake at high water level (Satellite image source: Tianditu).

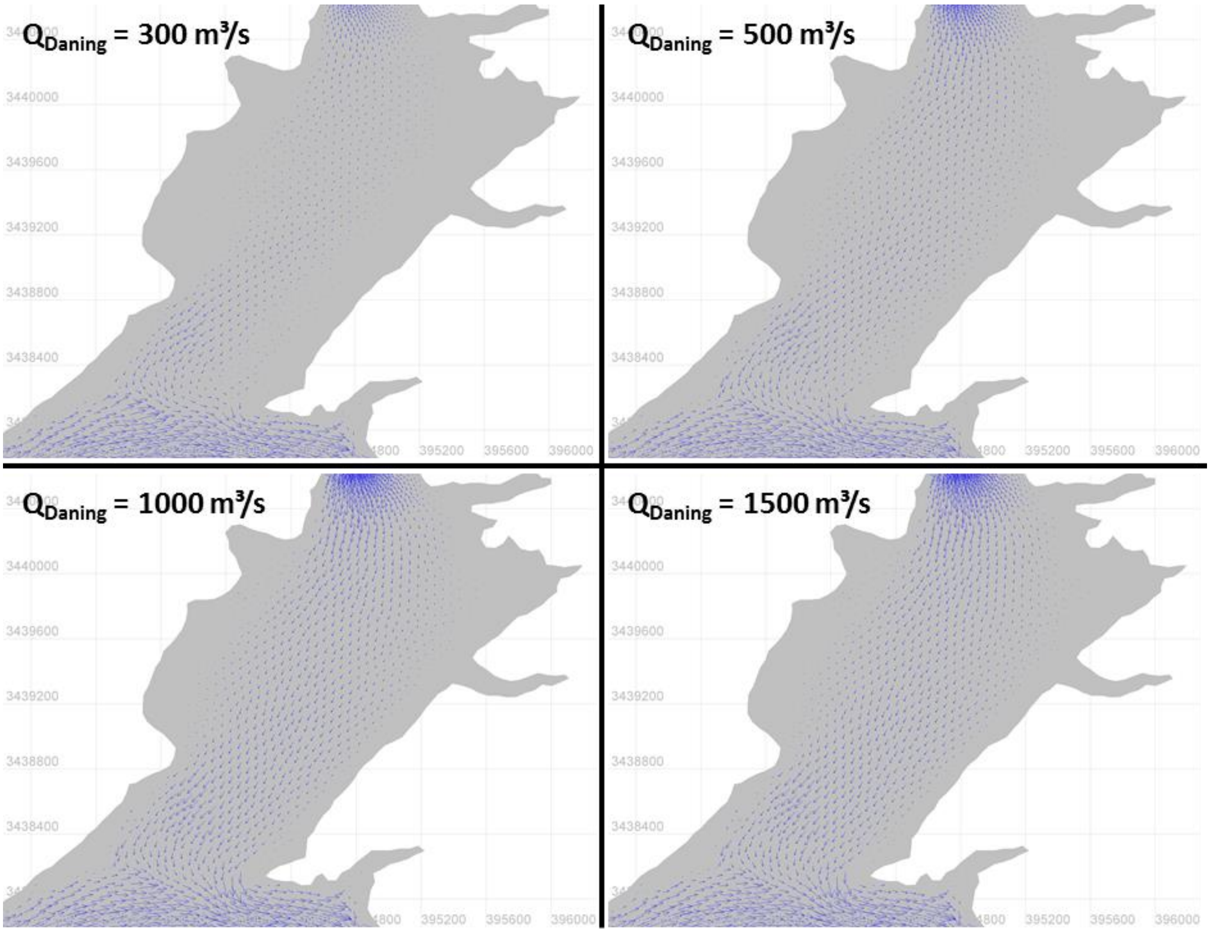


Figure V-27: Flow field in the Wushan Lake at low Yangtze water level of 150m.a.s.l. and varying discharge from the Daning River for constant discharge in the Yangtze of 12,000 m²/s

In the confluence area of the Daning River and the Yangtze River, a separate model domain, shown in Figure V-32, is set up to study the interaction of the Wushan Lake and Yangtze River in terms of water exchange, dissolved matter and algae concentration. There is a creek, a waste water treatment plant (WWTP) and two outlets releasing untreated waste water into this area. Water samples from these discharge locations were taken and analyzed. Based on these results, the concentrations of total phosphorus in Figure V-33 are selected to be used as boundary and initial conditions for the TELEMAC transport model.

One specific case in August 2011 is selected to present the transport behavior of the substances. The boundary conditions are shown in the Figure V-28. There was a rising and falling phase of the discharge in the Yangtze whereas the water level was steadily rising. During this period, high Chl α concentrations were detected by the MINIBAT in the Wushan Lake. Upstream boundary condition for the Daning River is set as 50 m^3/s.

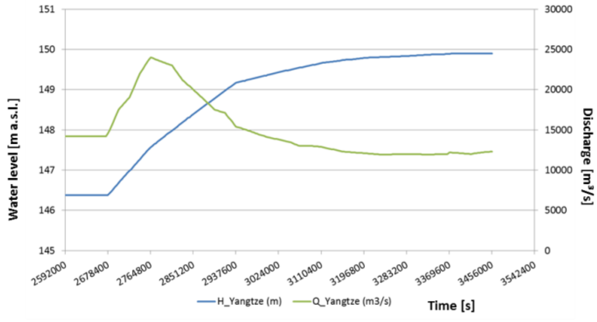


Figure V-28: 2D modelling boundary condition for the Yangtze River during August 2011.

The flow field simulated after 8 days (3,283,200 sec) of the modelling period is shown in the Figure V-29. In the circulation zones, higher flow velocities of about 0.05 m/s are found in the lower western area and lower velocities in the top right water zone. Since no stratification of the Lake is assumed the modelled flow velocities vary with water depth and show flow velocity of about 0.001 m/s at the Western bank of the Wushan Lake. Size, shape and direction of the circulation flow field are reflecting the interaction of the Wushan Lake with the Yangtze River indicating dynamic exchange of water, sediment and other substances. The near bank water bodies show very low flow velocities and, therefore weak interacting and exchange processes.

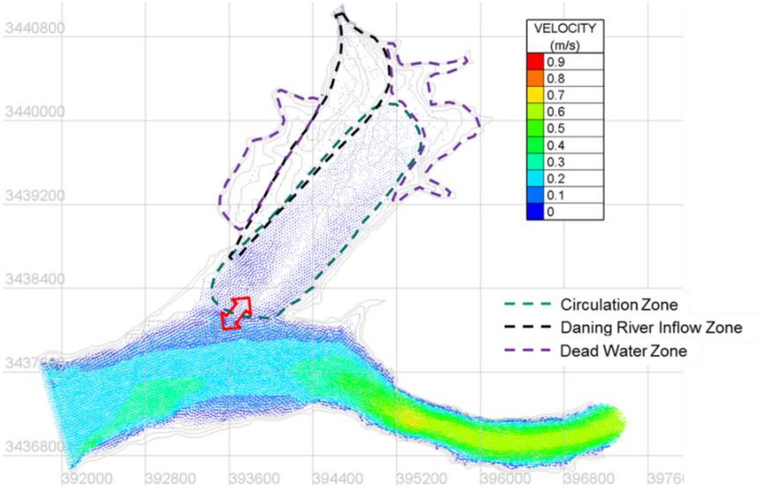


Figure V-29: Typical water zones of the Wushan Lake characterized by different transport and mixing potential.

To further understand algae movement in the surface layer of the Wushan Lake, transport of very fine particles is simulated as shown in the Figure V-30. There are three locations where suspended particles, representing algae cells, of very small fall velocity close to $2*10^{-7}$ m/s are released in the simulation. For each of the locations, 2000 particles are released and their trajectories are simulated over a 6 days period. All of these particles have the same physical properties. The red particles in the Yangtze River close to the WWTP are immediately transported downstream and only 12 are entrained at the interface and enter the circulation in the Wushan Lake. The black particles released in the Wushan Lake are slowly dispersed counterclockwise in the dominating circulation zone, after some time a few particles are entrained by the Yangtze River and transported downstream. The blue particles in the western near bank zone are moving slower. When entrained by the adjacent clockwise circulation zone (Figure V-30) of higher flow velocity they finally end up in the Yangtze due to both turbulent and advective water exchange at the interface. Reconsider the interpolated Chl α distribution in Figure V-9 both of the circulation zone and the Daning River inflow zone provide source of algae and ideal environment for algae bloom.

Figure V-30: Particle transport (Algae) in the Wushan Lake. The three colors represent particles released at different locations in the beginning of the model run: Red represent particles released in the Yangtze mainstream outside the mixing interface, black indicates particles in the large scale circulation zone , and blue are particles disposed to the western near bank recirculating water zone driven by the Daning River inflow .

3.5.4 Summary

Based on this study, circulation and mixing in the Wushan Lake will be reduced significantly with increase of the Daning River inflow and will disappear at a Daning River discharge beyond 1000 m^3/s On the average the Wushan Lake can be subdivided into three zones, characterized by hydrodynamic transport and mixing: (i) the large circulation zone directly and permanently driven by the Yangtze, (ii) the Daning River inflow zone depending on peak and duration of its discharge, and (iii) the two near bank dead water zones mainly resulting from the contour of the shoreline. The results of the TELEMAC2D tracer modelling enable to interpret and underline the MINIBAT measurements. The modelled tracer field (TP) in the Wushan Lake shows strong correlation with the interpolated surface Chl α distribution of the MINIBAT measured data. Modelling of particles transport provides further insight of the algae movement in the Wushan Lake.

3.6 Integration of MINIBAT monitoring data and water analyses with numerical modelling

3.6.1 Algal growth in relation to hydrodynamics and pollutant transport in the Wushan Lake

The contents of this section were originally published by Holbach et al. in the proceedings of the book ‘Integrated Water Resource Management’ (IWRM Karlsruhe 2012) (45).

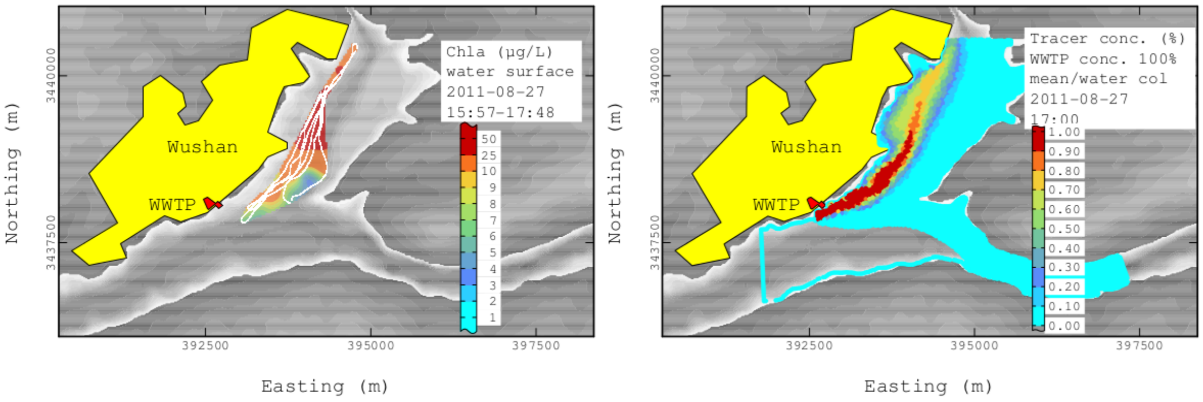


Figure V-31. Chl α concentration distribution (left), modeled tracer release from the WWTP (right) on 27 August, 2011.

Increasing eutrophication and algal bloom events in the Yangtze River Three Gorges Reservoir are widely discussed in relation to hydrodynamics and nutrient transport and distribution processes. Insights into water exchange and interaction dynamics between water masses related to large scale water level fluctuations in the reservoir are crucial to understand water quality and eutrophication dynamics. In this study, we therefore integrated water quality data recorded in situ and online with the MINIBAT towed underwater multi-sensor system with data obtained from simulations done with TELEMAC hydrodynamic 2D numerical modeling across the confluence zone of the Yangtze River and the Daning River in the Wushan Lake. Key scenario for the current study was a discharge peak and corresponding rising water level in the Yangtze River at its confluence zone with the Daning River following a heavy precipitation event in August 2011.

Water quality data obtained from MINIBAT measurements during this specific period suggest that Yangtze River main stream water flowed upstream into the Daning River. Hydrodynamic 2D numerical modeling supports that hypothesis and enables to specify water and substance origins. Observed algal blooming can only be partly explained by the 2D modeling approach. 3D effects like the stabilization of thermal stratification at the water surface forming good conditions for algal blooming cannot be simulated but were measured with the MINIBAT. However, input of higher nutrient loads from Yangtze River water and from waste water discharges (WWTP in Figure V-31) into the Wushan Lake are supported by the model and the field measurements and may have played a key role for the observed algal bloom formation.

3.6.2 2D nutrient discharge model for the Wushan Lake

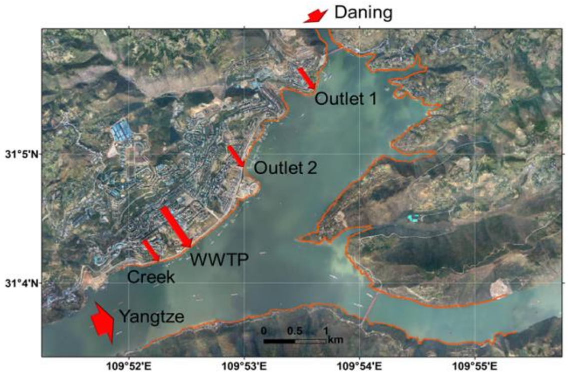


Figure V-32: 2D modelling boundary (orange dots) for the Wushan Lake at high water level (Satellite image source: Tianditu) with analyzed discharge locations along the Wushan shoreline.

From measured total phosphorus (TP) concentrations of several sewage water discharge locations along the Wushan shoreline (Figure V-32, Figure V-33) we estimated realistic TP inputs and established a reasonable nutrient pollution scenario around Wushan with estimated discharges (Table V-3).

In the numerical model a tracer is used to represent transport and mixing of conservative substances. The initial conditions of tracer (TP) in the model domain were set as 40 µg/l, 120 µg/l for the Yangtze water and 40 µg/l for the inflowing Daning water. Due to strong mixing the higher concentration of tracer in the Yangtze River is quickly diluted as compared with the concentration field of the tracer released from the creek and the WWTP having lower initial concentration.

Table V-3. Discharge boundary conditions for the nutrient pollution scenario.

	WWTP	Creek	Outlet 1	Outlet 2	Yangtze	Daning
Estimated Discharge (m³/s)	0.2	0.2	0.02	0.02	>12000	50

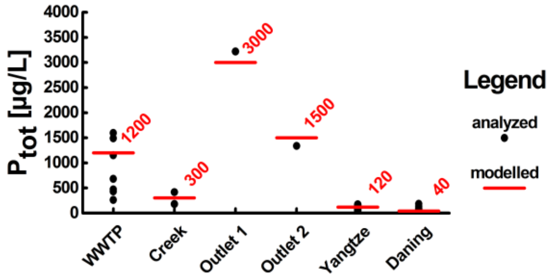


Figure V-33: Derivation of model P_{tot} discharge concentrations for several sewage water discharge locations along the Wushan shoreline from analyzed water samples.

The circulation flow field (Figure V-29) plays an important role for the distribution of dissolved substances in the Wushan Lake. Additionally, water quality in the lower part of the Daning River inflow zone is deteriorated significantly due to the nutrients from the untreated waste water of outlet 1. The impact of the waste water outlet 2 is relatively small and only has local effect in the vicinity of the outlet. Figure V-34 shows the comparison of tracer (TP) model results with MINIBAT measurement on 29 August, 2011. We can see that the major algae growth is not directly related to the 2D modelled P_{tot} distribution. The highest algae density can be found along the western shoreline of the Wushan Lake. There, P_{tot} inputs from Outlet 1 had a significant impact on algal growth in this slow flow area (Figure V-29). The much larger P_{tot} input from the Yangtze River and the WWTP only have minor direct impact. In this scenario, as seen before in chapter 0, there was a strong thermal stratification at the water

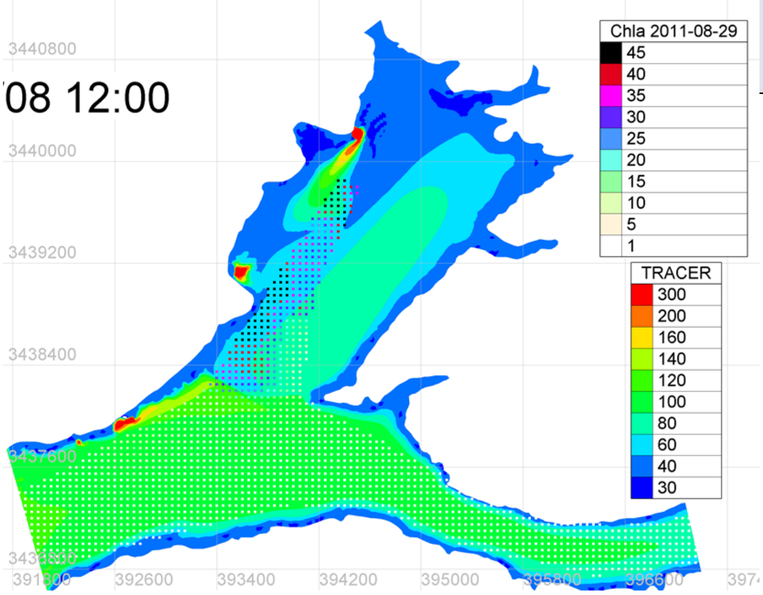


Figure V-34: Comparison of tracer (TP in µg/L) modelling with interpolated MINIBAT measurements of Chl α concentrations illustrated as colored dots (µg/L) (29 August, 2011)

surface on 29 August, 2011. Thus, the comparably small input of P_{tot} from Outlet 1 might have accumulated in the epilimnion, whereas the much larger P_{tot} inputs from the Yangtze River and the WWTP were mixed and diluted across the whole water column and might consequently have had less affected algal growth. Furthermore, the very slow flow conditions (Figure V-29) and long water residence times (Figure V-30) in these areas provide a fruitful basis for intense algal growth.

3.6.3 Water quality modelling with input of MINIBAT data, water analyses and hydrodynamic numerical modelling

The ‘MINIBAT’ project intended on one side to collect, evaluate and model multi-parametric water quality data in a spatial and/or temporal context on the basis of a multisensory system recording real data. On the other side the project intended to model spatial and temporal distribution of flow and transport characteristics of the TGR water bodies with numerical methods. The results of both approaches should mutually be integrated to improve the process understanding within the TGR ecosystems. This can work out very well when considering the transport and distribution dynamics of one pollutant (e.g. total phosphorus) and its possible effects on algae growth.

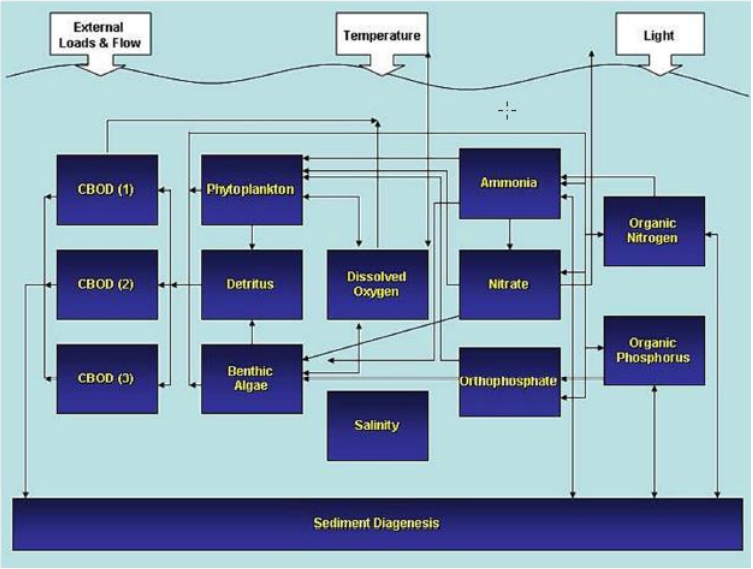


Figure V-35. Principles of the model WASP in a scheme.

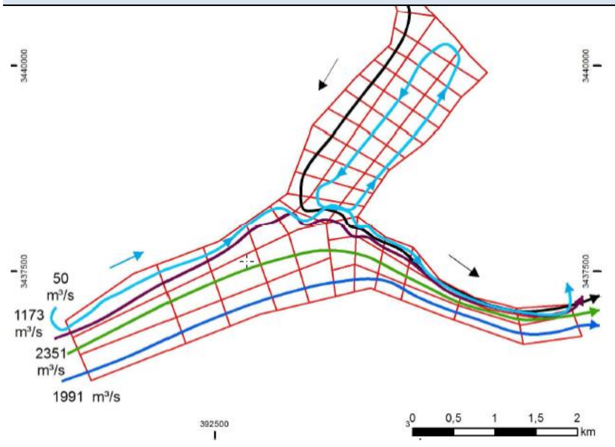


Figure V-36: Flows and flow paths simulated by the hydrodynamic TELEMAC model in the summer scenario.

To investigate the reasons of algae growth in more detail, data from measurements and geochemical analyses of water samples are imported into the water quality model. This model has the capacity to predict eutrophication and algae blooms in the future. It has been found that the calculation and modelling of algae growth with WASP can be done by the input of hydrological data and limnological data that provides the MINIBAT, plus results from geochemical analysis of water samples in the laboratory, to achieve the objective to get plausible results. The synthesis of all input data is drawn in the scheme of the principles of the WASP in Figure V-35: The nutrient data on the left directly influence a phytoplankton reaction, while temperature and light take effect on the whole system, thus lastly on the phytoplankton growth rate. Also the flows and flow velocities (Figure V-36) are of principle importance and were derived from the hydrodynamic TELEMAC model results of the ‘Numerical Modelling’ sub-project. Two different scenarios were set up: Winter with a few segments, and summer with more segments for a higher spatial resolution (Figure V-37).

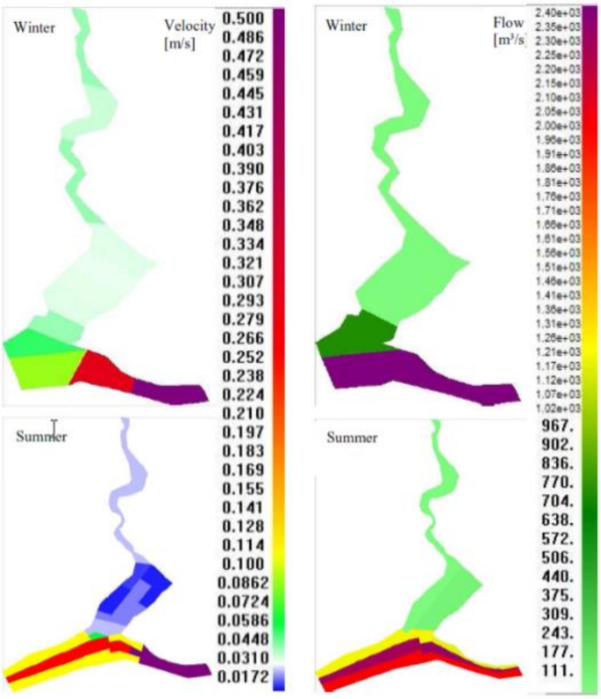


Figure V-37: Velocity and flow in different scenario setups of winter and summer.

Figure V-38 indicates August. Chl α can be understood as an indicator of the amount of algal biomass, because all algal species including cyanobacteria contain commensurate percentages of Chl α in their cell structure. The initial low values rise beginning from ca. 5 µg/L steadily up to 25 µg/L, which is nearly the beginning of an algal bloom.

The tendency of constantly positive algal growth in summer can change within weeks into a logarithmic trend, stagnancy, or slight decrease (Figure V-39), which can be caused by nutrient consumption and deficiency, self-shading of dense algae cell populations, oxygen depletion, and temperature fall in autumn. These mentioned parameters are also calculated in every time step in the model, so in the results all is observable and the values can be drawn in concentration maps or curve diagrams like demonstrated with Chl α, which allows a holistic understanding of the effects among them.

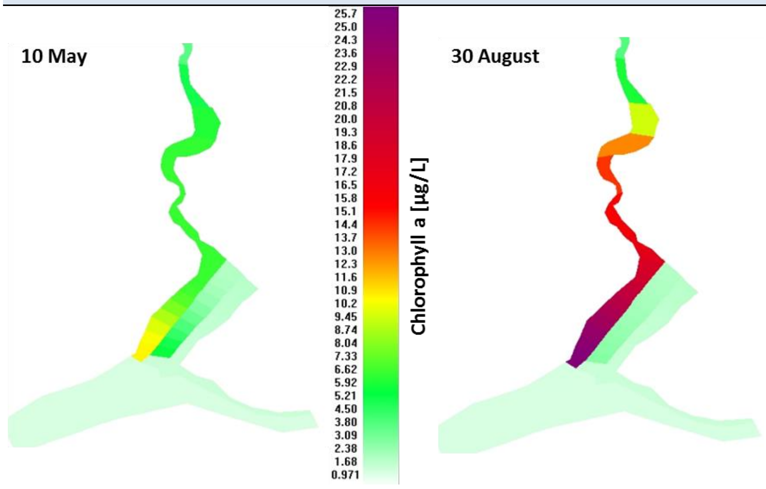


Figure V-38: Modelled spatio-temporal distribution of chlorophyll α in a summer time period between 10 May and 30 August.

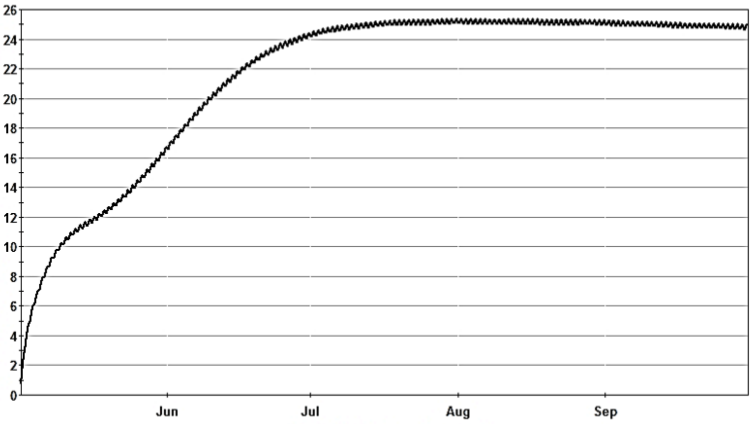


Figure V-39: Concentration of chl α in summer time period in a segment on the western Wushan Lake littoral area.

As a main outcome of the use of WASP, the approach to combine measurement data (MINIBAT) with hydrodynamic model data (TELEMAC) enabled the creation of a model on algal growth development for a defined and limited time period. Furthermore, it has been found by comparison of several configurations that the main factors to influence the phytoplankton growth in the model are the phytoplankton maximum growth rate per day, the death rate per day and the water flows which transport the algae in the streaming direction. Starting from that point, additional values can furthermore be added and directly tested for their effects on algae growth.

4 Summary

This project on (i) spatio-temporal resolved in-situ and on-line monitoring of the dynamics of water body relevant parameters by means of a towed under water multi sensor system (MINIBAT) and (ii) numerical modeling of pollutant transport dynamics aimed to understand the influences of the changed hydrodynamics caused by the operation of the Three Gorges Reservoir on water quality of the Yangtze River and its tributaries. Conceptionally, a monitoring approach was combined with a modelling approach allowing to feed the models with necessary data and to validate the model results.

The MINIBAT system was especially constructed for the requirements of this project and contains sensors for pressure, temperature, pH, electrical conductivity, oxygen saturation, turbidity, chlorophyll a, hydrogen sulphide, colored dissolved organic matter and photosynthetic active radiation. Furthermore, this system was equipped with a sampling system for five water samples developed within this project. The MINIBAT can be steered by its wings down to depths of 30 m when dragged behind a running vessel and can be used as profiling probe down to depths of above 200 m. The spatial position of the MINIBAT is recorded by the pressure sensor and a GPS on board of the dragging ship.

The spatio-temporal recorded data were evaluated by the use of geostatistical methods. Adapted variogram models were used to interpolate the data by means of kriging estimation. For this attempt, the locations of the single data had to be processed and filters had to be specified to produce reliable results. The program ISATIS from the producer Geovariance allowed to carry out three dimensional geostatistical modeling of the data recorded by the MINIBAT.

Numerical modeling of the hydrodynamic processes in the water bodies studied was carried out by HEC-RAS and TELEMAC2D. HEC-RAS was used for one dimensional modeling showing the fluctuation of the water level, the flow direction and the expansion of the water bodies over the seasons. The two dimensional models processed by use of TELEMAC2D provide information about the pathways of pollutants, their spatial concentration and residence time. The Water Quality Analysis Simulation Program (WASP) of the EPA (USA) was applied to model the development of algal blooms.

Between 2011 and 2014 nine fieldtrips were conducted in China with the destinations of the Daning River, the Xiaojiang River, the confluence zone of the Jialing River with the Yangtze River at Chongqing, the Xiangxi River, the Shennongxi River, the Yangtze at Wuhan and Yidu and the Taihu Lake.

It could be shown that the pollution from urban areas exists but that input of heavy metals can quickly be diluted by the large water masses of the Yangtze. Flooded cities occurred in the field investigation areas in the Wushan Lake and the Dachang Lake, but no respective hot spot of pollution was detected. The situation is more critical with respect to nutrients such as phosphorus, since large amounts are discharged by sewage and agriculture. Especially in the confluence zones and tributary backwaters, in which lake-like conditions can evolve due to locally extremely high water residence times, frequent algal blooms are a serious threat for water quality. Exemplarily, this was shown for the situation of the Wushan Lake at the confluence zone of the Daning River and the Yangtze River.

Based on the modeling results of this study, circulation and mixing in the Wushan Lake will be reduced significantly with increase of the Daning River inflow and will disappear at a Daning River discharge beyond 1000 m3/s On the average the Wushan Lake can be subdivided into three zones, characterized by hydrodynamic transport and mixing: (i) the large circulation zone directly and permanently driven by the Yangtze, (ii) the Daning River inflow zone depending on peak and duration of discharge, and (iii) the two near bank dead water zones mainly resulting from the contour of the shoreline. The results of the TELEMAC2D tracer modelling enable to interpret and underline the MINIBAT measurements. The modelled tracer field (TP) in the Wushan Lake shows strong correlation with the interpolated surface Chlorophyll-α distribution of the MINIBAT measured data. Modelling of particles transport provides further insight of the algae movement in the Wushan Lake. The MINIBAT measurements and geostatistical interpolations carried out for this location very well were reproduced by the numerical modeling with TELEMAC2D. Both approaches pointed to a sewage plant discharge pipe as important source for nutrients. A simulation for a changed location of the discharge of the sewage showed that there are possibilities to mitigate the situation (Figure V-40).

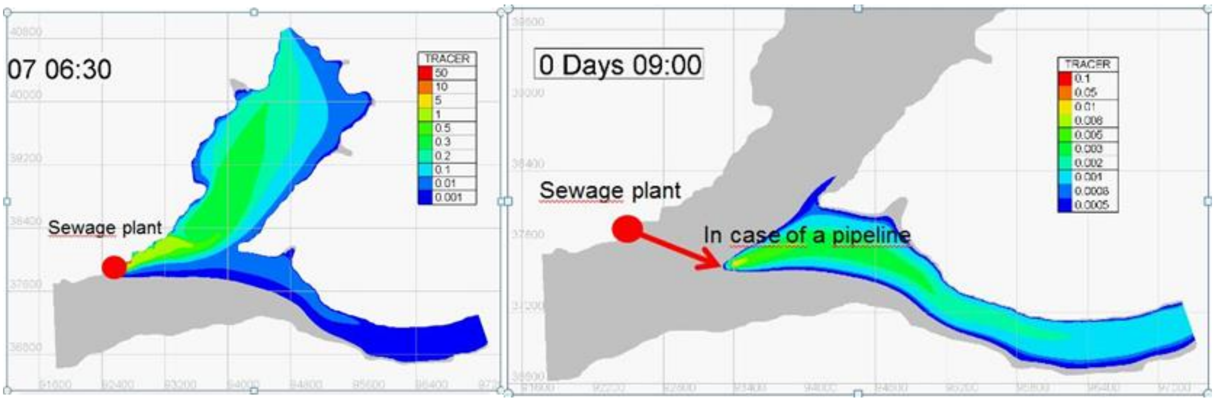


Figure V-40 TELEMAC2D model (left) and simulation (right) for the distribution of sewage plant discharge. The model shows the existing situation in which the high discharge of the Yangtze is pressing the sewage discharge into the Wushan Lake. The simulation depicts the situation in case of pipeline discharging the sewage in the middle of the Yangtze with the result that almost no sewage discharge reaches the Wushan Lake and can contribute by its nutrients to algal growth.

The environmental importance of backwater effluent into the tributaries could also be shown for the Xiangxi River in very detail, where the inflow of Yangtze water was driven by temperature and density differences and happened at intermediate depths. Since the Yangtze often contains higher loads of particulate matter and pollutants as the single tributaries, this effect has the potential to contribute to a decline the environmental conditions of the tributaries.

Impacts of the Three Gorges Reservoir on the hydrodynamics of the Yangtze also occur downstream of the dam due to discharge regulation at the dam and sedimentation of particles in the reservoir. However, hydrodynamic processes downstream of the dam are still influenced by the local conditions. The particle load of the Yangtze decreased between Yidu and Wuhan along the Yangtze run, most probably due to a Lake system between both cities acting as sediment traps. Ratios of stable isotopes of oxygen and hydrogen successfully were used to differentiate between various water bodies and to indicate the possible sources of tap water. The potential of this approach for further studies on the origin, residence times and hydrodynamic processes such as mixing of different water bodies is obvious.

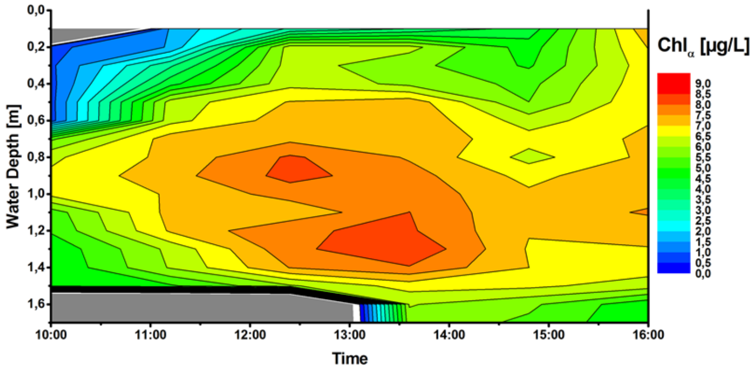


Figure V-41: Diurnal variation of chlorophyll *a* concentrations in the Taihu Lake near Wuxi recorded by the MINIBAT system on 08 April 2014.

Additionally, the operation of the MINIBAT was tested at conditions of shallow waters, which were successfully carried out at the Lake Taihu near Wuxi city. This Lake is also connected to the Yangtze River near Shanghai and is an important drinking water source. Besides several other advancements worked out for the MINIBAT system within this project regarding prevention of rolling over, interferences of electrical subsystems or the optimization of the sampling system, it became obvious that the shallow depths of only 2m in the Lake Taihu pose new challenges for the MINIBAT application. There, it is necessary to adapt the size of the wings and the steering precision to prevent accidents during the MINIBAT monitoring work. Here, the MINIBAT was also used for a whole day long as probe to monitor the algae activity during one day (Figure V-41).

Finally, it can be stated that this project successfully integrated monitoring and modeling approaches and demonstrated the applicability of the towed under water multi sensor system MINIBAT in various water bodies of the Yangtze and its connected tributaries and lakes downstream and upstream of the Three Gorges Dam. The flexibility of the MINIBAT system to be used on different kinds of vessels makes it an eminent contribution to the surveillance needs of the Yangtze system. However, further studies and investigations are needed to understand the algal blooms and backwater effects in the Yangtze in more detail. Furthermore, the economic development and intensive agriculture in the region of the Yangtze River require a permanent monitoring of the affected water bodies to ensure the availability of basic data for the development of water quality control concepts and technologies. For this purpose, the concept of this project provides an urgently needed fundament.

5 Publications, theses and conference contributions

5.1 Publications

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. Environmental Science and Pollution Research, 19(4), 1341-1344.

Holbach, A., Wang, L., Chen, H., Schleicher, N., Hu, W., Zheng, B., Norra, S. (2013): Urban Pollutant Plumes around Wushan and Dachang City in the Three Gorges Reservoir. In: Rauch, S., Morrison, G., Norra, S., Schleicher, N. (eds.): Urban Environment, 437-447.

Holbach, A., Floehr, T., Kranzioch, I., Wolf, A. (2013): Dilution of pollution? Processes affecting water quality in the River-style Three Gorges Reservoir. Environmental Science and Pollution Research 20(10), 7140-7141.

Holbach, A., Norra, S., Wang, L., Yuan, Y., Hu, W., Zheng, B., Bi, Y. (2014): Three Gorges Reservoir: Density pump amplification of pollutant transport into tributaries. Environmental Science & Technology, 48(14), 7798–7806.

Holbach, A., Wang, L., Chen, H., Schleicher, N., Hu, W., Zheng, B., Norra, S. (2013): 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. Environmental Science and Pollution Research 20(10), 7027-7037.

Hu, W., Wang, L.-J., Chen, H., Holbach, A., Zheng, B.-H., Norra, S., Westrich, B. (2012): Hu, Two-dimensional numerical modelling of dissolved and particulate pollutant transport in the Three Gorges Reservoir. Geophysical Research Abstracts, 14, EGU2012-13962

Holbach, A., Hu, W., Wang, L., Chen, H., Schleicher, N., Zheng, B., Westrich, B., Norra, S. Integrated water quality monitoring and modeling in the Three Gorges Reservoir, China. Steussloff IWRM Karlsruhe 2012, 132-138.

Kranzioch, I., Stoll, C., Holbach, A., Chen, H., Wang, L., Zheng, B., Norra, S., Bi, Y., Schramm, K.-W., Tiehm, A. (2013): Dechlorination and organohalide-respiring bacteria dynamics in sediment samples of the Yangtze Three Gorges Reservoir. Environmental Science and Pollution Research 20(10), 7046-7056. (Electronic version already available 2012)

Scholz-Starke, B., Ottermanns, R., Rings, U., Floehr, T., Hollert, H., Hou, J., Li B., Wu, L.L., Yuan, X., Strauch, K., Hu, W., 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. Environmental Science and Pollution Research 20(10), 7009-7026. (Electronic version already available 2012)

5.2 Theses

Fetzer, Jasmin (2013): The chemical condition of the Yangtze River middle reaches in China affected by various factors on spatial and temporal scales (Bachelor thesis at IMG, Karlsruhe Institute for Technology)

Leib, Simon (2014): Modelling of algae growth in the Three Gorges Reservoir, China (Master thesis at IMG, Karlsruhe Institute for Technology)

Holbach, A. (in preparation): Pollutant distribution dynamics in the Yangtze River Three Gorges Reservoir - Evaluation of driving forces (PhD thesis at IMG, Karlsruhe Institute for Technology)

Reid, L. (2012): Impact of urban systems on the water quality of the Three Gorges Reservoir, China (Diploma Thesis at IMG, Karlsruhe Institute of Technology)

Scheibelein, Alexander (in preparation): Stoffflüsse im Yangtze Three Gorges Reservoir (Master thesis at AGW/IMG, Karlsruhe Institute for Technology)

5.3 *Conference contributions*

Holbach, A. (2013): Aspects of water quality and pollutant dynamics in the Three Gorges Reservoir—Insights from MINIBAT measurements. International Conference on Ecological Environment in Three Gorges Reservoir, Yichang, China, 09.-10.12.2013.

Holbach, A., Wang, L., Bi, Y., Zheng, B., Norra, S. (2013): Density Current Intrusion Dynamics in a Reservoir's Tributary—Insights Derived from Space-time Kriging of Water Quality Data. 10th Annual Meeting of the Asia Oceania Geosciences Society, Brisbane, Australia, 24.-28.06.2013.

Holbach, A., Hu, W., Wang, L., Chen, H., Schleicher, N., Zheng, B., Westrich, B., Norra, S. (2012): Integrated water quality monitoring and modeling in the Three Gorges Reservoir, China. IWRM Karlsruhe 2012, Karlsruhe, Germany, 21.-22.11.2012.

Holbach, A., Wang, L., Chen, H., Schleicher, N., Hu, W., Zheng, B., Norra, S. (2012): Urban pollutant plumes around Wushan and Dachang City in the Three Gorges Reservoir. 11th Urban Environment Symposium, Karlsruhe, Germany, 16.-19.09.2012.

Holbach, A., Wang, L., Chen, H., Hu, W., Schleicher, N., Zheng, B., Norra, S. (2012): Impact factors on water quality in the confluence zone of the Daning River and the Yangtze River. European Geosciences Union General Assembly 2012, Vienna, Austria, 23.-27.04.2012

Hu, W., Wang, L.., Chen, H., Holbach, A., Zheng, B.-H., Norra, S., Westrich, B. (2012): Two-dimensional numerical modelling of dissolved and particulate pollutant transport in the Three Gorges Reservoir. European Geosciences Union General Assembly 2012, Vienna, Austria, 23.-27.04.2012.

Hu, W., Holbach, A., Chen, H., Wang, L., Zheng, B., Norra, S., Westrich, B. (2012): Hydrodynamic modelling of urban development in the Three Gorges Reservoir. 11th Urban Environment Symposium, Karlsruhe, Germany, 16.-19.09.2012.

Reid, L., Holbach, A., Hu, W, Wang, L., Chen, H., Zheng, B., Norra, S. (2012): Urban impacts on the water quality of the Yangtze and its tributaries Daninghe, Xiao Jiang and Jialing. 11th Urban Environment Symposium, Karlsruhe, Germany, 16.-19.09.2012.

Reid, L., Holbach, A., Hu, W., Wang, L., Chen, H., Zheng, B., Norra, S. (2013): Urban impacts on the water quality of selected water bodies in the Three Gorges Reservoir, China. European Geosciences Union General Assembly 2013, Vienna, Austria, 07.-12.04.2013.

5.4 References

(1) Nilsson, C.; Reidy, C. A.; Dynesius, M.; Revenga, C.: Fragmentation and flow regulation of the world's large River systems. Science 2005, 308, 405-408.

(2) Wu, B.; Zhang, X.X.; Zhang X.L.; Yasun, A.J.; Zhang. Y; Zhao, D.Y.; Ford, T.; Cheng, S.P.: Semi-volatile organic compounds and trace elements in the Yangtze River source of drinking water. Ecotoxicology 2009 18:707-714.

(3) McCartney, M. P.; Sullivan, C.; Acreman, M. C.: Ecosystem impacts of large dams. Background Paper Nr. 2 Prepared for IUCN/UNEP/WCD, 2001.

(4) International Commission on Large Dams. World Register of Dams. http://www.icold-cigb.org (accessed March 5, 2014).

(5) Lehner, B.; Reidy Liermann, C.; Revenga, C.; Vörösmarty, C.; Fekete, B.; Crouzet, P.; Döll, P.; Endejan, M.; Frenken, K.; Magome, J.; Nilsson, C.; Robertson, J. C.; Rödel, R.; Sindorf, N.; Wisser, D.: High resolution mapping of the world's reservoirs and dams for sustainable River flow management. Front. Ecol. Environ. 2011, 9(9), 494-502.

(6) China Three Gorges Corporation. http://cwic.com.cn/inc/sqsk.php (accessed October 16, 2013).

(7) Xu, Y.; Cai, Q.; Shao, M.; Han, X.; Cao, M.: Seasonal dynamics of suspended solids in a giant subtropical reservoir (China) in relation to internal processes and hydrological features. Quat. Int. 2009, 208, 138-144.

(8) Liu, L.; Liu, D.; Johnson, D.M.; Yi, Z.; Huang, Y.: Effects of vertical mixing on phytoplankton blooms in Xiangxi Bay of Three Gorges Reservoir: Implications for management. Water Research 2012, 46, 2121-2130.

(9) Yang, X.; Lu, X.: Ten years of the Three Gorges Dam: A call for policy overhaul. Environ. Res. Lett. 2013, 8, 1-5.

(10) Seeber, C.; Hartmann, H.; Xiang, W.; King, L.: Land use change and causes in the Xiangxi catchment, Three Gorges area derived from multispectral data. J. Earth Sci. 2010, 21(6), 846-855.

(11) Zhang, Q.; Lou, Z.: The environmental changes and mitigation actions in the Three Gorges Reservoir region, China. Environ. Sci. Policy 2011, 14 (8), 1132-1138.

(12) Holbach, A.; Wang, L.; Chen, H.; Hu, W.; Schleicher, N.; Zheng, B.; Norra, S.: 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. 2013, 20 (10), 7027-7037.

(13) Zhang, J.; Zheng, B.; Liu, L.; Wang, L.; Hunag, M.; Wu, G.: 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. 2010, 2, 1479-1490.

(14) Lin, J.; Fu, C.; Zhang, X.; Xie, K.; Yu, Z.: Heavy metal contamination in the water-level fluctuating zone of the Yangtze River within Wanzhou section, China. Biol. Trace Elem. Res. 2012, 145, 268-272.

(15) Ye, C.; Li, S.; Zhang, Y.; Zhang, Q.: Assessing soil heavy metal pollution in the water-level-fluctuation zone of the Three Gorges Reservoir. China J. Hazard. Mater. 2011, 191(1-3), 366-372.

(16) Audry, S.; Schäfer, J.; Blanc, G.; Jouanneau, J.-M.: Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). Environ. Pollut. 2004, 132, 413-426.

(17) Bianchi, T. S.: Estuarine chemistry. In Estuarine Ecology, 2nd ed.; Day, J.W.; Crump, B.C.; Kemp, W.M.; Yáñez-Arancibia, A. (Eds.); Wiley: Hoboken, N.J.; 2012, 39-85.

(18) Turner, A.; Millward, G.E. Suspended particles: Their role in estuarine biogeochemical cycles. Estuarine, Coastal Shelf Sci. 2002, 55(6), 857-883.

(19) Luo, Z.X.; Zhu, B.; Zheng, B.H.; Zhang, Y.: Nitrogen and phosphorus loadings in branch backwater reaches and the reverse effects in the main stream in Three Gorges Reservoir. China Environ. Sci. 2007, 27, 208-212 (in Chinese).

(20) Dai, H.; Zheng, T.; Liu, D.: Effects of reservoir impounding on key ecological factors in the Three Gorges Region. Procedia Environ. Sci. 2010, 2, 15-24.

(21) Ministry of Environmental Protection of China: Three Gorges Bulletin 2005 – 2011. Ministry of Environmental Protection — The People's Republic of China. http://english.mep.gov.cn/standards_reports/threegorgesbulletin/. Accessed 31 Jul 2012.

(22) Stüben, D.; Stüben, K.; Haushahn, P.: MINIBAT — A new, simple system for in-situ measurement, mapping and sampling of dissolved trace elements in aquatic systems. Underwater Syst. Des. 1994, 16, 5-14.

(23) 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.: The Yangtze-Hydro Project: a Chinese–German environmental program. Environ. Sci. Pollut. Res. 2012, 19(4), 1341-1344.

(24) Chehata, M.; Jasinski, D.; Monteith, M.C.; Samuals, W.B.: Mapping three-dimensional water-quality data in the Chesapeake Bay using geostatistics. JAWRA 2007, 43, 813-828.

(25) Murphy, R.R.; Curriero, F.C.; Ball, W.P.: Comparison of spatial interpolation methods for water quality evaluation in the Chesapeake Bay. J. Environ. Eng. 2010, 136(2), 160–171. doi: 10.1061/(ASCE)EE.1943-7870.0000121.

(26) Rathbun, S.L.: Spatial modelling in irregularly shaped regions: kriging estuaries. Environmentrics 1998, 9, 109-129.

(27) McBride, C.; Hamilton, D.; Gibbs, M.; White, P.; Stewart, L.: BioFish survey of Lake Taupo. Centre for Biodiversity and Ecology Research 2006, University of Waikato — report 68.

(28) Woodson, C.B.; Washburn, L.; Barth, J.A.; Hoover, D.J.; Kirincich, A.R.; McManus, M.A.; Ryan, J.P.; Tyburczy, J.: Northern Monterey Bay upwelling shadow

front: observations of a coastally and surface-trapped buoyant plume. J. Geophys. Res. 114, 2009, C12013.

(29) Haas, L.W.: Improved performance capabilities for the Acrobat towed instrument platform: data collection, calibration and interpolation/graphic visualization. Virginia Institute of Marine Sciences 2008 — final report.

(30) Journel, A.G.; Rossi, M.E.: When do we need a trend model in kriging? Math. Geol. 21, 1989, 715-739.

(31) Armstrong, M.: Basic linear geostatistics. 1998 Springer, Berlin.

(32) Holbach, A.; Norra, S.; Wang, L.; Yuan, Y.; Hu, W.; Zheng, B.; Bi, Y.: Three Gorges Reservoir: density pump amplification of pollutant transport into tributaries. Environmental Science & Technology, 48(14), 7798–7806.

(33) Kyriakidis, P. C.; Journel, A. G.: Geostatistical space-time models: A review. Math. Geol. 1999, 31 (6), 651-684.

(34) Journel, A. G.; Rossi, M. E.: When do we need a trend model in kriging? Math. Geol. 1989, 21 (7), 715-739.

(35) Scholz-Starke, B.; Ottermanns, R.; Rings, U.; Floehr, T.; Hollert, H.; Hou, J.; Li, B.; Wu, L.L.; Yuan, X.; Strauch, K.; Hu, W.; Norra, S.; Holbach, A.; Westrich, B.; Schäffer, A.; Roß-Nickoll, M.: 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. 2013, **20(10)**, 7009-7026.

(36) Roelke, D.L.; Pierce, R.H.: Effects of inflow on harmful algal blooms: some considerations. J. Plankton Res. 2011, 33, 205-209.

(37) Zhang, J.L.;, Zheng, B.H.;, Liu, L.S.; Wang, L.P.; Huang, M.S.; Wu, G.Y.: 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. 2010, 2, 1479-1490.

(38) Ji, D.B.; Liu, D.; Yang, Z.J.; Yu, W.: Adverse slope density flow and its ecological effect on the algae bloom in Xiangxi Bay of TGR during the reservoir impounding at the end of flood season. Shuili Xuebao (J. Hydraul. Eng.) 2010, 41, 691-696 (in Chinese).

(39) Xu, Y.; Cai, Q.; Han, X.; Shao, M.; Liu, R.: Factors regulating trophic status in a large subtropical reservoir, China. Environ. Monit. Assess. 2010, 169, 237-248.

(40) Holbach, A.; Wang, L.; Chen, H.; Schleicher, N.; Hu, W.; Zheng, B.; Norra, S.: Urban Pollutant Plumes around Wushan and Dachang City in the Three Gorges Reservoir. In: Rauch, S., Morrison, G., Norra, S., Schleicher, N. (eds.): Urban Environment, 2013, 437-447, Springer.

(41) Zhang, L.; Zhou, K.: Background values of trace elements in the source area of the Yangtze River. Sci. Total Environ. 1992, 25, 391-404.

(42) Federal ministry for the environment, nature conservation, and nuclear safety of Germany (BMUB). Chemische Gewässergüteklassifizierung, 2012. BMUB Website. http://www.bmub.bund.de/themen/wasser-abfall-

boden/binnengewaesser/fluesse-und-seen/schutzziele-und-bewertungsparameter/chemische-gewaessergueteklassifizierung (accessed March 6, 2014), in German.

(43) Yang, Z.; Liu, D.; Ji, D.; Xiao, S.; Huang, Y.; Ma, J.: An eco-environmental friendly operation: An effective method to mitigate the harmful blooms in the tributary bays of Three Gorges Reservoir. Sci. China Technol. Sci. 2013, 56, 1458-1470.

(44) Ponseti, M.; López-Pujol, J.: The Three Gorges Dam project in China: History and consequences. HMiC: Historia Moderna I Contemporania 2006, 151−188.

(45) Holbach, A.; Hu, W.; Wang, L.; Chen, H.; Schleicher, N.; Zheng, B.; Westrich, B.; Norra, S.: Integrated water quality monitoring and modeling in the Three Gorges Reservoir, China. Steussloff IWRM Karlsruhe 2012, 132-138.

(46) Holbach, A.; Floehr, T.; Kranzioch, I.; Wolf, A.: Dilution of pollution? Processes affecting water quality in the River-style Three Gorges Reservoir. Environ. Sci. Pollut. Res. 2013, 20(10), 7140-7141.

(47) Chen, J.; Wang, F.; Xinghui, X.; Zhang, L.: Major element chemistry of the Changjiang (Yangtze River). Chemical Geology 2002, 187(3-4), 231-255.

(48) Yang, S.L.; Milliman, J.; Li, P.; Xu, K.: 50,000 dams later: Erosion of the Yangtze River and its delta. Global and Planetary Change 2011, 75(1-2), 14-20.

(49) Lin, B.; Zhang, R.; Dai, D.; Tan, Y.: Sediment Research for the three gorges Project on the Yangtze River since 1993. In Ninth International Symposium on River Sedimentation 2004. Yichang, China, 29-37.

(50) Glaser, R.; Kremb, K.: Yangtze: Sicherheit vor Hochwasser? In Asien. Darmstadt: WBG (Wissenschaftliche Buchgesellschaft) 2007, 183–194.

(51) Zhu, Y.; Guo, X.-H.; Hu, W.; Qu, G.; He, G.-S.: Variations of Hydrological Regime in the Jingjiang Reach of the Yangtze River after Operation of the TGP. In EGU General Assembly 2012. 1.

(52) Gorchev, H.G.; Ozolins, G.: WHO guidelines for drinking-water quality. WHO chronicle 1984, 38(3), 104-108.

(53) EU: Richtlinie 98/83/EG des Rates über die Qualität von Wasser für den menschlichen Gebrauch. 1998-11-3, 1-29.

(54) Hu, B.; Wang, H.; Yang, Z.; Sun, X.: Temporal and spatial variations of sediment rating curves in the Changjiang (Yangtze River) basin and their implications. Quaternary International 2011, 230(1-2), 34-43.

(55) US-EPA: Water quality analysis simulation program (WASP) version 6.0. DRAFT: User's manual. Without year. URL: www.epa.gov/athens/wwqtsc/html/wasp.html (accessed on 28.01.2014)

(56) Shen, L.H.; Xu, X.; Guo, A.M.; Li, M.: Characteristics of large-scale harmful algal blooms (HABs) in the Yangtze River estuary and the adjacent east China Sea (ECS) from 2000 to 2010. Journal of Environmental Protection, 2011, 2, 1285-1294.

(57) Leib, S.: Modelling of algae growth in the Three Gorges Reservoir, China. (Unpublished master thesis at the Institute of Mineralogy and Geochemistry, KIT, 2014)

VI BIOVIRTUOS - Biomonitoring with Virtual Organisms

FKZ: 02WT1132

Technical University Munich

Karl-Werner Schramm

Dominik Deyerling

Cedrique Temoka

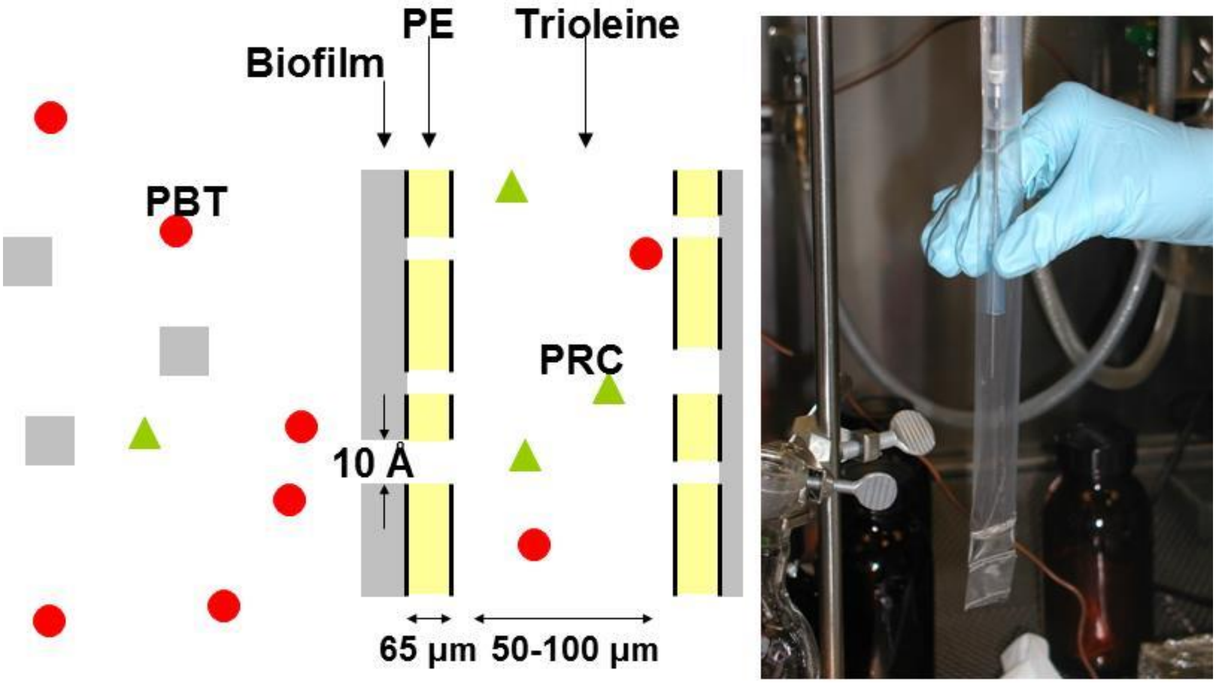


Figure VI-1: Virtual Organisms: left: Structure of device; right: lay-flat PE tubing enclosing a thin film of natural-like trioleine

Figure VI-2: Stainless steel containers for virtual organisms

Virtual Organisms (VO) are artificially designed to simulate a specific biological compartment such as for example the fat as a part of the lipidome of an organism. BIOVIRTOUS-project employs VO reflecting this fatty compartment because especially PBT are accumulating to a large extend in fatty tissues as an important part of the long lasting storage compartment of persisting and highly persistent compounds (PBT) of real organism's exposome. **V**O consists of lay-flat PE tubing enclosing a thin film of natural-like trioleine, a high molecular weight (FW. 885) natural lipid which can develop a biofilm during exposure. Therefore stable isotope labelled Performance Reference Compounds (PRC) are added into the VO-triolein to compensate environmental conditions at different sampling locations such as turbitity, temperature, biofouling etc. during exposure. PRC losses are then used to calculate the water volume sampled by the VO and thus to calculate the ambient water concentrations of the PBT. Seven **VO** are placed in stainless steel containers, which are usually deployed in water 2-4 weeks.

1 Chemical and Effect Oriented Exposomics: Three Gorges Reservoir (TGR)

Exposomic studies of the rapidly changing environment of the Three Gorges Reservoir (TGR) after its impounding is elaborated as a novel field of human and environmental research. Molecular exposomics is focused on the measure of all exposures to molecules and especially PBT-like compounds are of emerging interest due to their lifetime existence in the environment and humans.

Especially PBT have properties to estimate exposure to them more accurately. POP once marketed are expected to remain in the environment and biota for a long time and might peak even years after their use in the following generations of individuals (Figure VI-3)

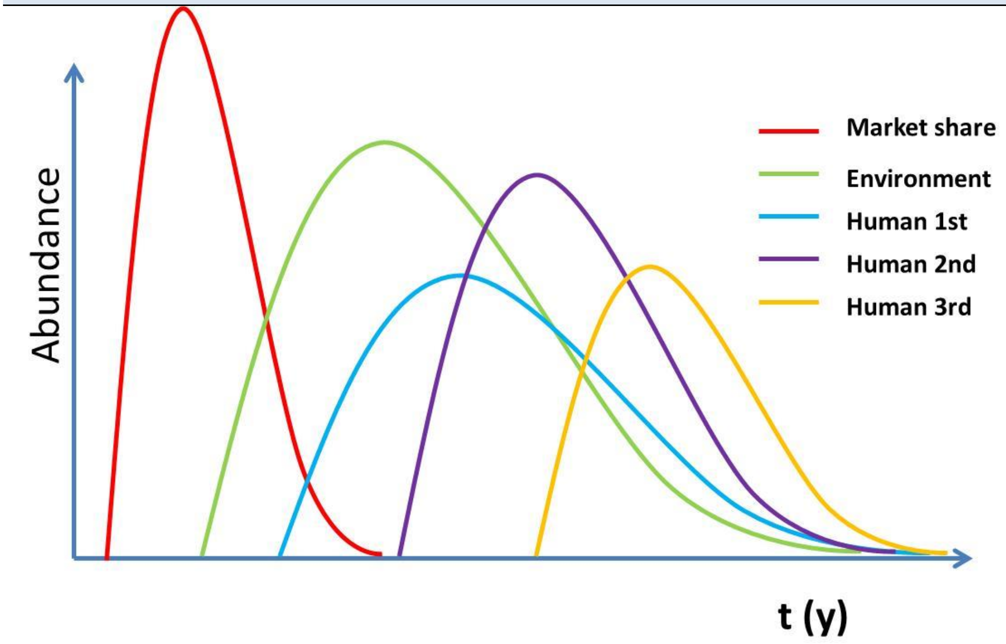


Figure VI-3: Abundance of PBT in human individuals at different generations in relation to their market share and their occurrence in the environment.

Theoretical considerations in general and particular for the TGR are deduced and presented using quantitative approaches for this research field

Since exposomics is strongly time-dependent a theory is presented to link extension of exposure, time and related effects. Similarity to the first law of thermodynamics is outlined. On top of this the integrated use of biomarkers is presented employing chemical analysis for biomarkers of exposure and effects, biomarkers in vivo, in vitro approaches and the link between chemical mixtures and the onset of disease and lethality. Besides real organisms also virtual organisms are favored to act as well defined sub-compartments such as fat of biota and with respect to time of exposure.

Exposomics is the perspective of risk evaluation and chronic exposures in the running century. It needs novel theories, approaches and integrated action between medical and environmental disciplines. The existing knowledge about molecular stressors has to be assembled and put into a context especially with respect to time resp. lifetime exposure of humans but also eco-toxicological findings by using highly conserved phylogenetic mechanisms to enable links between human and risks of environmental biota. The TGR is a good example not only to employ bio-monitoring of real but also virtual organisms due to the lack of established ecotopes in this changing environment so far.

Progress in understanding long-term risks requires a proper theory as well as novel tools such as virtual organisms. On top, multidisciplinary approaches and the utilization of existing knowledge about the exposure of the environment and humans have to be merged and directed into mutual concepts.

Effect-oriented and chemical analysis must be designed time-oriented to determine lifetime exposures of mankind and nature. Perspectively, a first attempt about exposomic theory and concepts is proposed and has to be developed experimentally further enclosing virtual besides of real organisms and compartments. Environmental and human exposomics have to be considered as a unified global issue in order to effectively utilize their mutual existing knowledge most effectively.

If biomarkers are considered in exposomics, an integrated approach is required to combine information about endogenous and exogenous abundance of chemicals and their relation to biomarkers of effect. Figure VI-4 shows an example how chemical exposure information can be combined with in-vitro and in-vivo data as well as the in-silico (risk model) approach by translation chemical information of mixtures into values to be comparable with effect information. In practice that means that for instance a fish liver should be analysed for chemical agonists relevant for the in-vitro and in-vivo endpoints determined in the fish and by fish cell lines or other phylogenetically related cell lines eg. from rat mice or humans. Finally those information must be related to the age and surface to volume ratio of organisms or its period of exposure since it is known that for many persistent compounds of emerging concern (PCEC) the exposure is indeed integrated in time and, thus, must be assessed before this background in relation to effect, resp. disease.

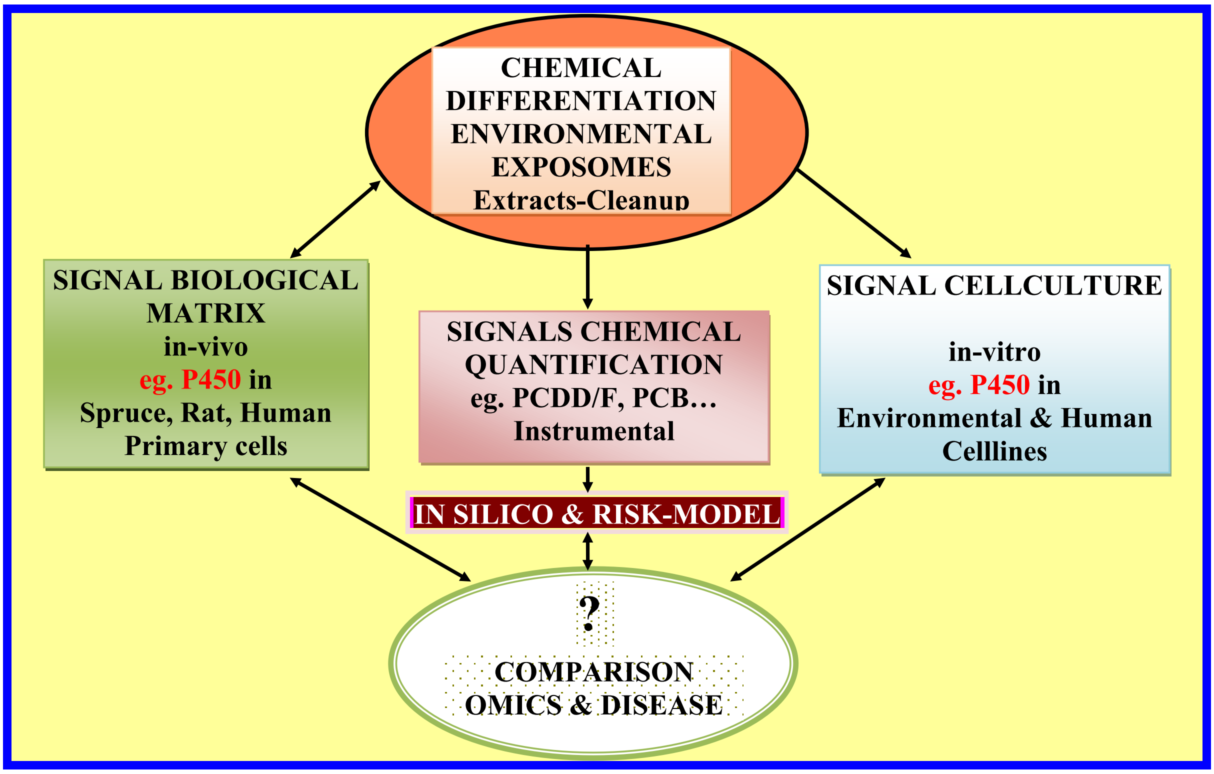


Figure VI-4: Potential holistic experimental and theoretical approaches to characterize environmental exposomes by means of chemical analysis, biomarkers of exposure, bioassay, and risk/effect modeling of tentative mixtures including translational comparisons between species and chemicals.

Recently exposomics has been structured as bottom-up or top down, which stands for measuring the exogenous environmental pressure and in case of molecular exposomics determining or modeling the chemical abundance in air, water, food etc. Top down molecular exposomics then is understood as endogenous exposure characterization by measuring chemicals in blood or other internal tissues and liquids. In the latter case non-invasive techniques are favorable to assess also ethically sensitive or protected species. For mammals, the investigation of hair has been found useful and received increasing attention because such a matrix is capable to reflect both top-down and bottom up exposomics. For improving the field of exposomics, the following demands have been stated recently and are extended here to environmental aspects:

- Developing a common language in a sense to develop a unifying concept for exposure. Since exposomics was targeting mankind, the language must also reflect the demands of ecoepidemiologists, ecotoxicologists and environmental researchers as well.
- Developing the exposome through biomarkers. However, for a biocenosis or biogeosystem imagination of biomarkers must arrive beyond the systematic of biomarkers in humans. In a biogeosystem also the presence or absence, resp. abundance of a species is probably biomarking the status of the system.
- Incorporation of exposure biomarkers into population studies, where a classic design integrates internal exposure data with external and genetic data also in a context of a suffering environment.
- Utilizing existing research studies such as running cohort studies, specimen banks and environmental monitoring programs. First approaches to link data from German environmental and human specimen bank have been executed finding some time delayed pattern between PCB in spruce needles and human blood
- Analysing the tremendous amount of data, harmonizing investigators by an international initiative and to translate the data into useful policy impacting the disease or well-being of a biogeosystem.
- Identification and production of less toxic chemical structures as an element of socialized prevention before we have understood and applied individualized therapeutics or measures. The efforts should include data generation, technology development, and data dissemination.

Three Gorges Dam (TGD) closure may result in even more drastic environmental alterations such as changes in the whole ecosystem structure and functioning. After the construction of TGD, the width of Yangtze River becomes wider and the depth becomes deeper and the biocenosis of the TGR started its succession. The water flow slows down significantly. Due to this dramatic changes and dynamics exposomics based only on species is currently difficult for this successive ecosystem. Therefore, other attempts have been executed to characterize the exposome of the TGA-biogeosystem.

Virtual Organisms (VO) are artificially designed to simulate a specific biological compartment such as for example the fat as a part of the lipidome of an organism. BIOVIRTOUS-project employs VO reflecting this fatty compartment because especially POP are accumulating to a large extend in fatty tissues as an important part of the long lasting storage compartment of persisting and highly persistent compounds of real organism's exposome. VO are normally representing a time period of 1-4 weeks 'living' at the sampling site. Thus VO provide a more averaged information about the POP in TGR in a bottom-up as well as top down approach because environmental and body concentrations can be deduced from the VOs. In this context VOs are very suitable for exposomic studies because time of exposure is well defined. In addition, the fate and accumulation of molecules targeted at particular persistent organic pollutants (POP) can be further reliably modeled in the food chain due to the existing knowledge about them; and since their properties are well known and their persistence allows also long-term estimations of effects based on approaches such as toxodose. The VO are exposed in TGR from Chongqing 600 km downstream to the dam attempting to characterize the impact of POP content in the main inflowing rivers during the season of depleting water levels typically in spring.

First results of POP concentrations back-calculated to water concentrations showed obvious regional variations of PAH, PCB and OCP levels in the reservoir and are compared to other matrices as well as effect oriented investigations such as Ah-receptor and ER-receptor agonists or antagonists. The comparison of chemical-oriented and effect-oriented analyses revealed large differences between known and unknown compounds, which caused EROD activity and ER-antagonits of sample extracts. Unknown compounds in TGR are suspected to be responsible for the high anti-estrogenic and EROD-activity in extracts of suspended particles.

To complement the exposome of TGA at the current conditions, the second matrix sediment has been selected.

In general, molecular exposomics demands crosstalk between different exposomes encompassing virtual organisms and real organisms up to human level. Due to the complexity exposomics also requires crosstalk between different disciplines covering environmental, biological, toxicological, systemic, medical disciplines etc.

Further time related approaches such as toxodose are necessary to quantify persisting and transient exposures up to lifetime exposomics within biological webs.

In this respect also the development and employment of VOs are of increasing importance as a surrogate of real organisms. In particular the dynamic situation in the TGR required such technique because the biocenosis is in a changing condition, which makes it difficult to use established real organisms for biomonitoring. Finally, time related approaches between VOs, biomonitors, and abiotic matrices seem promising to reveal more clear pictures between the abundance of persisting chemicals and their molecular effects resp. risk for ecosystems and humans.

Full paper: Schramm, K.-W., Wang, J., Bi, Y.*, Temoka, C., Pfister, G., Henkelmann, B., Scherb, H.: Chemical- and effect-oriented exposomics: Three Gorges Reservoir (TGR). *Environ. Sci. Pollut. Res.* **20**, 7057-7062 (2013)

2 Field data of related performance reference compounds in virtual organisms accurately monitor Polycyclic Aromatic Hydrocarbons in aqueous media

Performance Reference Compounds (PRC) spiked into Virtual Organism (VO) has been used to assess an analyte's *in situ* VO-water exchange kinetics. It is still a particular challenge to measure dissipation rate of highly hydrophobic PRCs in VO and only vanishingly small amounts of native lipophilic PAH should be available for uptake because of sorption to particulates and dissolved organic carbon. In this present work the evaluation of PAH-PRC-was established regardless certain environmental conditions (biofouling, pH, temperature) and the exchange kinetic was measured to enable the calculation of *in situ* sampling rates of chemicals using PRC with moderate and high hydrophobicity. Sixteen labeled 13C EPA-PAH compounds were chosen as PRC with log K_{OW} values ranging from 3.38 to 6.63. PRC Compounds with $K_{OW}<10^5$ were generally useful at up to 30 days with $k_{e,PRC}$ values ranging 0.03 to 0.19 day^{-1}.

Evaluation of the sixteen PRC release reveals a good performance of seven compounds, for which logKow values ranged from 3.38 (Naphthalene-13C6) to 4.84 (Fluoranthen-13C6) for exposure time from 7 days to 30 days. Relation between the concentration and time was described by a log-linear empirical function where the slope is referred to as the PRC elimination rate constant ($ke,_{PRC}$) (Figure VI-5). Probably, due to its high fugacity, $ke,_{PRC}$ of Naphtalene-13C6 was the highest with 0.19 day^{-1} and the lowest had Fluoranthen 13C6 with 0.03 day-1. Using Eq1, Naphthalene-13C6 and Acenaphtylen-13C6 had already attained equilibrium with $k_{e,PRC}\ t$ >1 for an exposure time of 30 days while Acenaphthen-13C6, Fluoren-13C6, Phenanthren-13C6, Anthracen-13C6 and Fluoranthen 13C6 were still in the linear stage with $k_{e,PRC}\ t$ <1 (Huckins et al, 2006). Sampling rate Rs for those compounds increased linearly with logKow. The other compounds with high Kow (logKow range 5.18 to 6.63) did not perform enough for this short period of deployments as their $ke,_{PRC}$ were lower than 0.01. Low $ke,_{PRC}$ does not mean that there was not isotropic exchange between high hydrophobic PRC compounds and their native analogues. Uncertainty of retained PRC compounds is now used to estimate maximal $ke,_{PRC}$ of high hydrophobic compounds.

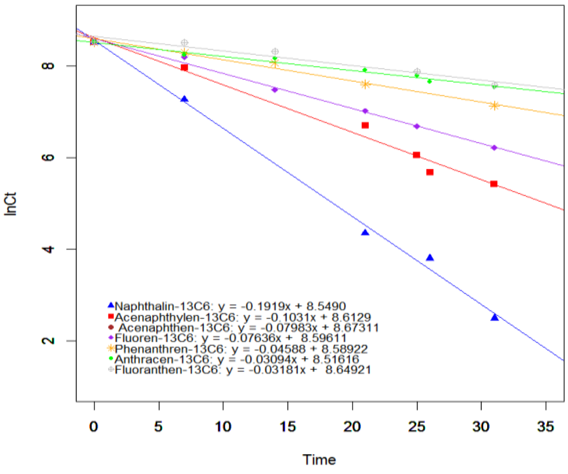


Figure VI-5: Exposure time of compounds in the log Kow range 3 to 5 as a function of PRC dissipation ln (N/N0) with N0 the amount present at t=0 and N the amount present at t. Connected data points represent measurements within 4 different studies during periods ranging from 7 to 30 days.

Highly hydrophobic PRC exhibit too low dissipation rates constant even after 30d. Measured values of sampling rate Rs show a linear increase of lower hydrophobic compounds with logKow < 4.84 following by the upper limit for compounds with log Kow ≥ 5.18. This deviation opposed other approaches where Rs slightly decline with increasing Kow presenting then a possible and substantial overestimation of pollutant concentrations.

Full paper is in preparation

Temporal variation and spatial distribution of PAH in water of Three Gorges Reservoir during the complete impoundment period

Bioavailable concentrations of polycyclic aromatic hydrocarbons (PAH) were investigated in water of Three Gorges Reservoir (TGR) using virtual organisms during the period of completely impounding water. The sampling sites spanned the whole reservoir from the upstream Chongqing to the great dam Maoping, covering more than 600 km long distance.. The sampling sites were MP (Maoping), GJB (Guojiaba), BD1 (Badong), BD2 (Badong), DN1 (Wushan), DN2 (Wushan), FJ (Fengjie), XJ1(Yunyang), XJ2(Yunyang), WZ (Wanzhou), CS (Changshou), CQ (Chongqing) (Figure VI-6).

∑PAH concentrations in water of TGR in the period of completely impounding water were 15-381 ng L^{-1}. ∑PAH concentrations increased from town or counties to big industrialized cities in TGR, indicating urbanization effects on PAH pollution in the water. Tributaries in TGR have a certain contribution of PAH pollution to the main stream of Yangtze river and their pollution could not be neglected.

The results of PAH showed obvious spacial distribution in TGR that modest to dramatic increases in ∑PAH concentrations were seen in water of TGR from down stream to upstream during the five time monitoring periods in the three years (Table VI-1). The concentrations of the total PAH in less urbanized Hubei area were characterized as homogenous relative to most heavily populated cities in Chongqing area ranged from 16 to 42 ng L^{-1} in the three years, whereas ∑PAH increased obviously from WZ and showed the highest levels to 354 and 381 ng L^{-1} in CS and CQ. The total PAH concentrations increased obviously from town or counties to big industrialized cities, suggesting that PAH in water reflect the urbanization effects. CQ and CS may be a major PAH source to the downstream reservoir.

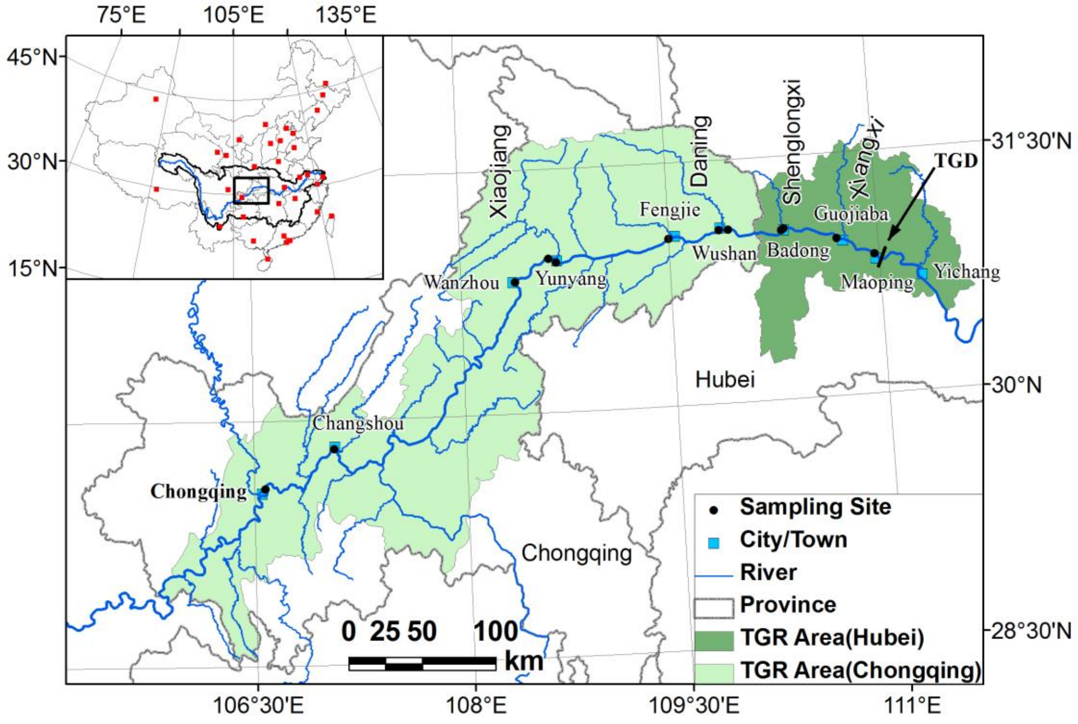


Figure VI-6: Scheme of sampling sites. The sampling sites are MP (Maoping)), GJB (Guojiaba), BD1 (Badong), BD2 (Badong), DN1 (Wushan), DN2 (Wushan), FJ (Fengjie), XJ1 (Yunyang), XJ2 (Yunyang), WZ (Wanzhou), CS (Changshou), CQ (Chongqing)

The composition of 16 priority PAH (grouped by the ring number in compounds) was at similar percentages for 5- and 6-ring compounds in TGR from upstream to downstream. Whereas, the 3-ring and 4-ring PAH portions were considerably higher in water from big city CQ and CS than from town or counties in Hubei area.

The first time of impounding water in TGR to reach water level of 135 m was in June 2003. After flood season of 2006, the water level reached to 156 m and during this primary operation period, the lowest water level was 135 m. Until 2008 the engineering construction of the Three Gorges project was near to completion. In November 2008, the reservoir started to retain water to water level of 172.8 m. In October 2009 started the second time of storing water in the reservoir and to rise the water level to 171.4 m. In October 2010 started the third time of water storage in the reservoir and for the first time the water level rised to the designed height of 175 m. From now on, the Three Gorges project goes into its normal operation period with water level fluctuations from 145 to 175 m. Our sampling campaign in May 2008 was exactly in the period of primary operation period. The second sampling campaign in May 2009 was just after the first time of storing water to 172.8 m. And the third sampling campaign in May 2011 was after the first time of water storage to the designed height of 175 m. There were obvious temporal variations of PAH concentration in TGR for the five times monitoring in the three years. Similar variation was observed in 2009 that ∑PAH of 2009-2 was generally higher than 2009-1 and the water flow was lower than 2009-1. 2008-2 and 2009-1 had similar water flow, ∑PAH in these two periods were also similar.

High flow volume of water dilutes pollutant concentration in 2008 and 2009. However, exception was in 2011 because ∑PAH were lower compared to the other two years whereas water flow volume was also much lower.

Table VI-1: ∑PAH concentrations for the 16 individual PAH (ng L^{-1}) in water from dam to upstream of TGR in 2008, 2009 and 2011

Note: "-" indicates no data available because no sampling in these sites

	2008-1 *May 4-11*	*2008-2* *May 11-Jun 4*	*2009-1* *Apr 29-May 13*	*2009-2* *May 13-Jun 7*	*2011* *Apr 24-May 19*
MP (Maoping)	42	33	39	23	19
GJB (Guojiaba)	19	21	22	17	18
BD1 (Badong)	19	16	34	28	22
BD2 (Badong)	17	-	32	22	20
DN1 (Wushan)	-	-	-	-	32
DN2 (Wushan)	-	-	-	-	28
FJ (Fengjie)	-	-	-	-	34
XJ1 (Yunyang)	-	-	-	-	37
XJ2 (Yunyang)	-	-	-	-	36
WZ (Wanzhou)	15	26	58	46	43
CS (Changshou)	354	103	91	294	80
CQ (Chongqing)	166	-	129	381	159

The wastewater treatment capacity is improved every year because the number of urban sewage treatment plant in TGR is increased from 56 in 2008 to 71 in 2010. Until April 2011, there are 155 wastewater treatment plants running in TGR and treatment ability reaches to 25 million tons/day. Therefore, the large scale of construction of wastewater treatment plant and management measures for reducing wastewater discharge and saving energy in TGR could have contributed to the decrease of pollution in 2011.

The ∑PAH in MP was 23, 11.6, 16.9, 6.4 and 1.9 ng L^{-1} higher than in GJB respectively in the five times monitoring period (Table VI-1), indicating Xiangxi river (XX) had PAH pollution input to the main stream of Yangtze river. The results show that the contribution of ∑PAH from Xiangxi river in 2011 were very low compared to 2008 and 2009. The reason for the decrease of PAH in Xiangxi river may also be the result of the comprehensive treatment and management for the river. ∑PAH in BD1 were 2.3 ng L^{-1} higher than in BD2 in 2008, 3.1 and 6.3 ng L^{-1} higher in 2009 and 1.7 ng L^{-1} higher in 2011 (Table VI-1), indicating Shenlongxi river (SL) also had PAH pollution input to the main stream but its contribution was lower than XX river. In 2011, 4 sampling sites were added to monitor PAH contribution of the tributaries Daning river (DN) and Xiaojiang river (XJ). After the two tributaries, ∑PAH in the main stream increased 4.3 ng L^{-1} and 0.8 ng L^{-1} respectively (Table VI-1). Among the 4 monitored tributaries in 2011, XJ contributed lowest PAH of 0.8 ng L^{-1} to the main stream and DN contributed highest PAH of 4.3 ng L^{-1} among the four rivers. The annual average flow of the four tributaries are XX 65 m^3 s^{-1}, SL 20 m^3 s^{-1}, DN 106 m^3 s^{-1}, and XJ 127 m^3 s^{-1}, respectively.

Compared with the flow of the main stream Yangtze, their inputs are small and the discharge at the two sites of each tributary is approximately equal. Therefore, percentages of increased total PAH concentrations in the main stream after the four tributaries were 10.9%, 8.4%, 15.3% and 2.2% in 2011 for XX, SL, DN and XJ respectively. Pollution from tributaries could not be neglected.

Ratios of PAH with similar molecular weights have been used as indices for source apportionment. If anthracene/ anthracene+ phenanthrene (ANT/(ANT+PHE)) < 0.1 and benz[a]anthracene/ benz[a]anthracene+ chrysene (BaA/(BaA+CHR)) < 0.2, a petrogenic source is suggested; for a pyrogenic source, ANT/(ANT+PHE) would be > 0.1 and BaA/(BaA+CHR) > 0.35. Fluoranthene/ fluoranthene+ pyrene (FLUO/(FLUO+PYR)) < 0.4 are for a petrogenic source, between 0.4 and 0.5 for liquid fossil fuel (vehicle and crude oil) combustion; Indeno[1,2,3-c,d]pyrene/ indeno[1,2,3-c,d]pyrene+ benzo[g,h,i]perylene (INP/(INP+BghiP)) < 0.2 are possibly for a petrogenic source, between 0.2 and 0.5 for liquid fossil fuel (vehicle and crude oil) combustion. The ANT/(ANT+PHE) in TGR was higher than 0.1 except CQ. The BaA/(BaA+CHR) was smaller than 0.2 except CQ and CS in 2008 and 2009. In 2011 the ratio of most sites was higher than 0.2. The source was neither pure petrogenic nor pure pyrogenic, thus should be their mixture. The sources had obviously changed in 2011 since the ratio of BaA/(BaA+CHR) were much higher than 2008 and 2009. But the cause of the change in sources in 2011 is unknown. It may be related with the newly running express highway for moving around the dam and further study needed to clarify it. FLUO/(FLUO+PYR) was less than 0.4 except CQ and CS, indicating PAH in the downstream of TGR was characterized as petrogenic source. The ratio in CS was between 0.4 and 0.5 and CQ was higher than 0.5, indicating that the source in CS was mainly from liquid fossil fuel (vehicle and crude oil) combustion and in CQ was characteristics of coal, grass or wood combustion. Ratio of INP/(INP+BghiP) in 2008 was between 0.2 and 0.5 and 83% of the ratio in 2011 was between 0.2 and 0.5, indicating that the possible source was liquid fossil fuel (vehicle and crude oil).

But 75% of the ratio in 2009 was higher than 0.5 and suggests combustion of biomass and coal. During the monitoring period in 2009 rainfall was higher than the other two years, indicating rainfall causing higher impact of pollutants scavenging from air masses originating from urban cities.

Downstream and upstream TGR have different PAH sources. Chongqing and Changshou are big cities in the upstream area of TGR. Local discharge, ship activities and air pollution may have been the main source of PAH. In the downstream area especially Hubei area of TGR, the main source of PAH may be ship activities and oil spillage.

PAHs in TGR were investigated employing VO during the drawdown season late April and early June of the completely impounding water years in TGR. The successful application of virtual organisms in TGR provides an efficient method for monitoring and surveillance trace pollutants in TGR. The results of the study showed clear distribution pattern of PAH in different areas of TGR and the variation in different water impounding year and the pollution status is dynamically related with anthropogenic activities, suggesting PAH could be used as marker compound or indicator in the network monitoring system to surveil and trace the industrial pollution status in TGR.

The total PAH concentrations increased from town or counties to big industrialized cities, indicating urbanization effects on PAH pollution in water. Different composition of 16 priority PAH in cities and towns in TGR suggests different pollution sources from industrialized cities to rural area. Decrease of PAH concentration was observed after 175 m water impounding in TGR. Several reasons contribute to this decrease. Comprehensive treatment and management measures like construction of wastewater treatment plants and phasing out old and non standard ships resulted largely to reduce wastewater discharge. The dry weather in 2011 may caused less impact of pollutants into the water of TGR from atmosphere. Sedimentation is another important reason for decreasing pollution in water after 175 m water impounding because of the increase of water volume and slow down of water velocity.

Our study only reflects PAH pollution in TGR in drawdown period of a year during which normally water quality is the best compared to other seasons (dry season from November to April, flood season from June to August, and impoundment from September to October). Monitoring should be considered in other periods of the TGR operation cycle.

Obvious decrease of PAH concentration was observed after 175 m water impounding in 2011 in TGR. Several factors may account for this decrease, including execution of comprehensive treatment and management measures in TGR, less rainfall in 2011 and sedimentation effect caused by the dam. Passive sampling method has been successfully applied in the investigation of trace PAH in water of TGR and proved to be a useful and efficient tool for the management and sustainable development of the big reservoir. The results of the study provide valuable information about PAH pollution in the whole reservoir including some tributaries and the pollution status is dynamically related with human activities. Therefore, PAH could be used as marker compound or indicator in the network monitoring system to survey and trace the pollution status in TGR.

Full paper: Wang, J., Henkelmann, B., Bi, Y.*, Zhu, K.*, Pfister, G., Hu, W.*, Temoka, C., Westrich, B.*, Schramm, K.-W.: Temporal variation and spatial distribution of PAH in water of Three Gorges Reservoir during the complete impoundment period. *Environ. Sci. Pollut. Res.* **20**, 7071-7079 (2013)

3 PAH distribution and mass fluxes in the Three Gorges Reservoir after impoundment of the Three Gorges Dam

Mass fluxes of polycyclic aromatic hydrocarbons (PAH) were calculated for the Three Gorges Reservoir (TGR) in China, based on concentration and discharge data from the Yangtze River. Virtual Organisms (VO) have been applied during four campaigns in 2008, 2009 (twice) and

2011 at sampling sites distributed from Chongqing to Maoping. The total PAH mass fluxes ranged from 110 to 2,160 mgs^{-1}.

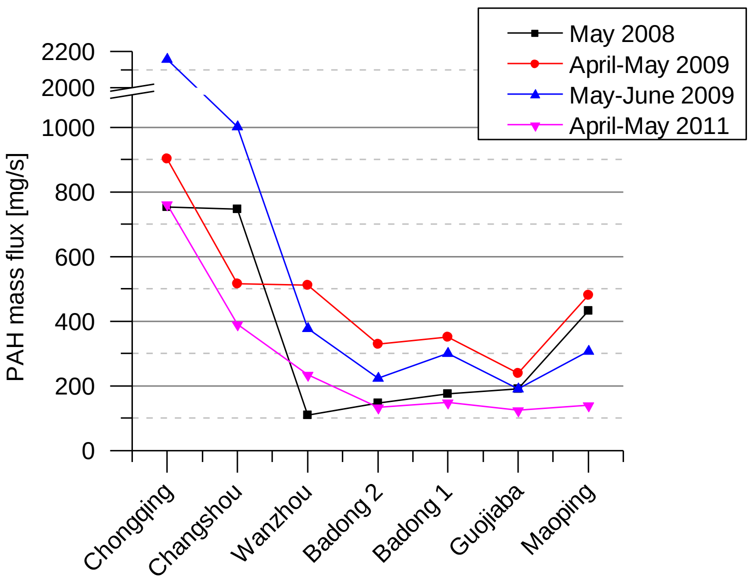


Figure VI-7: Total PAH mass flux from Yangtze river in mg/s determined with concentration data from 2008, 2009 and 2011

Highest loads were determined at Chongqing with a decreasing trend towards Maoping in all four sampling campaigns. PAH remediation capacity of the TGR was found to be high as the mass flux reduced by more than half from upstream to downstream. Responsible processes are thought to be adsorption of PAH to suspended particles, dilution and degradation. Furthermore, the dependence of PAH concentration upon water depth was investigated at Maoping in front of the Three Gorges Dam. Although considerable differences could be revealed, there was no trend observable. Sampling of water with self-packed filter cartridges confirmed more homogenous PAH depth distribution. Moreover, PAH content of suspended particles was estimated from water concentrations gathered by VO based on a water-particle separation model and subsequently compared to PAH concentration measured in water and in filter cartridges.

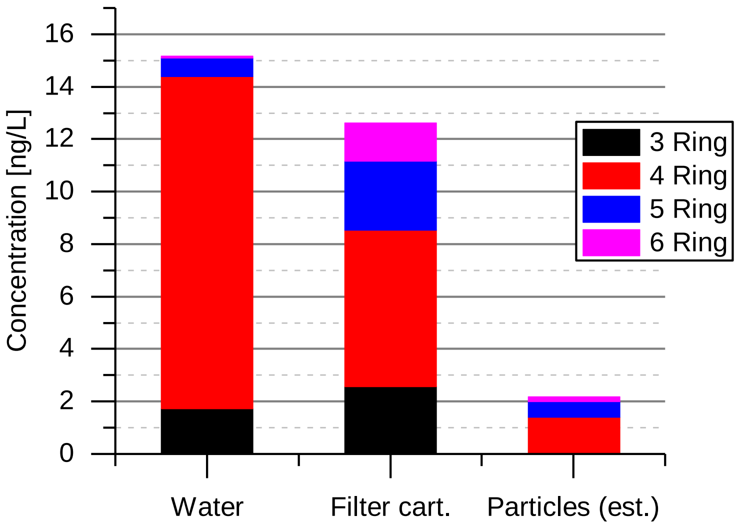


Figure VI-8: Total PAH mass flux from Yangtze river in mg/s determined with concentration data from 2008, 2009 and 2011

It could be shown that the modeled data predicts the concentration caused by particle-bound PAHs to be about 6 times lower than PAHs dissolved in water.

Besides, the model estimates the proportions of 5- and 6-ring PAHs being higher than in water phase.

Full paper: Deyerling, D., Wang, J., Hu, W.*, Westrich, B.*, Peng, C.*, Bi, Y.*, Henkelmann, B., Schramm, K.-W.: PAH distribution and mass fluxes in the Three Gorges Reservoir after impoundment of the Three Gorges Dam. *Sci. Total Environ.*, DOI: 10.1016/j.scitotenv.2014.03.076 (2014)

4 Depth profile of selected pharmaceutical traces and polar pesticides at Maoping

Active water sampling on self-packed sampling cartridges was carried out in September 2013 at Maoping in front of the Three Gorges Dam. For the analysis, a new analytical method was developed including high volume enrichment of the analytes (approx. 300 L) as well as a suitable laboratory cleanup and measurement via LC-HRMS.

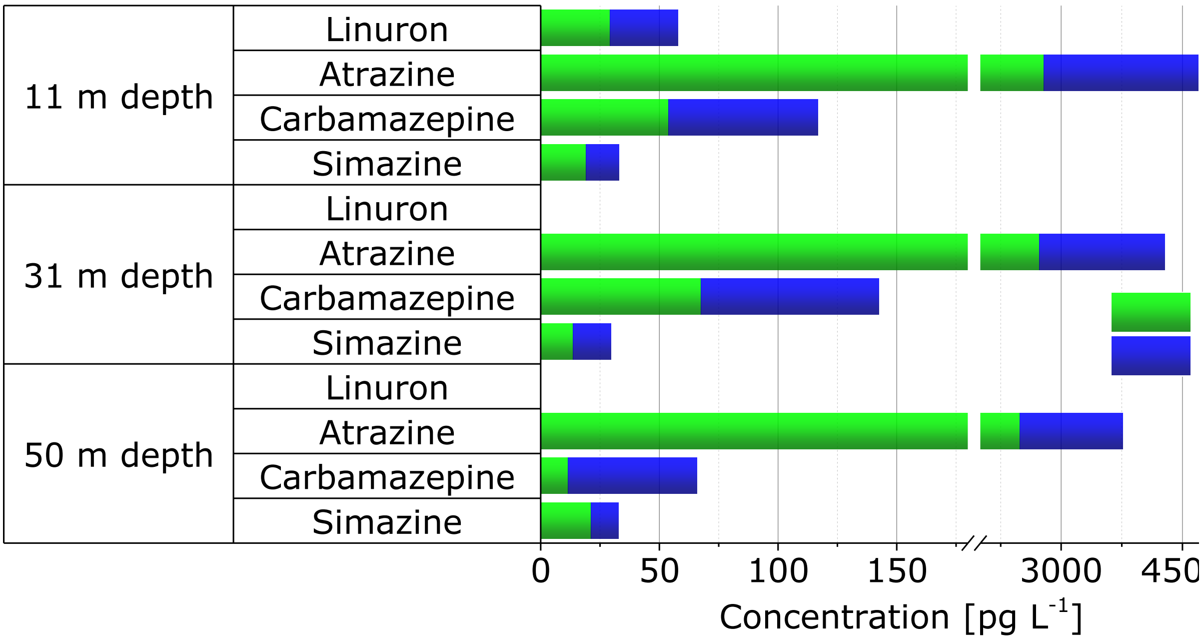


Figure VI-9: Water concentrations in different water depths of the Yangtze River at Maoping (China); the graph illustrates the amount of analyte found in master and backup cartridges as well as the total analyte concentrations Figure VI-9 presents first results of the water samples taken in September 2013 at Maoping in front of the Three Gorges Dam. Furthermore, Sulfamathoxazole and Naproxene could not be found in any of the samples and are therefore omitted in the plot. Obviously, the compounds seem to have a comparable distribution in the water body. Highest values were determined for the herbicide Atrazine which was detected within a ng L^{-1} range. The concentrations indicated were in the lower pg L^{-1} range. The results support the general expectation that water concentrations within the reservoir tend to be very low due to dilution.

Extended Abstract: LC-MS in der Umweltanalytik, Leipzig, 16-18.6.2014

5 Contamination status of dioxins in sediment cores from the Three Gorges Dam area, China

In order to screen dioxin pollution in sediment of Three Gorges Dam (TGD) area, three sediment cores were obtained from two sites in 2010~2011; each core was divided into different samples with every 10 cm depth. Sediment dating determined by radiometry

(137Cs, 210Pb) and concentrations of dioxins were analyzed by high-resolution gas chromatography/mass spectrometry. The results indicated: Sediment dating showed no significant difference among all the samples from the same core and the two locations (ANOVA, $p > 0.05$). The total amount of polychlorinated dibenzo-p-dioxins (PCDD)/Fs in all sample ranged from 30.7 to 371 pg/g dry weight (d.w.), with the mean value of 66.2 pg/g d.w. PCDDs occupied 60.33~85.22 % of dioxins in each sample, and PCDFs contributed to a very small extend. There was no significant difference in the dioxin concentration between 2010 and 2011 and in the two locations (t test, $p > 0.05$), but the vertical distribution of dioxins showed significant different in different depths.

There was no significant difference of dioxins concentration between GJB and MP (t test, $p > 0.05$), and there was no marked difference in the three sediment cores (ANOVA, $p > 0.05$). OCDD was the main congener and occupied 94.08~99.08 % of PCDDs.

The concentrations of total PCDD/Fs from MP in 2010 and 2011 were 76.2 and 71.3 pg/g d.w., respectively. The vertical distribution of dioxins in the two sediment core was shown in Figure VI-9.

Sample A4 showed significant different from other samples. Results of PCA test indicated that in core of MP in 2010, A3, A4, A7, and A8 could not be clustered into other samples. The higher concentration of OCDF in A3, the higher concentrations of OCDD and 1,2,3,4,5,7,8-HpCDD in A4, the higher concentration of OCDD in A7, and the higher concentration of 2,3,7,8-TCDF in A8 made the four samples significantly differed from others samples in the same core. In the core of GJB in 2010, the higher concentrations of 2,3,7,8-TCDD and OCDD in A1 and the higher concentration of OCDD in A2 made the two samples markedly differed from other four samples. In the core of MP in 2011, the higher concentrations of 1,2,3,4,6,7,8-HpCDD, OCDD, and OCDF in A7 made it markedly differed from other samples. It could be concluded that concentrations of dioxins in different depths showed evident difference, which meant the spatial heterogeneous of the concentration of dioxins in the sediment core.

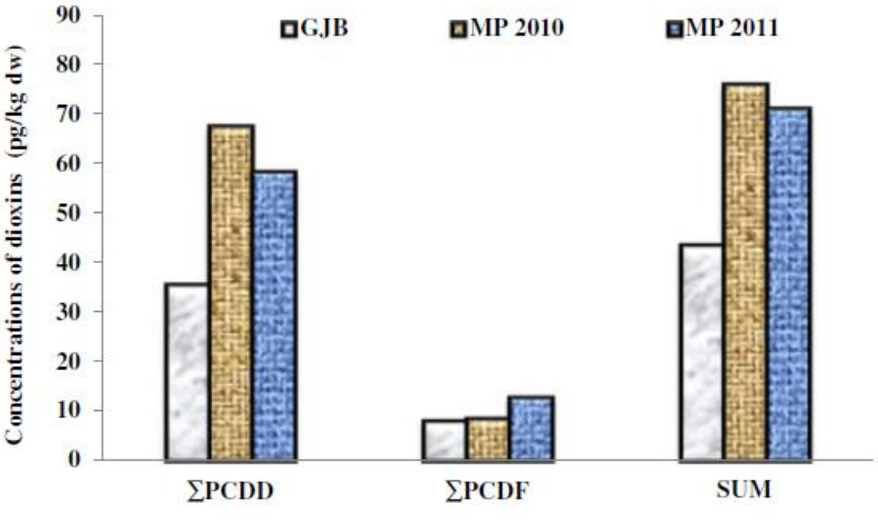


Figure VI-10: The concentration of PCDDs and PCDFs in GJB core and MP core

Toxic equivalent (TEQ) (WHO 2005, Humans) of samples ranged from 0.15 to 1.60 pg/g d.w.; the mean was 0.41 pg/g d.w. No significant difference was found in TEQ between 2010 and 2011(t test, $p > 0.05$). It could be concluded that the distribution of dioxins showed the spatial heterogeneity which resulted from the strong mixing and sediment deposition characteristics. Dioxin concentration in sediment cores was low with very low environmental risk potential. Dioxins at the two sites nearby the dam had the same origin, and exogenous input was the main source. It is the first report on the dioxins concentrations in sediment cores in the TGD area.

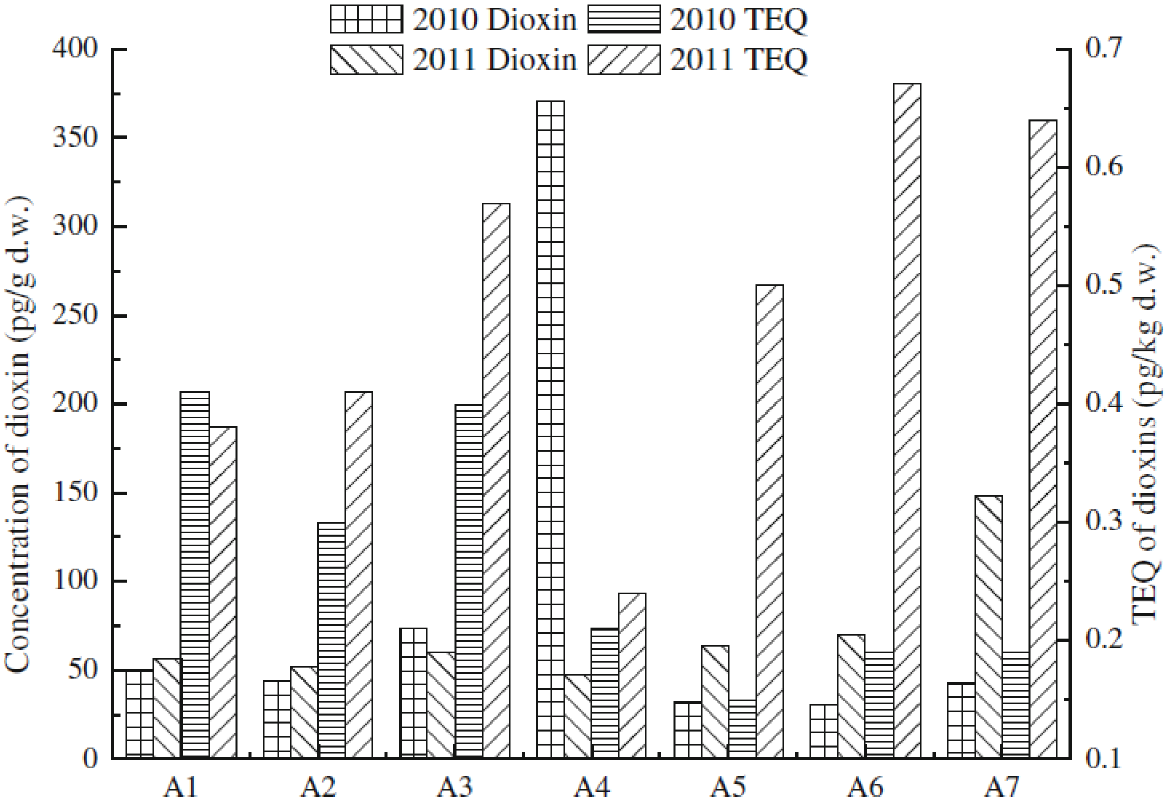


Figure VI-11: The vertical distribution of dioxins and TEQ value (WHO 2005) in the sediment core MP in 2010 and 2011

Full paper: Chen, L.*, Bi, Y.H.*, Zhu, K.X.*, Hu, Z.Y.*, Zhao, W.*, Henkelmann, B., Bernhöft, S., Temoka, C., Schramm, K.-W.: Contamination status of dioxins in sediment cores from the Three Gorges Dam area, China. *Environ. Sci. Pollut. Res.* **20**, 4268-4277 (2013)

6 Aryl hydrocarbon receptor (AhR) inducers and estrogen receptor (ER) activities in surface sediments of Three Gorges Reservoir, China evaluated with in vitro cell bioassays

Two types of biological tests were employed for monitoring the toxicological profile of sediment cores in the Three Gorges Reservoir (TGR), China. In the present study, sediments collected in June 2010 from TGR were analyzed for estrogen receptor (ER)- and Aryl hydrocarbon receptor (AhR)- mediated activities. The estrogenic activity was assessed using a rapid yeast estrogen bioassay (YES), based on the expression of a green fluorescent reporter protein (Figure VI-12).

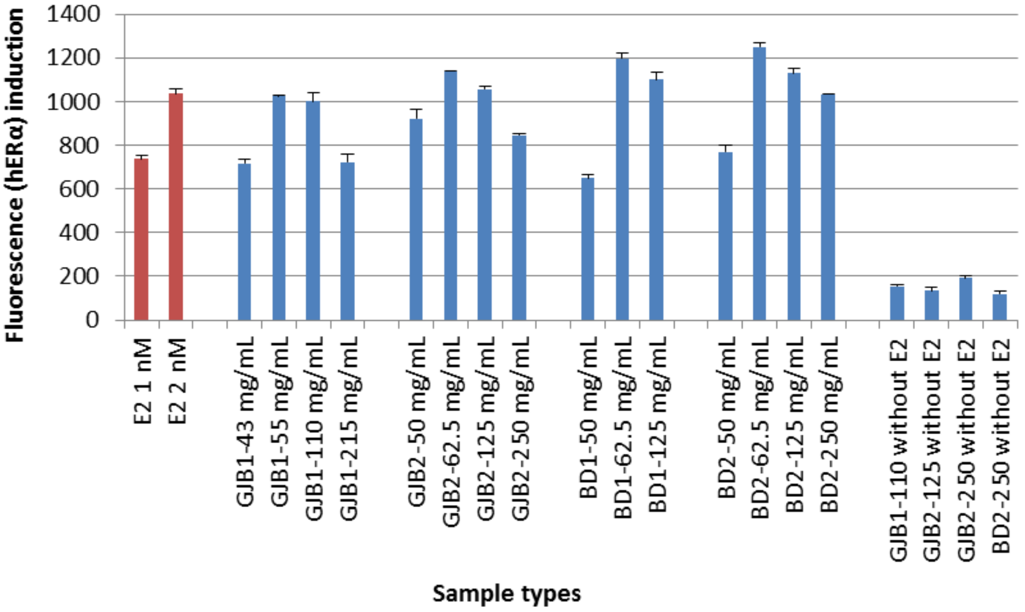


Figure VI-12: Estrogenic activities in sediment extracts from GJB and BD in co-administration of 1 nM Estradiol (E2) yeast bioassay system were presented with relative fluorescence induction. The relative fluorescence inductions of some of the dilution levels which had been shown estrogenic potency without the addition of E2 were also presented. 1 nM E2 and 2 nM E2 co-cultured with carrier solvent only were used as relevant controls.

Weak anti-estrogenic activity was detected in sediments from an area close to the dam of the reservoir and weak estrogenic activities ranging from 0.3 to 1 ng E2 EQ g^{-1} dry weight sediment (dw) were detected in sediments from the Wanzhou to Guojiaba areas. In the upstream area Wanzhou and Wushan, sediments demonstrated additive effects in co-administration of 1 nM E2 in the yeast test system, while sediments from the downstream Badong and Guojiaba area showed estrogenic activities which seemed to be more than additive (synergistic activity). There was an increasing tendency in estrogenic activity from upstream of TGR to downstream, whilst this tendency terminated and converted into anti-estrogenic activity in the area close to the dam.

The AhR activity was detected employing rat hepatoma cell line (H4IIE). EROD activities were found homogenously distributed in sediments in TGR ranging from 200 to 311 pg TCDD EQ g^{-1} dw for total AhR agonists and from 45 to 76 pg TCDD EQ g^{-1} dw for more persistent AhR agonists (Figure VI-13). The known AhR agonists PAH, PCB and PCDD/F only explained up to 8% of the more persistent AhR agonist activity in the samples, which suggests that unidentified AhR-active compounds represented a great proportion of the TCDD-EQ in sediments from TGR.

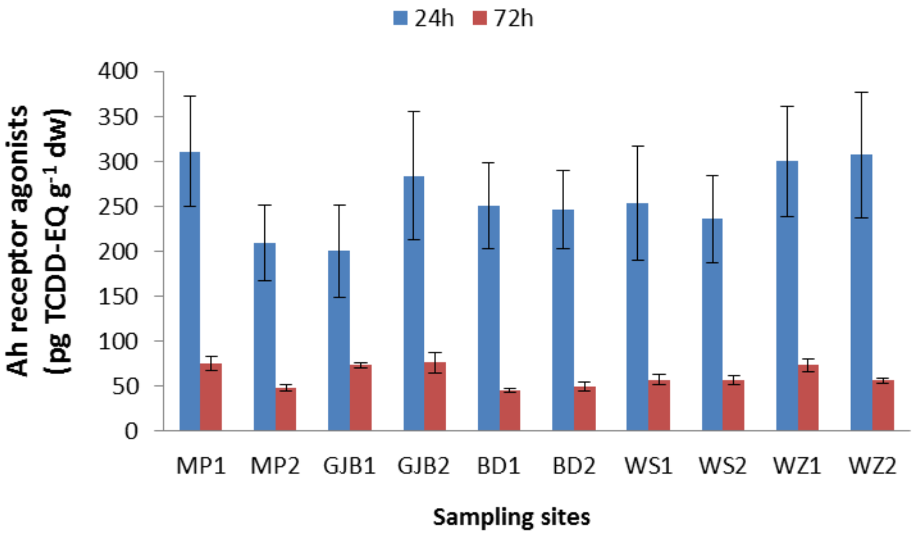


Figure VI-13: EROD results after 24 and 72 hours incubation (pg TCDD-EQ g^{-1} dw, mean ±SD) with extracts of sediments from TGR

TEQ_{bio} values of the samples extracts were obtained by comparing EROD activities to TCDD concentration-response curve and are presented in Figure VI-14. All samples also induced obvious EROD activities after 72 h exposure, although the EROD induction and TEQ_{bio} levels of 72 h incubation were lower than those of 24 h. The TEQ_{bio} levels of VO sample extracts after 24 h of incubation (TEQ_{bio_24h}) ranged from 90.5 to 652.2 pg TCDD g^{-1} lipid and after 72 h of incubation (TEQ_{bio_72h}) ranged from 14.0 to 177.3 pg TCDD g^{-1} lipid. Both $TEQ_{bio-24h}$ and $TEQ_{bio-72h}$ showed in general an increasing trend from downstream TGR to upstream, and both values in 2011 were relatively higher than those in 2008 but lower than 2009.

Virtual organisms (VO) deployed at five to eight sites in the Three Gorges Reservoir (TGR), China for five periods in 2008, 2009 and 2011 were used to determine the water exposure of aryl hydrocarbon receptor (AhR) agonists (Figure VI-14).

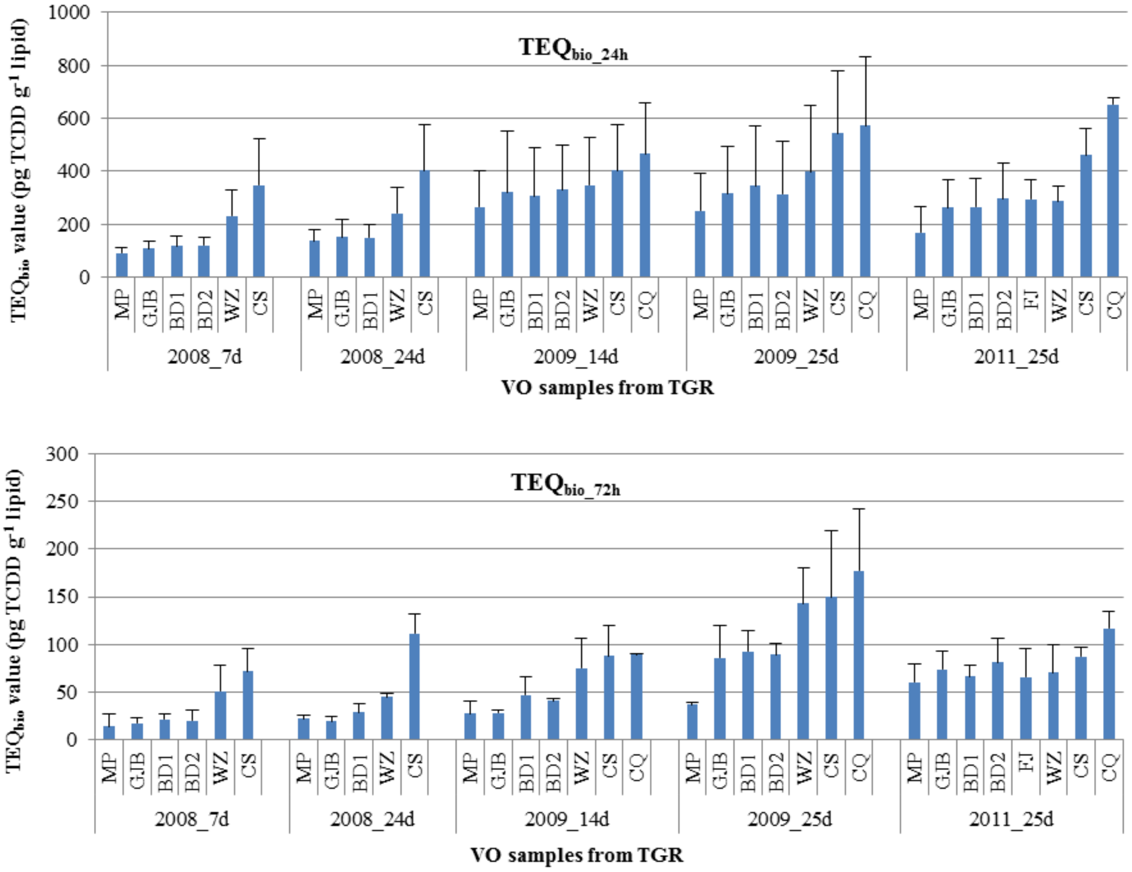


Figure VI-14:: Bioassay-derived TEQs in VOs from TGR determined in five periods. Bars represent the mean ±SD of triplicate analysis. TEQ_{bio} was obtained by comparing the EROD activities of samples to the TCDD concentration-response curves.

The results show that the extracts of VO could induce AhR activity significantly, whereas the chemically derived 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) equivalent (TEQ_{cal}) accounted for <11% of the observed AhR responses (TEQ_{bio}) (Table VI-2). Unidentified AhR-active compounds represented a greater proportion of the TCDD equivalent in VO from TGR. High TEQ_{bio} value in diluted extract and low TEQ_{bio} in concentrated extract of the same sample was observed suggesting potential non-additive effects in the mixture. The levels of AhR agonists in VOs from upstream TGR were in general higher than those from downstream reservoir (Figure VI-14), indicating urbanization effect on AhR agonist pollution. The temporal variation showed levels of AhR agonists in 2009 and 2011 were higher than those in 2008, and the potential non-additive effects in the area close to the dam were also obviously higher in 2009 and 2011 than in 2008, indicating big changes in the composition of pollutants in the area after water level reached a maximum of 175 m.

Although the aqueous concentration of AhR agonists of 0.8-4.8 pg TCDD L^{-1} in TGR was not alarming, the tendency of accumulating high concentration of AhR agonists in VO lipid and existence of possible synergism or antagonism in the water may exhibit a potential hazard to local biota being exposed to AhR agonists.

Table VI-2: Chemical-derive TEQs based on concentrations of PAH and PCB (pg TCDD g^{-1} lipid)

	Sampling time	MP	GJB	BD1	BD2	FJ	WZ	CS	CQ
TEQ_{PAH}	2008_7d	0.920	0.781	1.315	1.142	-	1.147	1.800	-
	2008_24d	0.791	1.825	1.610	-	-	3.923	3.598	-
	2009_14d	0.346	0.703	0.980	1.121	-	1.316	1.211	2.347
	2009_25d	0.668	0.935	1.213	1.299	-	1.829	3.920	6.403
	2011_25d	0.608	0.488	1.121	1.089	1.936	1.988	2.591	12.510
TEQ_{PCB}	2008_7d	0.009	0.007	0.007	0.007	-	0.007	0.007	-
	2008_24d	0.018	0.010	0.025	-	-	0.022	0.010	-
TEQ_{cal}	2008_7d	0.929	0.787	1.322	1.148	-	1.153	1.807	-
	2008_24d	0.809	1.835	1.635	-	-	3.945	3.608	-

Note: The TEQ_{PCB}s were calculated by multiplying the measured concentrations by the corresponding TEF proposed by the World Health Organization (Van den Berg et al., 2006). The TEQ_{PAH}s were calculated by multiplying the measured concentrations by the corresponding REPs (relative potencies) proposed by references Villeneuve et al. (2002) and Nakata et al. (2003). TEQ_{cal} is the sum of TEQ_{PAH} and TEQ_{PCB}. The symbol "-" indicates no data available because sampling was not done in these sites.

The findings of estrogenic potential and dioxin-like activity in TGR sediments provide possible weight-of-evidence of potential ecotoxicological causes for the declines in fish populations which have been observed during the past decades in TGR.

Full papers

Wang, J., Bovee, T.F.H.*, Bi, Y.*, Bernhöft, S., Schramm, K.-W.: Aryl hydrocarbon Receptor (AhR) inducers and Estrogen Receptor (ER) activities in surface sediments of Three Gorges Reservoir, China evaluated with in vitro cell bioassays. *Environ. Sci. Pollut. Res.* **21**, 3145-3155 (2014)

Wang, J., Bernhöft, S, Pfister, G., Schramm, K.-W.: Water exposure assessment of aryl hydrocarbon receptor agonists in Three Gorges Reservoir, China using SPMD-based virtual organisms. Sci. Tot. Environ. in press (2014)

7 *Conclusive Summary*

The development and employment of Virtual Organisms (VO) to characterize the status of the water quality in the Three Gorges Reservoir (TGR) revealed important data about

- The spatial and seasonal water quality based on chemical analysis which increases from Chongqing to the dam for many persisting organic pollutants (POP)

- The spatial and seasonal water quality based on bioassay analysis for AhR interaction and estrogens which increases from Chongqing to the dam for many POP
- The seasonal mass transport across the dam during low water regime
- The homogeneity of the pollution in the cross-sectiona area in front of the dam to verify the feasibility of mass transport calculations
- The contribution to the pollution of the reservoir for the most important tributaries during low water regime

Many reasons were discussed for the pollution, among them the ship traffic, increasing urbanization and development as well as the instrial city of Chongqing as a main source of pollution. On the other hand the reservoir has been shown to exhibit substantial losses of pollution (up to 80 % from Chongqing to the dam) after being substantially contaminated at Chongqing. These losses can be attributed to ecological services based on degradative processes (biotic and abiotic) and volatilization of chemicals from the water phase.

The investigation of sediment cores from the reservoir and selected tributaries wittness their homogeneity and young age. Their low contamination status with respect to pollutants and their young age with respect to sedimentation pinpoint to their recent formation which is mainly based on low contaminated eroded material.

All in all, the Biovirtous project generated first data about the status of PBT and estrogenicity of the whole reservoir as a basis for further follow-up investigations and risk assessments. The VO will also help to estimate the potential contamination status of future fish populations of the food market based on TGR. Due to the high reproduceability of the VO their future utilization in other projects or by authorities is feasible. The VO performance allows the seasonal cost-effective investigation of PBT in TGR in a short time along the whole stretch of the huge reservoir. In addition the VO results can be compared to other Chinese reservoirs of societal interest such as the Danjiangkou-Reservoir connected to the Yangtze and surving Beijing as a drinking water reservoir (Wang et al. 2014).

Wang, J., Song, G., Li, A., Henkelmann, B., Pfister, G., Tong, A.Z., Schramm, K.-W.: Combined chemical and toxicological long-term monitoring for AhR agonists with SPMD-based virtual organisms in drinking water Danjiangkou Reservoir, China. *Chemosphere* **108**, 306-313 (2014)

8 Summary

Project BIOVIRTUOUS developed and utilized Virtual Organisms (VO) to characterize the status of water quality in the Three Gorges Reservoir (TGR). TGR exhibit substantial losses of pollution (up to 80 % from Chongqing to the dam) after being contaminated at Chongqing. These losses can be attributed to ecological services based on degradative processes and volatilization of chemicals from the water phase.

The contribution to the pollution of the reservoir for the most important tributaries during low water regime could be evaluated as a basis of environmental management. Homogeneity investigations of the pollution in the cross-sectiona area in front of the dam allowed the verification of total mass transport calculations of pollutants.

The investigation of sediment cores from the reservoir and selected tributaries wittness their homogeneity and young age. Their low contamination status with respect to pollutants and their young age with respect to sedimentation pinpoint to their recent formation which is mainly based on low contaminated eroded material. All in all the BIOVIRTUOUS generated first data about the status of persistent bioaccumulative toxins (PBT) and estrogenicity of the whole reservoir as a basis for further follow-up investigations and risk assessments. VO were very effective to estimate the potential contamination status due to their high reproduceability and allowed seasonal cost-effective investigation of PBT in TGR in a short time along the whole stretch of the huge reservoir.

VII MICROTOX - Transformation, Bioaccumulation und Toxicity of Organic Micropollutants in the Three Gorges Reservoir

FKZ: 02WT1141

RWTH Aachen University

Björn Scholz-Starke
Ye Yuan
Peng Zhang
Stephan Heister
Michael Hennig
Ursula Rings
Katrin Strauch
Tilman Floehr
Josef Theo Koch
Armin Zoschke
Sarah Könemann
Hongxia Xiao
Yan Yan
Oliver Thelen
Burkhard Schmidt
Richard Ottermanns
Martina Roß-Nickoll
Henner Hollert
Andreas Schäffer

1 Problem definition and structure of the MICROTOX project

It was broadly considered badly necessary to conduct a comprehensive technology assessment addressing the impact of the building of the Three Gorges Dam (TGD) and of the impounded reservoir (TGR). The reported research project aimed at an integrated assessment of the TGR impacts on ecology, ecotoxicology and environmental behaviour of organic pollutants. More specifically, the fate of relevant model pollutants (here: a commonly used rice herbicide) was investigated, relating the altered fluctuation regimen with observable degradation patterns. Furthermore, the bioaccumulation of parent and metabolized substances was assessed in a realistic simulation environment. The ecotoxicity of sediments and waters of the TGR was described by using a comprehensive test battery on the biological organisation level from cell to organism. Three self-contained work packages resulted:

- Fate and behaviour of environmental pollutants
- Bioaccumulation and magnification in aquatic food webs
- Ecotoxicity of sediments and analysis of biomarkers of toxic stress

Finally, the results were used for a merged monitoring strategy to prevent the environment from excess exposure and effects of xenobiotics.

The Three Gorges Reservoir occupies an area of more than 1000 km² over a length of 663 km from the Chinese provinces Sandouping over Chongqing to Hubei. This project is considered to have substantial impacts on the environment in China. The construction of the dam began in the year 1993 and was finished in 2006. The impounding of the reservoir has begun already in the year 2003. Formerly urban and industrial areas were flooded and more than 1 million people had to be resettled. In spite of the great economic benefit for the whole region regarding shipping, flood control and electrical power generation concerns were formulated in China and worldwide on the drastic sociological, ecological and ecotoxicological impacts as a consequence of the building of the very large dam (Wu et al. 2004).

The flooding of large agricultural and industrial areas after the impounding of the dam and the runoff from adjacent areas (agriculture, aquaculture, households, industry) inevitably lead to the release of high amounts of organic and inorganic pollutants and nutrients (Yang et al. 2010, Henderson et al. 2007, Moeckel et al. 2008). Thus, the input of contaminants directly into the reservoir or via tributary side reaches of the Yangtze River has to be largely reduced. We aimed in a first step at analysing the status-quo of the chemical concentrations and their ecotoxicological impact. The contamination level of the feeder rivers is much higher than in European Rivers, consisting of numerous problematic substances, such as heavy metals, persistent organic pollutants (POPs), pesticides, endocrine disruptors and others (Xue et al. 2008, Fu et al. 2003). Soluble pollutants adsorb to detritus particles and disappear from the water column (sink), but are possibly remobilised (secondary source). This process is the main reason of the non-satisfying state of European water bodies according to the water framework directive (Netzband 2007, Malaj et al 2014). The significant reduction of the flow velocity of the TGR waters leads to the sedimentation of large amounts of suspended sediments (about 1.2 kg/m³).

Following the eutrophication sediments or even the water body could become anoxic. Therefore, particle-bound pollutants could reach an anoxic environment, which could develop through microbial biofilms at the surface of particles. Solubility, degradation rates, degradation pathways and finally bioaccumulation and ecotoxicological processes could be altered. The possible fate and behaviour of a pollutant in the reservoir is illustrated by Figure VII-1.

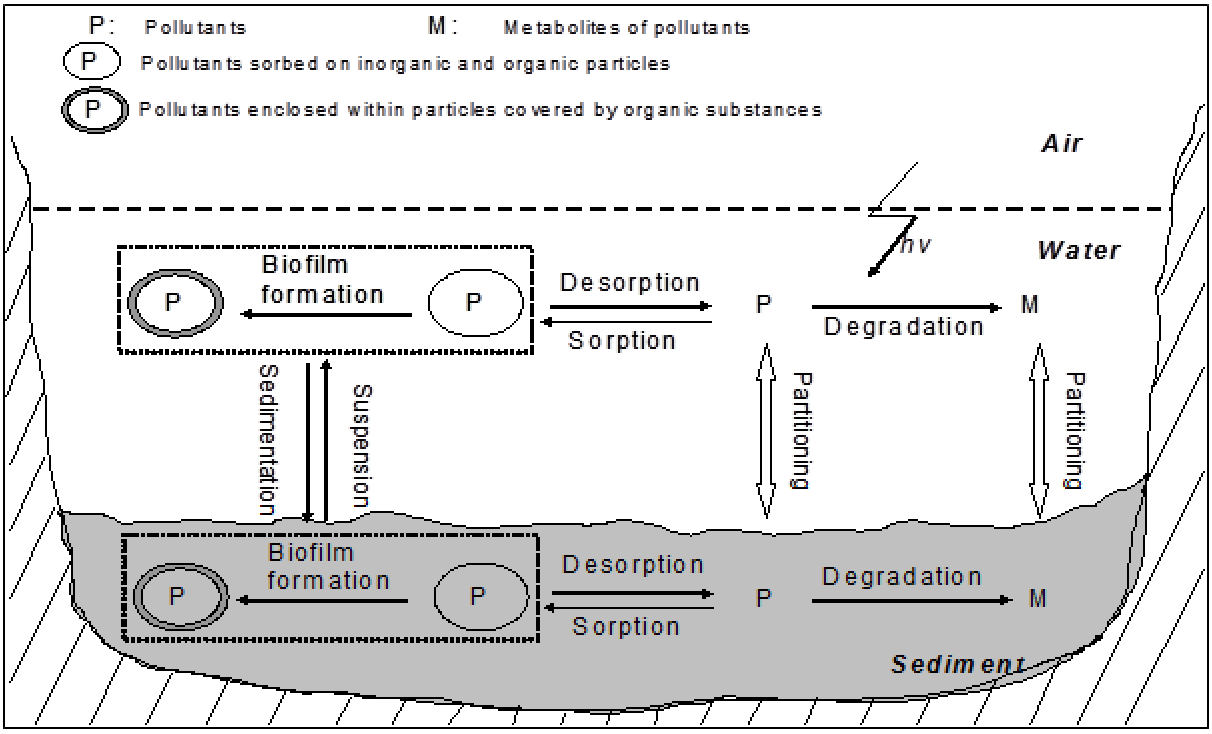


Figure VII-1: Fate and behaviour of organic pollutants in the reservoir: 1) Biotic and abiotic degradation. 2) Sorption on organic and inorganic particles. 3) Distribution between water and sediment. High concentrations of nutrients increase microbial activity, stimulating the degradation of pollutants, reducing the bioavailability through encapsulation within biofilms.

Profound knowledge about the behaviour of pollutants in the reservoir, the fate and the effects on organism that live there are not only important prerequisites for an hazard assessment of the reservoir ecosystem, but are also of great importance for the people living there, who interact directly via drinking water use and fishery with the ecosystem TGR. Such data that are analysed in an integrative concept are so far lacking.

MICROTOX is a sub-project within a joint project that aims at the investigation of the situation at the newly created 'Three-Gorges-Reservoir-ecosystem` to enable for a sustainable management of the impacted area. The aims of the project comprise the investigation of the transformation, bioaccumulation and ecotoxicity of organic micropollutants. Since the dam was primarily built for reasons of power generation (CO_2-neutral 182000 MW) and flood control (20 billion € property damage caused by the flood event in 1994), it could be seen as a contribution to fight the consequences of climate change. Specific goals of the reported project are the description of the fate of model pollutants and the assessment of the potential bioaccumulation and ecotoxicity in the TGR-area. An overview of the three modules of the project is given in Figure VII-2 and Table VII-1.

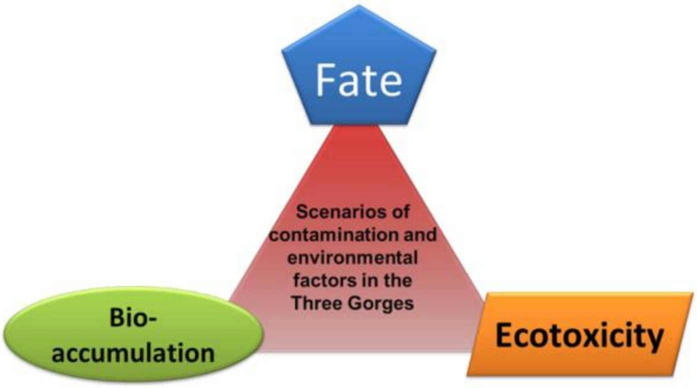


Figure VII-2: The sub-project 'MICROTOX' within the joint Yangtze-Hydro joint projects is divided in three synergistic modules. The modules exchange information and share scenarios of contamination.

Table VII-1: The organizational structure of the MICROTOX project.

Work package	Personnel involved
Project coordination and management	Björn Scholz-Starke, Andreas Schäffer, Martina Roß-Nickoll, Henner Hollert
I **Fate and behaviour of environmental pollutants**	Ye Yuan, Peng Zhang, Stephan Heister, Michael Hennig, Burkhard Schmidt, Andreas Schäffer
II **Bioaccumulation and magnification in aquatic food webs**	Björn Scholz-Starke, Richard Ottermanns, Ursula Rings, Katrin Strauch, Martina Roß-Nickoll
III **Ecotoxicity of sediments and analysis of biomarkers of toxic stress**	Tilman Floehr, Hongxia Xiao, Josef Koch, Armin Zoschke, Sarah Könemann, Yan Yan, Oliver Thelen, Henner Hollert

The results of the three modules have been finally amalgamated to an integrative monitoring strategy.

2 Prerequisites of project execution

The project required *intense cooperation* with Chinese partners, in particular during sampling campaigns and for data exchange. The project management prepared since approximately ten years by concluding cooperation agreements and in field trips with Chinese experts for an effective project execution. The experiments and sampling campaigns have already been planned in personal talks with our Chinese project partners from Tongji University, Shanghai, and Chongqing University. Dr. Lingling Wu, Tongji University, investigated sediment samples with bioanalytical methods at our Institute for about two years.

The Institute for Environmental Research has many years of experience in national and international basic and applied joint research projects investigating the *fate and effects of organic micropollutants in water, soils and sediments*. Most of the methodologies had been available in advance of the reported project and it was expected that a time-consuming phase of establishing the methods could be skipped. In particular, the development of combined cell-based, in vitro biotest-batteries is focused by our institute, in order to describe the potential ecotoxicological effects of particle bound contamination (e.g. Ahlf et al. 2002, Keiter et al. 2009). To broaden the assessment of toxic effects of organic micropollutants, the group of Prof. Hollert developed further 'weight of evidence'-methods as a combination of bioassays, chemical analysis and in-situ inventories of e.g. histopathology of fish organs or macrozoobenthos communities. The approach is well published as the TRIAD-approach and its further development (Chapman & Hollert 2006).

The *behaviour and degradation of environmental chemicals* has been investigated at the Institute with special emphasis on the analysis of bound residues. Our methodologies can show how natural processes contribute to a remobilisation of chemicals. It has been found that pollutants bound to organo-clay minerals are protected from microbial degradation and have therefore been stable for very long periods. Furthermore, we developed methods to decrease the amount of pollutants in contaminated soil and sediments ('phytoremediation').

The Institute of Environmental Research is well known for its *ecological modelling* approaches of the effects of plant protection products across Europe. There have been increasing demands and awareness of regulatory bodies to model processes that cause effects on individuals, populations and ecosystems. Toxicokinetic-toxicodynamic models calculate effects based on internal concentrations of chemicals (Preuss et al. 2008, 2009). At the ecosystem level, trophic interactions between species trigger the extrapolation of effects from the laboratory and the field, for which successful approaches have been developed in the past decades (Hommen et al. 1992, Hommen & Ratte 1997).

Despite great efforts to establish good cooperation between Chinese and German institutional partners, it was difficult to obtain e.g. necessary data for the calibration of the ecological modelling part. Meetings, exchange of opinions and demands, even the signing of

‘Memoranda of understanding’ did not lead to data exchange. It was recommended by the responsible persons of the Changjiang Water Resources Protection Institute to move to another region, because the TGR is a politically sensitive area.

3 Planning and execution of the project

The BMBF has granted with the allocation decision from 17th August 2010 project funding for the period from 1st August 2010 to 31st July 2013 (36 months). By granting a cost-neutral extension to twelve additional months, the project duration has been extended until 31st July 2014.

The subproject MICROTOX is made by a composite of the three modules ‘Fate’ (3 work packages), ‘Bioaccumulation’ (7 work packages) and ‘Ecotoxicology’ (8 work packages). All actions carried out in frame of the project, which are reported here, have led in consequence to solutions or solution approaches of the previously formulated hypotheses of scientific and practical problems. With only a few unforeseen developments adjustment to the original project plan have become necessary, which led to the development of alternative research strategies.

The module ‘bioaccumulation’ waived the originally planned laboratory experiments to contaminant uptake in living fish. In the AQUATOX model data for calibration of the pollutant uptake and accumulation of in the Three Gorges Reservoir present fish species were sufficiently (in this case: trophic guilds) available. Considerable effort was conducted to closely cooperate with institutions that are entrusted by the Chinese government with the monitoring of the ecological situation in the Three Gorges Reservoir. Therefore, interviews with the staff of the ‘Institute of Hydroecology’ and the ‘Changjiang Water Protection Institute’ in Wuhan have taken place. While the latter institution referred to the political sensitivity of the study area and thus rejected cooperation, the exchange of data on organism densities and nutrient status of the Three Gorges Reservoir has been agreed with the Institute of Hydroecology. Unfortunately, the contact itself was not answered even after the examination of a ‘memorandum of understanding’. Thus, the work on the simulation models had to be continued with pure literature data.

The ‘Fate’ module has been extended for an additional sociological study to investigate the usage of pesticides in an area of concern by interviews with farmers, pesticide shop owners and retailers.

The ‘Ecotoxicology’ module has also been extended by a more detailed investigation of *in situ* markers in the model fish species *Pelteobagrus vachellii*. Based on the results of the analysis of water and sediment the histology of liver and kidney was given priority towards vitellogenin analysis. Also, the content of PAH metabolites in fish bile was included in the monitoring programme due to the occurrence of PAHs as priority pollutants in the Yangtze River, based on the literature review, as well as sediment and water analysis. After dialogue with the Chinese partners instead of a superficial investigation of 15 sampling sites the focus was given to four sites with major tributaries in regular distance along the reservoir (Chongqing, Fengdu, Yunyang, Wushan) in addition to one area of particular interest (Kaixian) in the Yangtze River watershed and a reference site (Pengxi River Wetland Nature Reserve). Per each site along the reservoir at three spots sediment has been sampled in order to understand the impact of the local tributaries on the Yangtze River, as the literature research had revealed a serious contamination of several side rivers along the mainstream. The investigation of water samples was initiated by a close cooperation with the WATERUSE project, who sampled water at the same areas in the same time period. A data exchange between MICROTOX and WATERUSE has been realized. The Chinese local authorities denied the installation of suspended particulate matter traps, thus suspended particulate matter could not be included in the monitoring programme. Instead of the bacteria contact assay with *Arthrobacter globiformis* a microbial community analysis of the sediment samples has been performed in cooperation with Prof. Xiaowei Zhang, State Key Laboratory of Pollution Control and Research Reuse, Nanjing University. The output of the novel community analysis approach was considered more beneficial with additional interconnections between the endpoints from the other bioassays. Furthermore, a second PhD student (M.Sc. Hongxia Xiao) was integrated in the module to work on the effect directed analysis of key pollutants and to continue the research based on the results and insights of the current investigations.

4 State of the art – methodologies and scientific literature

4.1 European Water Framework Directive – A Model for Chinese River basins

The European Water Framework Directive (EWFD) aims at a good ecological and chemical state of all European River basins until the year 2015 by reducing emissions and immissions from point and non-point sources (Förstner 2002, Hollert et al. 2007a). The conceptual approaches (monitoring strategies, regulatory frameworks) that have been applied in the EU are suitable to be transferred to other situations, in particular in China (Hollert et al. 2007b). Regardless the intense measures that were set in practice in Europe in the last decades and that meliorated the water quality significantly, the striven good ecological state could not be reached. Sediments are not only potential sinks of water-soluble chemicals. Remobilization processes during e.g. flood events lead to recurring pollution of the water bodies. Thus at present time, the investigation of sediments has been intensified (Hollert et al. 2009).

4.2 Sediments reflect past and recent contamination of surface waters

Especially by the European network SedNet and by initiatives of the SETAC North America (Wenning & Ingersoll 2002), sediments were focused by scientists and the public in recent years. There is clear evidence from literature that contaminated sediments affect the biocoenoses of invertebrates and cause adverse effects in fish (Chen & White 2004, White et al. 1998). Since the water quality has been significantly meliorated by technical measures in the past years, the era of non-regulated industrialization left highly contaminated sediments for the next decades (SedNet 2004). Sediment-bound pollutants are remobilized by bioturbation (Power & Chapman 1992), flood events (Hollert et al. 2000) or dumping of sediments (Koethe 2003). In particular, flood events can cause the release of highly contaminated sediments that are dumped in areas where drinking water is gathered from.

Sediment assessment is of major importance in developing and newly-industrialized countries all over the world, because of the well-documented adverse effects of contaminated sediments on fish populations. Contamination can enter the human food chains and influence the drinking water resources if bound to particles in the water phase.

4.3 Detection of Organic micropollutants in environmental samples

Nowadays, very low limits and high specificity of detection of organic pollutants can be realized. In the past, in particular lipophilic substances were detectable by direct coupling of gas chromatography and mass spectroscopy while polar substances had to be derivatized first. The LC-MS-MS technology allows for direct detection of polar and non-polar substance without previous treatments. Consequently, substances in soils are detectable even after many years of aging and in very low concentrations (Jablonowski et al. 2008). An estimation of the bioavailability of pollutants and specific analyses are possible by extracting the pore water of soils and sediments after equilibration via solid phase microextraction fibres (SPME) (Styrishave 2008). An additional option of quantitative analytics of pollutants refers to radiolabeling of substances; the total balance of degradation and distribution over different media can be followed. The described methodology enables for a comprehensive assessment of the exposure to pollutants in experimental designs.

4.4 Bioaccumulation in aquatic food webs

The scientific field of the (computerized) modelling of ecotoxicological effects and processes is currently developing towards an important tool in science to gain insights into underlying mechanisms. It is considered relevant for scientists, regulators and the industry (see e.g. Preuss et al. 2009, Grimm et al. 2009). New toxicokinetic-toxicodynamic approaches in effect modelling combine the uptake, accumulation and elimination with observed effects in laboratory ecotoxicological experiments. Internal concentrations within the aquatic organisms determine the effects on each individual (Preuss et al. 2009). On ecosystem level, interspecific trophic interactions are focused by recent researchers (Strauss & Ratte 2002, Jankowski 2005). An important step towards a relevant and realistic assessment of field-effects based on the bioaccumulation of xenobiotic substances and the resulting bioconcentrations is a proper extrapolation from the laboratory to the field, which can be done by well-validated computer models (Hommen et al. 1993, Hommen & Ratte 1997). Complex ecological and ecotoxicological models integrate information on all aspects of the processes that occur in an ecosystem and lead to the bioaccumulation of substances in aquatic organisms and finally cause toxic effects (Park et al. 2008).

5 Cooperation

Generally, the common topic ‘interactions between toxicants, water and sediment’ of the five sub-projects within the joint Yangtze-Hydro project offered a variety of opportunities to data and knowledge exchange. In this chapter, we sketch briefly our cooperative activities with our German and Chinese partners from science, government and industry.

Joint workshops in Germany and China, as well as frequent project meetings (from the level of project managers to processor level) served the intense exchange of experiences in a challenging scientific environment.

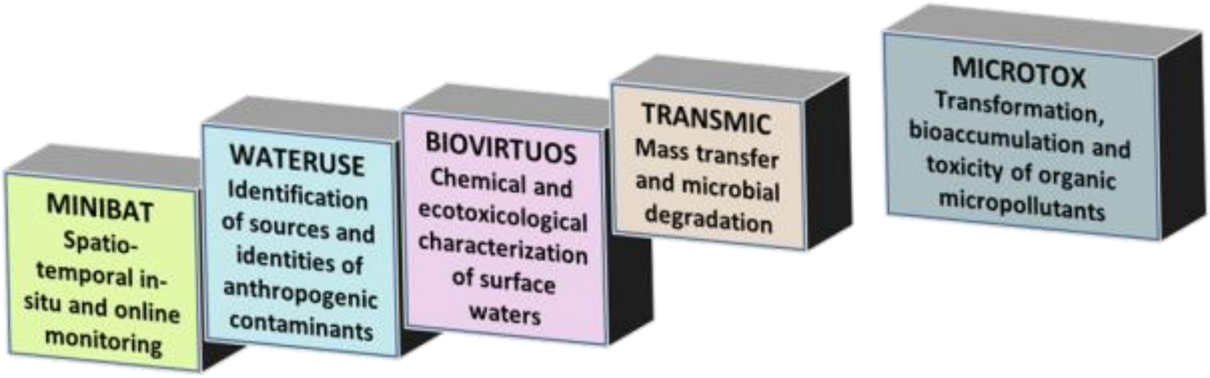


Figure VII-3: Five independent but cooperating sub-projects participate in the joint Yangtze Hydro-project.

5.1 Project meetings and workshops

- **‚Yangtzientists‘ PhD Meetings**

– Interconnection within Yangtze Hydro & Geo Network between PhD candidates
2012 January 26-27 - TZW Karlsruhe (Hydro)
2012 September 5-6 -IWW Biebesheim (Hydro)
2013 June 13-14 - University Kiel (Hydro & Geo)
2013 October 21-22 - RWTH Aachen (Hydro & Geo)

- **Yangtze Hydro Network Meetings**

- Interconnection within Yangtze Hydro Network
2010 September 100 - IWW Mülheim a.d. Ruhr

2010 November 30 - KIT Karlsruhe
2011 March 10 - TZW Karlsruhe
2011 May 9-10 - University Gießen
2011 August 02 - IWW Mülheim a.d. Ruhr (WATERUSE & MICROTOX)
2013 November 12 - RWTH Aachen

- **Sino-German Workshops**

– Interconnection between German and Chinese scientific institutions

2011 March 27 – April 2 – Tongji University, Shanghai, China 'Workshop on Interactions in the Water System – in the Frame of the Sino German Yangtze Project'

2011 November 28-29 – RWTH Aachen University, Aachen, Germany 'Processes in the Yangtze River System-Experiences and Perspectives'

2012 September 21-23 – Tongji University, Shanghai, China 'Processes in the Yangtze River System - 10th Anniversary of Sino-German Cooperation'

5.2 Sampling campaigns

Telephone and Skype-conferences were used to prepare for the three sampling campaigns and experimental work in China. The sampling was planned and conducted together with the German partners from the WATERUSE project as well as with people from the MINIBAT and the TRANSMIC project. The Chinese groups of Prof. Dr. Lingling Wu (Tongji University, Shanghai), Dr. Junli Hou (East China Sea Fisheries Research Institute) and of Prof. Dr. Xingzhong Yuan (Chongqing University, College of Resources and Environmental Science) were absolutely essential in identifying the sampling sites, in contacting the local authorities and in shipping and providing materials. We met several high-ranked local authorities for getting the permission to enter the political and militarily sensitive areas of the Three Gorges Reservoir area.

Table VII-2: Cooperation partners that made the sampling campaigns possible.

Organization	Contact	E-Mail
Chongqing University College of Resource and Environmental science No. 174 Shazhengjie 400030 Shapingba, Chongqing	Prof. Dr. Xingzhong Yuan MSc Li Bo MSc Yuyuan Wu	xzyuan63@yahoo.com.cn
Tongji University Institute of Environmental Science and Engineering 1239 Siping Road 200092 Shanghai	Assistant Prof. Dr. Lingling Wu	Wulleco@hotmail.com
East China Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences ECSFRI, CAF Laboratory of Biology and Germplasm Resources in Aquacuture 300 Jungong Road 200090 Shanghai	Prof. Dr. Junli Hou	Junlihou01@gmail.com
IWW Rhenish-Westfalian Institute for Water Research Institute for Water Ressources Management Justus-von-Liebig-Straße 10 D-64584 Biebesheim am Rhein Moritzstr. 26 D-45476 Muelheim an der Ruhr	Dipl.-Ing. Anja Wolf Dr. Axel Bergmann	a.wolf@iww-online.de a.bergmann@iww-online.de
Karlsruhe Institute of Technology (KIT) Institute of Mineralogy and Geochemistry (IMG) Adenauerring 20b 76131 Karlsruhe, Germany	Dipl.-Geoecol. Andreas Holbach Dr. Stefan Norra	andreas.holbach@kit.edu stefan.norra@kit.edu
Water Technology Center (TZW) Environmental Biotechnology Karlsruher Straße 84 76139 Karlsruhe, Germany	M.Sc. Irene Kranzioch Dr. Andreas Tiehm	Irene.Kranzioch@tzw.de thiem@tzw.de

5.3 Joint Publications

A number of publications have been published or prepared to be published soon as collaborative actions within the joint Hydro projects.

Table VII-3: Joint publications within the joint Yangtze Hydro-projects.

Author	Year	Title	Source
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 KW, Subklew G, Tiehm A, Temoka C, Wang J, Westrich B, Wilken RD, Wolf A, Xiang X, Yuan Y	2011	The Yangtze-Hydro Project: a Chinese - German environmental program.	Environmental Science and Pollution Research 19: 1341-1344
Holbach A, Floehr T, Kranzioch I, Wolf A	2013	Dilution of pollution? Processes affecting the water quality in the river-style Three Gorges Reservoir.	Environmental Science and Pollution Research. DOI 10.1007/s11356-012-1252-y
Scholz-Starke B, Ottermanns R, Rings U, Floehr T, Hollert H, Hou J, Li B, Wu Ll, 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.	Environmental Science & Pollution Research 20:7009-7026. DOI 10.1007/s11356-013-1504-5.
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 literature review on the ecotoxicological status of the Yangtze River region.	Environmental Science and Pollution Research 20: 6934-6971. DOI 10.1007/s11356-013-1666-1.
Floehr et al.	2014	A glimpse in the black box – Mutagenic effects of sediments and genotoxic impacts on fish of the Yangtze Three Gorges Reservoir, China	In preparation
Yuan Y, Zhang P, Schmidt B, Schäffer A	2014	A Metabolic study of 14C-radiolabeled 3,4-Dichloroaniline in a water-sediment system	Submitted for publication (Chemosphere)

6 Fate and degradation of organic model pollutants

6.1 Introduction

Rice is the third consumed cereal product in the world. In 2012/13, 466 million tons of rice was worldwide consumed (International Grains Council 2013). In order to get better harvest, pesticides are widely used in modern rice cultivation. In 2006 and 2007, approximately 5.2 billion pounds of pesticides were used worldwide; of which herbicides comprise 40%, followed by insecticides (17%) and fungicides (10%) (Grube et al 2011). Such huge consumptions have resulted in a series of environmental problems. The parent organic compounds or the corresponding transformation products remain either in the soil or ultimately enter into the aquatic sediment, and may subsequently accumulate in food chains. Regarding the toxicological potential of these pesticide residues and their corresponding metabolites remaining in environmental compartments, the fate of these xenobiotics in the environment has been intensively studied.

Xenobiotics enter the environment either by deliberate actions such as releases during production and usage of pesticides, waste disposal, or accidently by chemical spills, storage facility leakage, atmospheric deposition (Northcott & Jones 2000). Soils / sediments are important environmental sink sites for xenobiotics; they therefore play an essential role in the fate and behaviour of xenobiotics released to the environment. Several different and often simultaneous fate processes are involved while xenobiotics are reaching terrestrial soils and aquatic sediments, i.e., physical transport losses such as volatilization, leaching of parent compounds and metabolites; chemical reactions such as photolysis, hydrolysis, oxidation; biological degradation, and portioning such as bioaccumulation and binding to matrices (Northcott & Jones 2000).

In fact, a considerable number of xenobiotics and/or their metabolites remain in soils/ sediments in the form of so called ‘residues’. These residues include labile and non-extractable residues (NER). NER affect the long-term partitioning, bioavailability and toxicity of xenobiotics in soil and sediment (Kästner et al. 2014). Therefore, the mechanisms of bound residues formation and the related binding processes have been paid great attention to. According to a definition from Fuhr et al (1998), ‘Bound residues represent compounds in soil, plant, or animal which persist in the matrix in the form of the parent substance or its metabolite(s) after extractions. The extraction method must not substantially change the compounds themselves or the structure of the matrix’. In fact, the use of various organic solvents and different types of extraction procedures has direct influences both on the fraction of extractable residues and ‘non-extractable residues’ (Gevao et al. 2000). In order to remove some confusions about NER, Weller et al (1998) proposed a set of definitions: covalently bound residues that are covalently bound to the substrate; soluble covalently bound residues that are extracted along with the matrix by a specific extraction procedure, (e.g. humic fractions); adsorbed residues which are bound to the matrix by reversible non-covalent interactions and entrapped residues which are retained within the matrix by steric effects. According to a recent definition (Kästner et al. 2014) also microbial derived biogenic residues such as amino acids and phospholipids may form NER as part of the previously xenobiotic parent substance. In our studies, the definition is also applied on the premise of extraction methods (solvent shaking extraction with methanol and Soxhlet-Extraction). The proportion remaining in the matrix after a series of extraction procedures is defined as ‘non-extractable residues’.

Since Propanil, as well as other structurally related pesticides form 3,4-dichloroaniline (DCA) as primary and main degradation product, we conducted fate studies both on DCA and Propanil in water sediment systems.

6.2 Material and methods

6.2.1 *Sediment/soil and water samples*

(i) DCA study

The study site is located in a hamlet of the city of Vercelli in Northern Italy (51 ° 01'N, 11 ° 41'E). Sediments and water samples were collected from rice growing areas in May 2012.The sediments were stored with a sealed container under a layer of native water at 4°C in the dark after transportation to Germany, water samples were also stored at 4 °C.

(ii) Propanil study

Non-agricultured (NA) soil and agricultured rice soil (RS) were sampled in June 2012 from Baijiaxi River, a secondary tributary of the Yangtze River near Kaixian County, Chongqing, China. For NA soil, five shallow samples (3-5 cm) were taken near by the non-agriculture estuary of Baijiaxi River and Pengxi River at different water levels (168-173 m). RS was sampled from 6 rice fields located at different water levels (166-171 m). Each rice field was sampled 5 times at a shallow level. The soil samples were mixed thoroughly. River water was sampled near the Pengxi River and stored in plastic buckets. All samples were cooled at 4°C and transported to Germany.

6.2.2 *Preparation of the test system*

Natural sediments contain a lot of impurities, such as leaves, stones, etc. Therefore, the wet sediments and soils were sieved before use. Fractions < 2mm were used in this study, others were discarded; the native water samples were also filtered. 100 mL of the sieved sediment sample was put into a 500 mL flask; 300 ml water sample was then added, and then the flask was closed with aluminium foil. Before applications, the apparatus was placed on a rotary shaker (50 rpm) for two weeks at 20 ° C in the dark in order to equilibrate. During this period, matter and energy exchange achieved gradually stability between water phase, sediment phase and gas phase.

Sediment that was temporarily flooded by water and dry before water addition - in order to simulate the flooding situation – is termed ‘soiliment’ in the following.

All incubation experiments were performed in triplicate. After application, the flasks were closed with an absorption device containing soda lime (15 g) for trapping $^{14}CO_2$ released during incubation. All samples were incubated under the same conditions as described for the equilibrium period. Incubation periods were 4h, 2 days, 7 days, 15 days, 28 days and 56 days for DCA water-sediment system study and 4h, 2 days, 7 days, 17 days, 35 days, 50 days, 63 days and 92 days for the Propanil study. In the latter study flooding events were simulated between 30 days and 60 days.

6.2.3 ***Usage of ^{14}C-labeled substances***

Radiolabeled compounds provide a sensitive possibility to trace and balance the fate of contaminants in environmental chemistry studies. By means of measuring radioactivity as well as combining with chromatographic separation techniques, the studied substance and its metabolites can be sensitively detected on both qualitative and quantitative aspects. In our studies ^{14}C labelled Propanil and DCA were used. In order to obtain more stable chemical properties, the ^{12}C atoms of benzene ring were substituted by ^{14}C atom in a statistical manner (uniformly ring-^{14}C-labeled).

6.2.4 ***Scope of the study***

The fate of Propanil and 3,4-DCA in a laboratory water-sediment system were studied in order to:

- Evaluate the total recovered radioactivity.
- Evaluate the partitioning of the radioactivity in different phase (water phase, sediment phase and mineralization) with time
- Evaluate the sediment-associated radioactivity, in terms of the extractable fractions and non-extractable residues.
- Determine Propanil/DCA derived metabolites with thin layer chromatography (TLC), high performance liquid phase chromatography (HPLC), Gas chromatography-mass spectrometry (GC-MS).
- Examine how microbial activity changed in sediments during the incubation period and the relationship between mineralization and microbial activity by DMSO-Test.
- Determine the sites of sorption of radioactivity in NER fractions by means of a particle fractionation procedure.

In summary, by using chemical and analytical methods, useful information on the metabolism of Propanil and DCA and their converted products could be obtained. This will help to deepen the understanding of their impact on the aquatic environment.

6.3 Results and discussions

6.3.1 3,4-DCA water-sediment study

(i) Mass Balance

On the whole, after application of DCA, the radioactivity remaining in the water phase reduced rapidly; conversely, a rapid partitioning of radioactivity to the sediment phase was observed. Regarding the sediment phase, the extractable radioactivity increased at the beginning and decreased gradually after 7 d; the formation of NER showed a continuous increase with time. Mineralization to CO_2 increased linearly after 7 d. Results obtained from this study clearly indicated that DCA was ultimately converted to NER and CO_2.

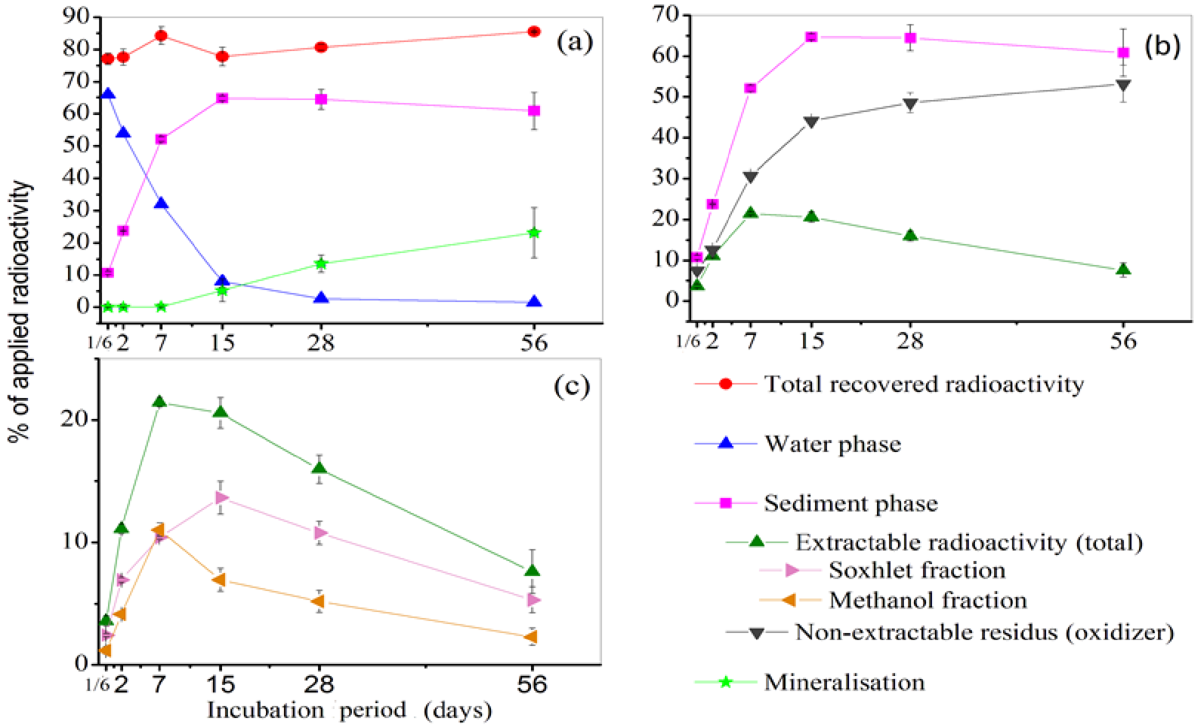


Figure VII-4: Distributions of radioactivity among the respective phases. Percentages refer to total radioactivity applied in the water-sediment system. (a): Total recovered radioactivity and partitioning of radioactivity among 14CO2, water, and sediment phase; (b):partitioning of the sediment-associated radioactivity; (c): partitioning of the radioactivity among the extractable residues.

To sum up, the partitioning results of radioactivity observed in this experiment agreed with literature using the same test system (Heim et al. 1994). Due to a low water solubility (580 mg/L) and log K_{OW} (= 2.7), after 56 days, only 1.3% of applied radioactivity was found in the water phase; the extractable radioactivity decreased to 7.6%; conversely, non-extractable residues increased to 53.2%. DCA or its metabolites were rapidly adsorbed or bound on the sediment matrix.

(ii) Fractionation of non-extractable residues

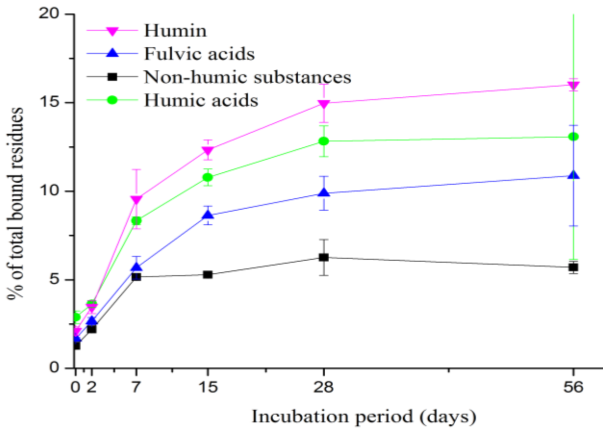


Figure VII-5: Distributions of non-extractable residues among sub-fractions of sediment organic matter. Percentages refer to radioactivity of non-extractable residues (= NER amounted to 53.3% of the originally applied radioactivity after 56 days).

Soil organic matter is an important constituent of soil regarding the fate of xenobiotics. Humus substances (HS) play a key role in the adsorption processes of xenobiotics to soils and the formation of NER. Therefore, in this study the NER associated with the sediment was further separated into non-humic substances (NH) which included salts, cations, other organic substances (such as carbohydrates, fats and amino acids) as well as other inorganic substances, humic acids (HA), fulvic acids (FA) and humin (HU), to obtain information of NER in the sub-fractions of SOM. Figure VII-5 shows the distributions of ^{14}C-NER in individual humic sub-fractions and NH. Percentages refer to radioactivity of non-extractable residues.

(iii) Mineralization and microbial activity

Most of soil microorganisms (prokaryotes, eukaryotes, aerobes and anaerobes) are able to reduce dimethyl sulfoxide (DMSO) to dimethyl sulphide (DMS). Therefore the amount of the DMS produced could be used to determine microbial activity in soil (Alef et al. 1989). In this study, this method is adapted to describe the potential correlation between the microbial activity in sediments and the amount of mineralized radioactivity over the whole incubation period.

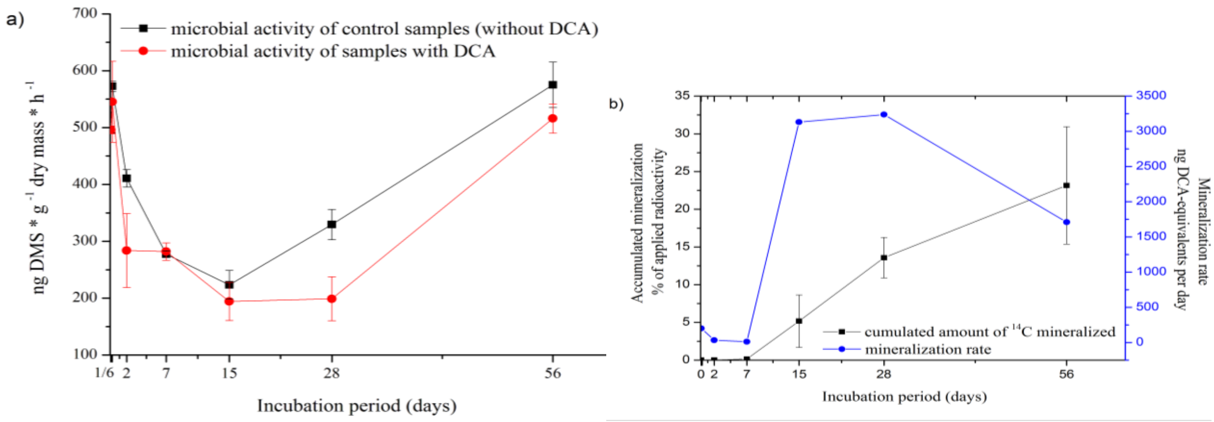


Figure VII-6: a): Microbial activity of sediment samples determined using reduction of dimethylsulfoxide (DMSO) to dimethylsulfide (DMS); b): mineralization of the ^{14}C-labeled DCA in sediment. Mineralization rate (ng DCA-equivalents/day) as ratios of cumulated mineralized amounts and incubation periods

Figure VII-6 shows the results of mineralization of the ^{14}C-labeled DCA as cumulative amounts in sediments and the rates of mineralization (mineralized DCA-equivalents per day) described as ratios of the cumulative mineralization amounts and the incubation times.

(iv) Analysis of the extracts

(a) Thin layer chromatography results

Several metabolites were detected by using different analytical techniques described below. DCA formed dichloroacetanilide, DCAA (an activated conjugating intermediate due to acetylation of DCA. DCAA could be detected in the soils and culture to which DCA or herbicides such as Propanil, diuron were applied (Tixier et al 2000) and tetrachlorazobenzene, TCAB (TCAB has a log KOW of 5.53 to 6.69 and the solubility in water is calculated to be 1 µg/L (NTP 2009). Therefore, TCAB migrated quickly into the sediment phase, rather than remaining in the water for an extended period, both of potential toxic concern, however at low concentrations, since the main fate of DCA was formation of NER.

The TLC results of three different extracts (ethylacetate extracts of the water phase, methanol- and Soxhlet extracts of the sediment phase) are presented in Table VII-4.

(b) High-performance liquid chromatography

The HPLC analysis results of the samples (ethylacetate-, methanol- and Soxhlet extracts) are described in this chapter, which can be compared with the TLC results. The metabolites were identified by

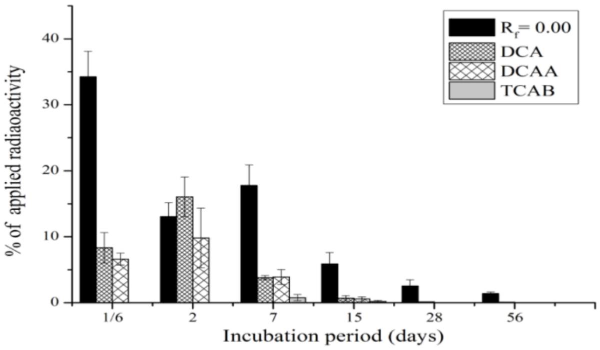


Figure VII-7: Trends of DCA and its metabolites in the ethylacetate extracts of the water phase with time (TLC analysis). Percentages refer to total radioactivity applied in the water-sediment system.

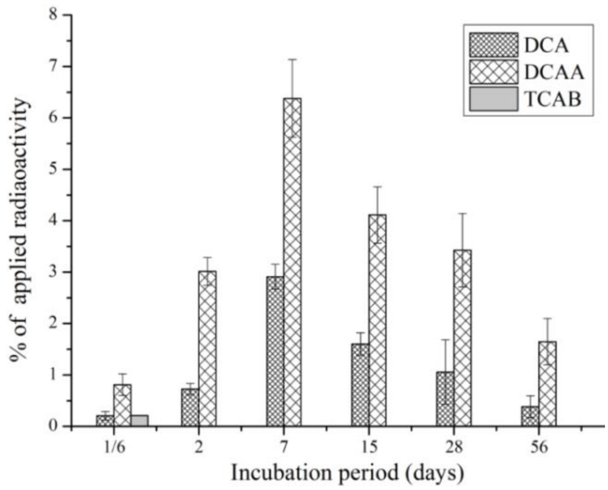


Figure VII-8: Trends of DCA and its metabolites in the methanol extracts of the sediment phase with time. Percentages refer to total radioactivity applied in the water-sediment system.

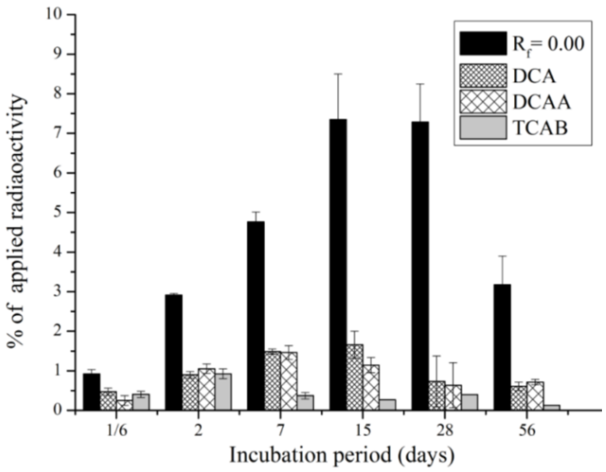


Figure VII-9: Trends of DCA and its metabolites in the Soxhlet extracts of the sediment phase with time. Percentages refer to total radioactivity applied in the water-sediment system.

comparing the retention times of corresponding non-labelled standards which were detected with UV detector (254 nm).

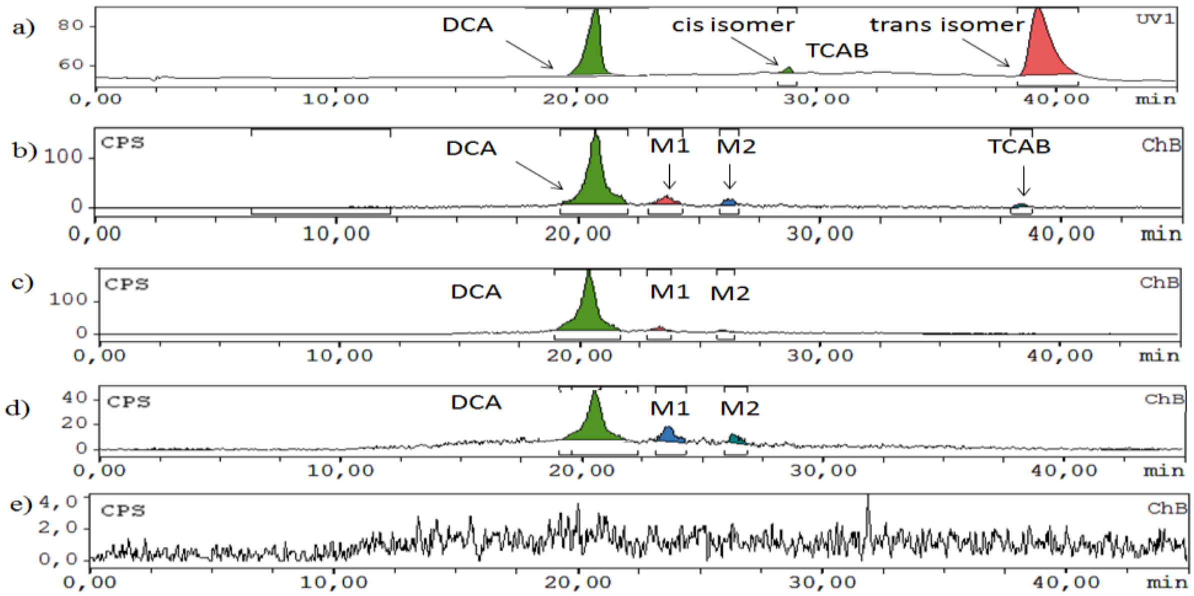


Figure VII-10: HPLC results of ethylacetate extracts of the water phase. a) UV chromatogram of the non-labelled standard (254 nm); b) radio-chromatogram of sample (the second parallel: p2) at 4h; c): sample (p2) at 7days; d): sample (p2) at 15 days; e): sample (p2) at 56 days. M1: unknown metabolite 1; M2: unknown metabolite 2.

(c) Gas chromatography-mass spectrometry

Table VII-4: Confirmation of TCAB formation in ethylacetate extracts of the water phase and Soxhlet extracts of the sediment phase by GC-MS. FSM: full scan mode; SIM: selected ion monitoring (ions: 320, 173, 145); LOD: limit of detection.

		Water ethylacetate extracts						**Sediment Soxhlet extracts**					
	LOD (µg mL^{-1})	**4h**	**2d**	**7d**	**15d**	**28d**	**56d**	**4h**	**2d**	**7d**	**15d**	**28d**	**56d**
FSM	1	d.	d.	n.d.	n.d.	n.d.	n.d.	d	d	D	d	d	n.d.
SIM	0.01	d.	d.	d.	n.d.	n.d.	n.d.	d	d	D	d	d	d.

d.: detected in samples; n.d.: not detected in samples.

6.3.2 *Propanil study with flooding simulations*

(i) Balance of radioactivity

The results of the fate of the radioactivity in different compartments (NER in sediment, water phase, and mineralization) are illustrated in Figure VII-12 and Figure VII-11.

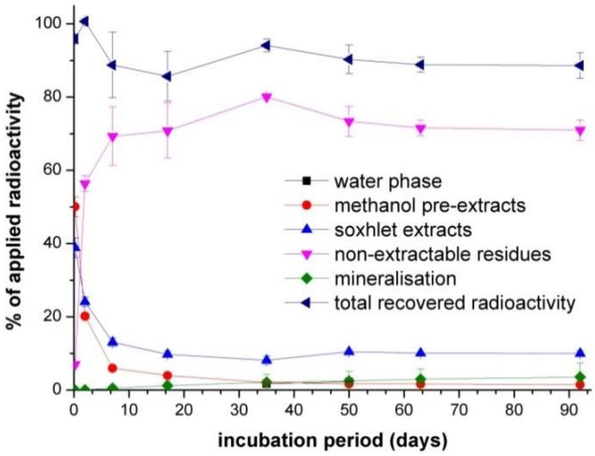


Figure VII-12: Balance of radioactivity for non-agricultured soil (NA) in the course of 92 d. All measuring points are triplicates.

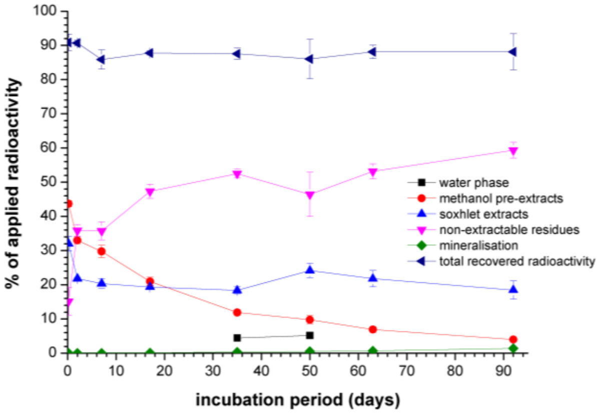


Figure VII-11: Balance of radioactivity for rice soil in the course of 92 d. All measuring points are triplicates.

For non-agricultured soil (NA) (Figure VII-12) the recovered radioactivity is from 85.7 % (17 d) to 100.7 % (2 d). Losses can be explained by minor losses during the workup procedure. The extractable radioactivity (ER) in NA decreased within the 92 d (88.9 % ± 1.7 % at 4 h to 11.4 % ± 0.9 % at 92 d). Hence, an increase of NER was observed until day 35 (7.0 % ± 0.5 % at 4 h to 80.1 % ± 0.6 % at 35 d), whereas NER decreased slightly to 71.0 % ± 2.8 % (92 d), obviously influenced by the water phase. Except at 4 h, less radioactivity was extracted with MeOH than with the Soxhlet-apparatus (MeOH: 1.5 % ± 0.2 % and Soxhlet: 10.0 % ± 0.7 % at 92 d), therefore Soxhlet was the more relevant method to extract exhaustively. Weak mineralization to $^{14}CO^{2}$ occurred within the experiment (3.8 % ± 0.3 % at 92 d). During the flooding period, a small amount of radioactivity passed into the water phase obviously due to remobilization of sediment adsorbed residues.

As for rice soil, extractable radioactivity from soiliment reduced with time (75.7% at 4h to 22.4% at 92d), NER increased (15.2% to 59.3%), mineralisation was low (max.1.4% at 92d). During flooding period (30d – 60d), small amounts of Propanil and DCA were detected (1%-4%) in the water phase which indicated release/interchange between water and sediment.

(i) Mineralisation and microbial activity measurement (DMSO-Test)

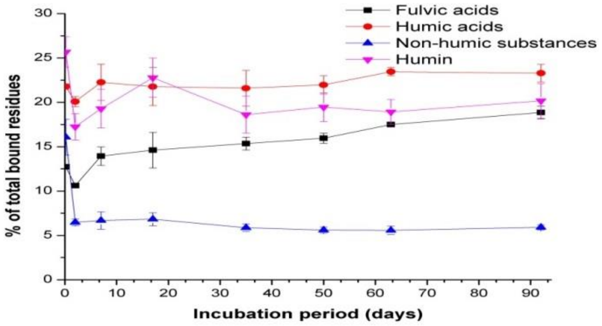


Figure VII-13: Distributions of non-extractable residues among sub-fractions of sediment organic matter, non-agricultured soil (NA). Percentages refer to radioactivity of non-extractable residues.

In the first dry period of non-agricultured soil (NA), a faster mineralization to${}^{14}CO_2$ was observed, compared to the wet period (2.1 % ± 0.1 % at 30 d and 2.8 % ± 0.0 % at 60 d). In the second dry period, Propanil and potentially its metabolites were mineralized stronger than in the wet period before, but more slowly compared to the first dry period (3.8 % ± 0.3 % at 92 d). This data might relate to a more difficult access to O_2 for microbes in the submerged soil, resulting in a slower mineralization. In the entire experiment of NA soil the microbial activity of the control groups was lower than in the applied approaches. At the beginning of the experiment the control group showed a strong increase of the microbial activity. In the course of the first two periods the microbial activity declined strongly (809 ng DMS * g^{-1} * h^{-1} at 35 d and 610 ng DMS * g^{-1} * h^{-1} at 50 d), whereas in the second dry period a slight rise of the microbial activity was observed (777 ng DMS * g^{-1} * h^{-1} at 92 d). Until day 92, the DMSO turnover rate stayed between794 ng ± 31ngDMS * g-1 * h-1 (63 d) and 1142 ng ± 25 ng DMS * g-1 * h-1 (7 d).

Figure VII-14 shows the data of microbial activity determined in rice soil. Similarly to the NA soil, the microbial activity of the rice soil control groups was also lower than in the applied approaches. The microbial activity in soiliment and the amount of mineralized radioactivity

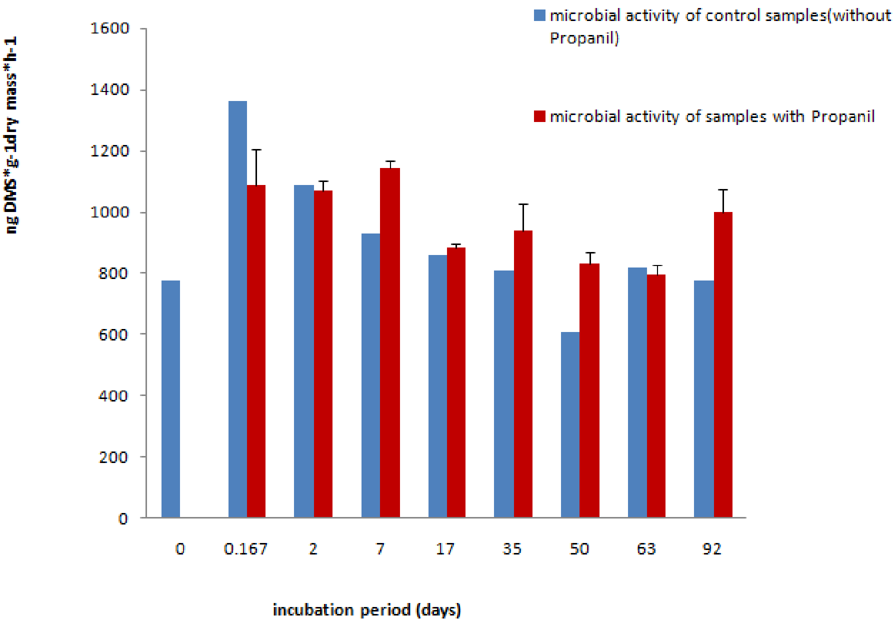


Figure VII-14: Microbial activity determined using reduction of dimethylsulfoxide (DMSO) to dimethylsulfide (DMS) from rice soil (top) and non-agricultural soil (NA) (bottom).

are clearly correlated.

(ii) Fractionation of the humic substances

Soil organic matter is an important constituent of soil regarding to the fate of xenobiotics. In order to characterize further NER of Propanil in sediment, humic matter was fractionated as described above for DCA in non-humic substances (NHS), humic acids (HA), fulvic acids (FA) and humin (HU). Figure VII-13 and Figure VII-15 show the distributions of ^{14}C-NER in individual humic sub-fractions and NHS. Percentages refer to radioactivity of non-extractable residues.

In NA soil (Figure 14), within the entire experiment the order of the fractions' percentages of total bound residues was: HA>HU>FA>NHS, whereas for RS soil (Figure 15), NER related HA and FA take up relative similar portions while most of the radioactivity stayed in HU fractions, which indicated different results due to different types of soils.

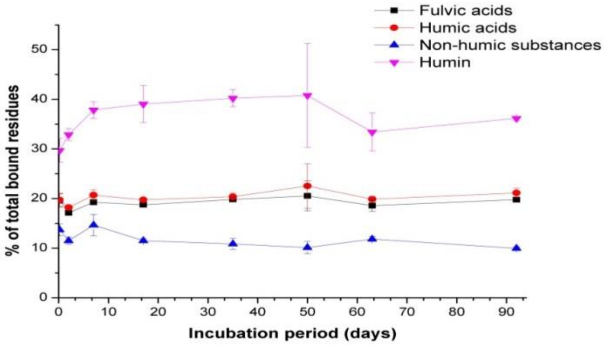
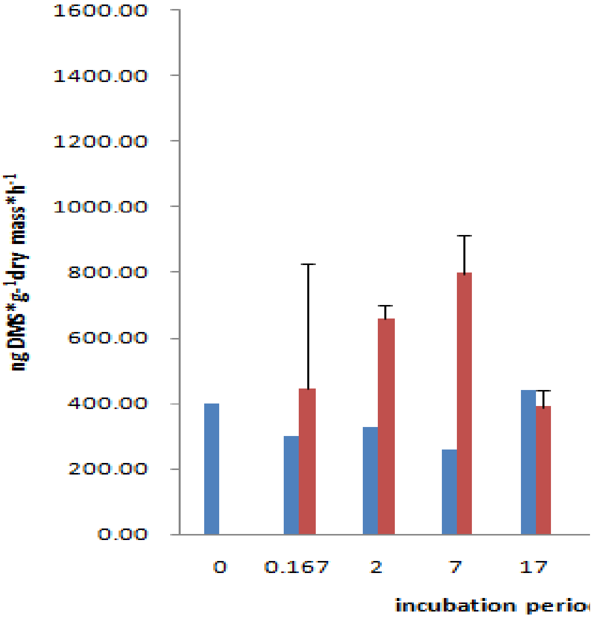


Figure VII-15: Distributions of non-extractable residues among sub-fractions of sediment organic matter, rice soil (RS). Percentages refer to radioactivity of non-extractable residues.



(iii) Analysis of the extracts with Radio-TLC, Radio-HPLC and GC-MS

The results of TLC analysis of the extracts were similar to the HPLC results. Analysis of the metabolites was conducted by co-chromatography with the reference substances Propanil, DCA and TCAB. The Rf-values (Radio-TLC) were for Propanil 0.55-0.63, for DCA 0.66 to 0.79 and for TCAB 0.89 to 0.95. Retention times (Radio-HPLC) were for Propanil 21.1 min, DCA 19.7 min, the cis-form of TCAB 28.7 min and for the trans-form of TCAB 39.2 min.

In the methanol pre-extracts of NA (Figure VII-16) a fast decrease of the Propanil concentration was observed (50.1 % ± 2.7%at 4 h to 0.3 % ± 0.1%at 92 d). The metabolite DCA appeared in the MeOH-extracts at day 2 (8.1% ± 0.5%) and decreased rapidly until day 92 (0.6 % ± 0.1%). Except in one parallel on day 7 (0.3 %, n=1), no TCAB could be extracted with MeOH. After 4 h incubation only Propanil was detected in the Soxhlet-extracts. The amount of Propanil decreased until day 35 (1.3 % ± 0.3 %). After a slight increase of Propanil after the wet period, it decreased until day 92 to 1.1 % ± 0.1 %. The amount of DCA in the

Soxhlet-extracts followed a similar trend. During and after the wet period the amount of DCA rose until day 92 (4.4 % ± 1.5 %). Except after 4 h and after 2d TCAB could be detected in some parallels with Radio-HPLC, but most on day 92 with 2.0 % of the applied radioactivity (n=2); this shows that TCAB might be extracted better with an exhaustive extraction method. Due to the small amount of radioactivity in the water phase extracts, it was difficult to detect substances; only in some parallels DCA could be identified with at most 1.7 % ± 0.1 % (60 d) of applied radioactivity. From the previous experiments the strong affinity DCA to sediment is obvious.

Measurements using GC-MS were conducted with full scan mode (FSM) and selected ion monitoring (SIM). The retention time of TCAB was 23.25 min. As tested with the reference substance (TCAB) ions with m/z = 320, 173 and 145 (base peak) were characteristic of TCAB; the relative intensity of the signals was about 30%, 40% and 100%, respectively. The molecular ion (m/z = 320) with the highest abundance is $[C_{12}H_6N_2{}^{35}Cl_3{}^{37}Cl]^{\bullet+}$. The fragments (m/z = 173 and 145) with the highest abundance are $[C_6H_3N_2{}^{35}Cl_2]^{\bullet+}$ and $[C_6H_3N_2]^{\bullet+}$, respectively. For NA soil, TCAB seems to be formed; however Soxhlet-extracts had to be thoroughly cleaned up before analysis. All MS of the measured extracts didn't show the definite signals identified from TCAB standard, i.e., we only have some indication that TCAB was present in the samples. With FSM, there is an indication for the formation

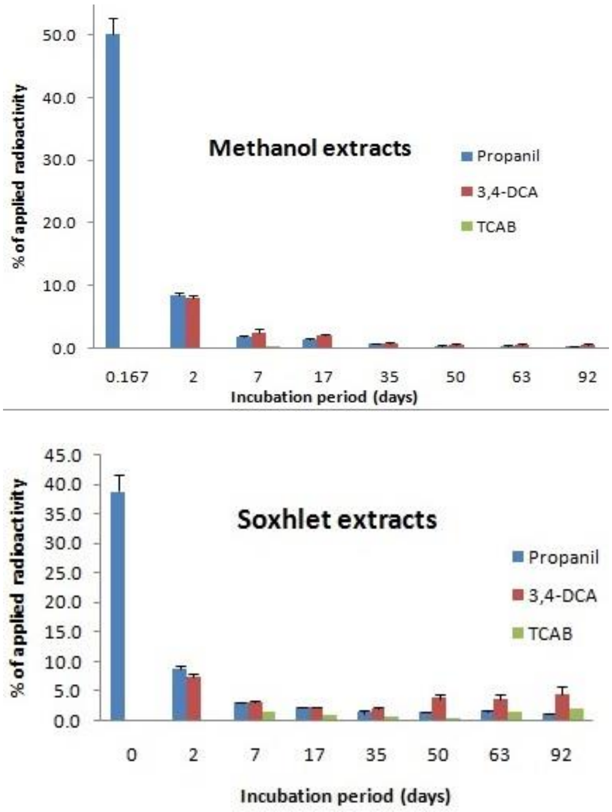


Figure VII-16: HPLC results of the MeOH and Soxhlet extracts of non-agricultured soil (NA)

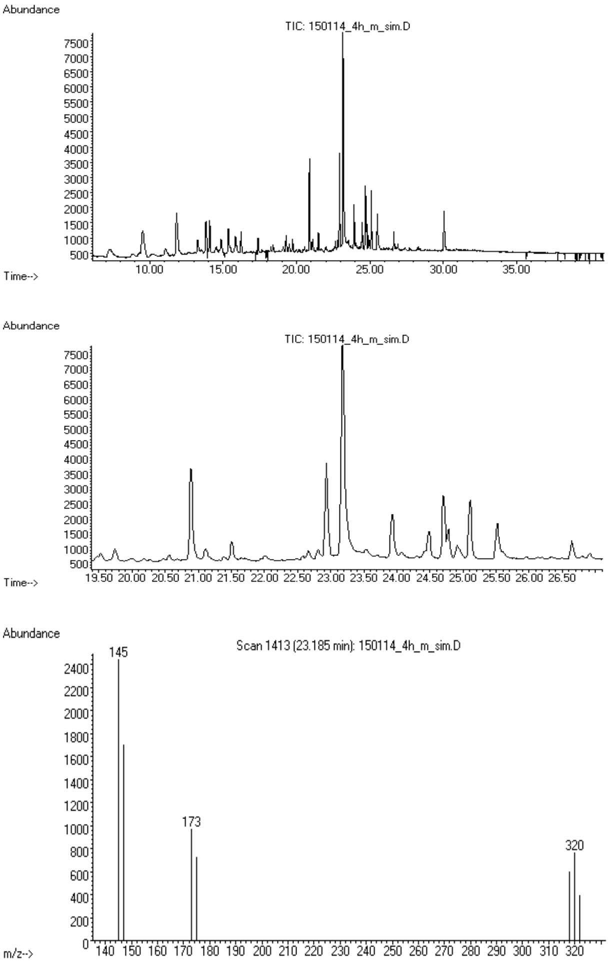


Figure VII-17: Representative GC/MS chromatogram and mass spectra of 4 h sediment methanol pre-extract by SIM (RS).

of TCAB on day 2, 7 and 17; however using the selected ion monitoring mode (SIM) TCAB was found on every measuring day except that after 4 h incubation. The sample after 7 d produced the highest peak at this retention time in both modes, so it was concentrated and measured again in FSM. MS and the retention time of extract and standard were comparable to each other, so TCAB was detected clearly in the Soxhlet sample after 7 d. Figure VII-16 shows the HPLC results of distribution of radioactivity in the soiliment extracts and water phase extracts with time. Percentages refer to total radioactivity applied in the water-soiliment system. As time goes by, Propanil degraded to its second metabolites 3,4-DCA. Further metabolite TACB were also detected in many rice soil samples by GC-MS (SIM) (Figure VII-17).

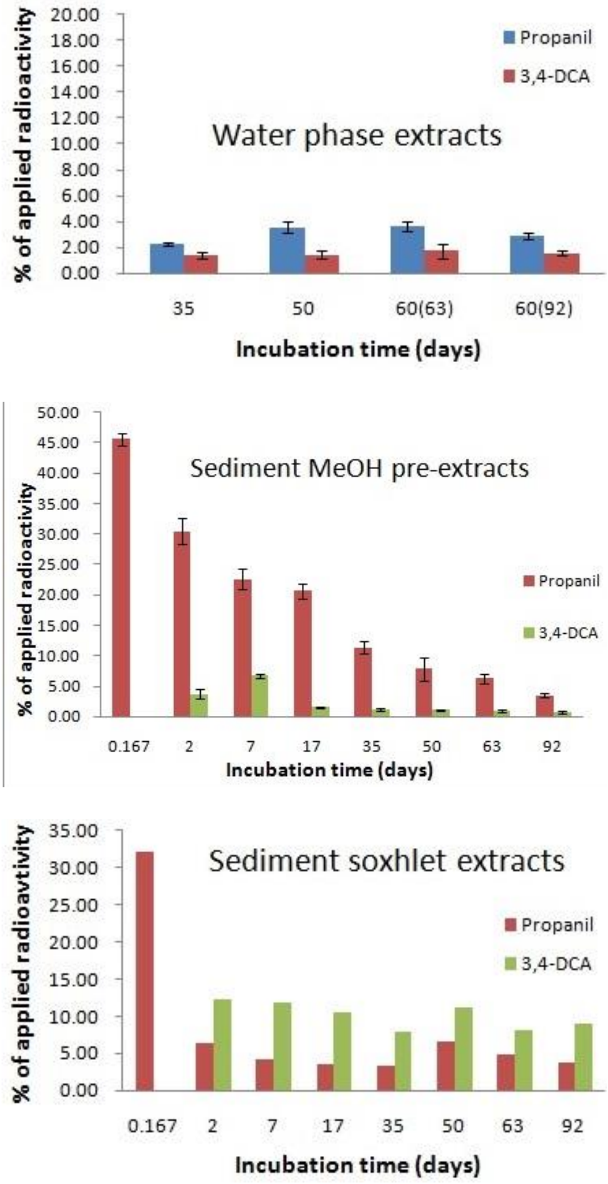


Figure VII-18: HPLC results of distribution of radioactivity in the soiliment extracts and water phase extracts with time (RS). Percentages refer to total radioactivity applied in the water-soiliment system.

6.4 *Conclusion*

6.4.1 *3,4-DCA study*

The present study on mechanisms of DCA degradation in rice cultivation is of importance to assess the environmental risk of DCA in the Three Gorges Reservoir Region. DCA is a central toxic metabolite of Propanil and other pesticides and represents a priority pollutant. After application of DCA to water sediment test system, DCA (Figure VII-19) showed a relatively high initial loss due to volatilization (F) and binding to sediment and suspended particulates in the water column (C) which resulted in the disappearance of the radioactive regarding to the mass balance. During the incubation period, DCA was rapidly converted to mainly NER and was mineralized to CO_2 (E). DCA and its two metabolites (A&B) demonstrated a high adsorption affinity to the sediment. In addition, the effect of DCA-derived residues on the microbial diversity should be further examined with molecular biological methods. The binding mechanisms and the structures of DCA-derived residues to humic substance should also be studied, because it may relate the potential bioaccessibility of the NER for the microorganisms and higher levels species. In terms of environmental risk assessment of sediment bound xenobiotics the remobilization potential of such residues, e.g., by flooding events and the potential bioavailability of particle bound residues for organisms should be studied.

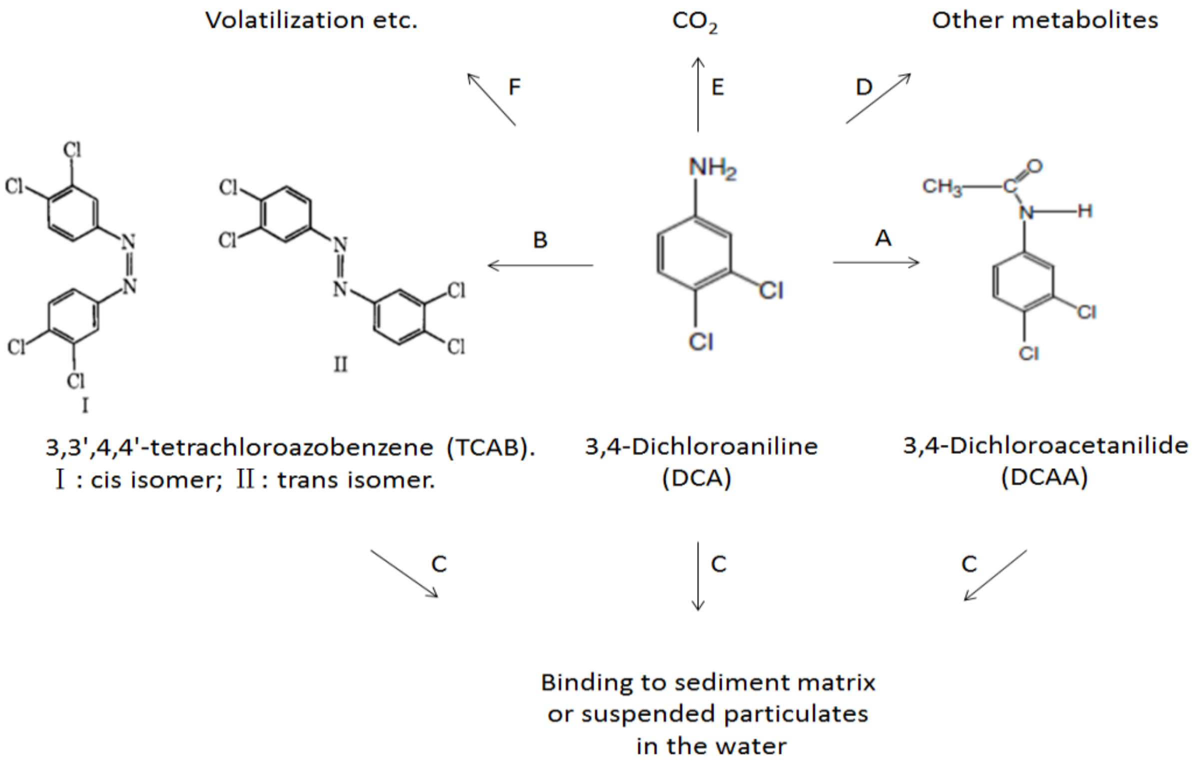


Figure VII-19: Degradation pathway of 3,4–dichloroaniline in the present study.

6.4.2 ***Propanil study***

The studies of the rice herbicide Propanil with flooding situation is a lab scope simulation of the realistic fluctuation zone situation in the TGR area. For the rice paddy soil study with radiolabelled Propanil, extractable radioactivity from soiliment reduced with time (79.0% at 4 h to 23.7% at 92d) while NER increased (15.8% to 62.6%) with an overall low mineralization rate (max.1.4% after 92d). During flooding period (30d – 60 d), small amounts of Propanil and DCA were detected (1%-4%) in water which indicates a partial release from the sediment into the water. Further metabolites of Propanil - via the formation of 3,4-DCA - were DCAA and TACB which were detected in many samples by GC-MS (SIM mode). The potential toxicity of DCAA and TCAB should be investigated. Due to the high amounts of NER formed, more information on the binding mechanism and the structures of these residues is needed; corresponding experiments are currently in progress.

Propanil is widely used in rice cultures in Asian countries. We showed that critical substances are formed by its degradation: besides the well-known DCA the two follow-up products DCAA and TCAB were present in the sediments for which very limited data on fate and ecotoxicity are available.

7 Bioaccumulation and -magnification in aquatic food webs of the Three Gorges Reservoir area

7.1 Introduction and research question

The sub-project ‘bioaccumulation’ aimed at 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 water body of the TGR, including and focusing on the tributary rivers. For this purpose, we quantified the internal concentrations of chosen model pollutants in ecologically and economically important fish species, under the influence of pollution scenarios representative for worst-case situations at the TGR. We analysed different agricultural land use patterns and nutrient loads under the fluctuating water level regime caused by the mode of operation of the dam. The concept of this integrated modelling procedure required input data from various scientific disciplines such as ecotoxicology, environmental analysis, ecology and hydrology.

The following milestones were planned and successfully reached during the project duration: First, a work-in-progress-version of a bioaccumulation model was drafted, published as a conceptual, integrative model (Scholz-Starke & Ottermanns et al. 2013). Second, the calibration of the finally complex ecosystem model (realised in the AQUATOX simulation environment) took place and the verification of expected organism densities and environmental parameters was conducted. Finally, the bioaccumulation of model pollutants in aquatic food webs in several different exemplified exposure scenarios was predicted.

7.2 Conceptual approach

In the following, the definition and development of conceptual approach is described in detail because of the very complex processes and manifold interactions between biotic and abiotic components of the TGR-ecosystem section that has been simulated.

Our studies followed an *integrated modelling approach* to gain a comprehensive overview on factors and mechanisms that trigger the bioaccumulation of organic pollutants in the TGR system. Integrated Environmental Modelling (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 combined and coupled several specialized modules to focus on TGR-specific environmental and ecological conditions (Figure VII-20). The AQUATOX model suite (Park et al. 2008) was used as an interconnected modelling framework. It linked the eight modules EXM, FWM, HDM, SDM, BAM, ETM and RAM of our approach seamlessly. The modules were implemented either as integrated sub-models within the AQUATOX modelling environment or as external models. Adequate input values were 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 fulfils the requirements for an aquatic environmental risk assessment, as evaluated by Echeverría et al. (2003) for AQUATOX.

- **Exposition module (EXM)**

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-azo-benzene (TCAB) were modelled by the hydrodynamic module (HDM). Estimated concentrations of these model substances are handed over to the chemical fate module of AQUATOX.

- **Food web module (FWM)**

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. AQUATOX 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 (HDM)**

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 volume, flow velocity, discharge and inflow rates delivered by the external 1-D 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.

- **Site-Descriptor module (SDM)**

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 (BAM)**

The bioaccumulation module describes the adsorption of the model pollutants (e.g. TCAB) to detritus particles by chemical characteristics. An adsorption coefficient can be modelled 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 modelled via uptake factors in the AQUATOX environment and exported as bioconcentration factors (BCFs). Based on the loading of pollutants on the surfaces of detritus particles or concentrations within the algae, BAM models the accumulation of these substances in the higher aquatic surrogate species of the TGR-food web (esp. fish) also via uptake factors.

- **Ecotoxicological module (ETM)**

Based on the estimated internal pollutant concentrations provided by BAM, ecotoxicological effects of the model substances are estimated in 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 human 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 (RAM)**

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).

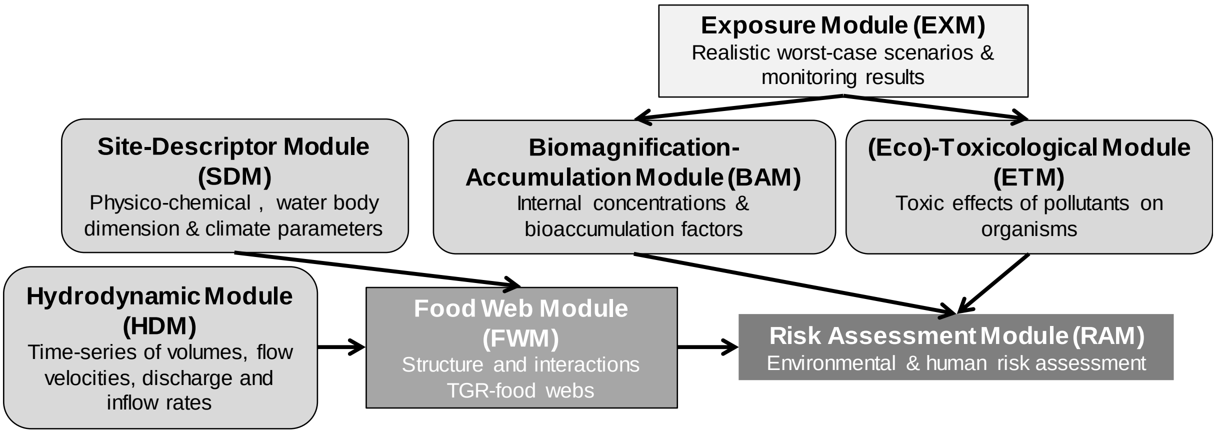


Figure VII-20: Conceptual 'Integrative modelling' approach.

7.3 Criteria for model selection

The whole complexity and the basic mechanism of the unique hydrological, biological and ecotoxicological situation of the TGR can best be reflected by an ecological model for environmental risk assessment, as shown by the reviews cited in Lei et al. (2008).

Existing bioaccumulation models were searched by means of the internet-based literature engine 'google scholar' (http://scholar.google.de/). The keywords were 'bioaccumulation model', ‚fish', ‚aquatic', ‚organic'. As a result, 6 models were identified. Those were 'FISH',

'FOODWEB', 'KABAM', 'BAF-QSAR', 'AQUAWEB' and 'ACC-HUMAN'. On the other hand, a report of the US Environmental Protection Agency (US EPA) evaluated the most complex bioaccumulation models ECOFATE, RAMAS ECOTOXOCOLOGY, BASS, TRIM.FATE und AQUATOX (Imhoff et al. 2004). The following summarizes the results of the query for bioaccumulation models. The criteria were chosen to define a 'best-fit-all-in-one-model' and had been adapted to practicability reasoning.

In sum, 11 bioaccumulation models were found (Table VII-5) and compared by seven the criteria for the usability in the context of the MICROTOX project (Table VII-6). As can be seen from Table VII-7, the only model that fulfilled all the criteria was the AQUATOX model (Park et al. 2008), which was used in the project from then on.

Table VII-5: List of the models compared for theirs use in the MICROTOX project for the evaluation of bioaccumulation and biomagnification in the TGR ecosystem. Modified after Strauch 2012.

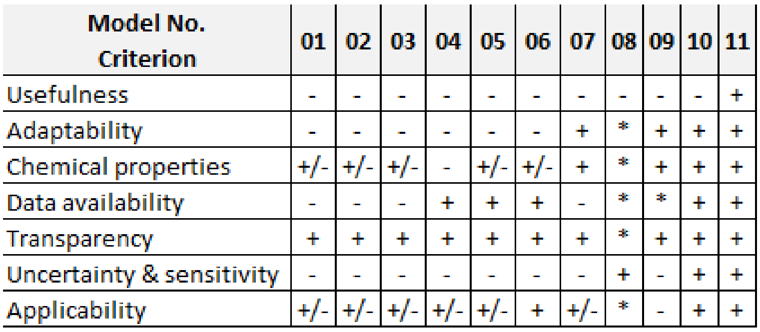
No.	Model	Website
01	ACC-HUMAN	http://www.itm.su.se/page.php?pid=117
02	FISH	www.trentu.ca/academic/aminss/envmodel/models/Fish2.html
03	FOODWEB	www.trentu.ca/academic/aminss/envmodel/models/Foodweb200.html
04	KABAM	http://www.epa.gov/oppefed1/models/water/#kabam
05	BAF-QSAR	www.rem.sfu.ca/toxicology/models/baf-qsar/
06	AQUAWEB	www.rem.sfu.ca/toxicology/models/aquaweb/
07	ECOFATE	www.rem.sfu.ca/toxicology/models/ecofate/
08	RAMAS-ECOTOX	www.ramas.com/ramas1.htm#tox
09	BASS	www.epa.gov/ceampubl/fchain/bass/BASS-dl.html
10	TRIMFATE	www.epa.gov/ttn/fera/trim_fate.html
11	AQUATOX	www.epa.gov/ttn/fera/trim_fate.html

Table VII-6: Criteria for model evaluation. Modified after Strauch 2012.

Criterion	Definition
Usefulness	The model should fit on the research question.
Adaptability	The model should be suited to be adapted to a great number of site-specific characteristics.
Chemical properties	The model should regard the properties of a model substance, as far as relevant for the bioaccumulation behaviour.
Data availability	For the ease of setting up a simulation scenario, the model environment should contain some scenarios readily available for further adaptations.
Transparency	Model assumptions and equations should be well documented.
Uncertainty & sensitivity	The model should offer good oppportunities for the quantification of the most important model parameters.
Applicability	The model should be well tested, maintained and documented.

We decided to 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 (EPA) 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, behaviour 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's species communities. We describe the consecutive adaptation steps that were 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 bioaccumulation of pollutants is desired. The definition of scenarios included 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 is characterized by lake species (USGS 2008) and the predefined 'Rum River' scenario (Park et al. 2005) characterized by flowing water specialists, respectively.

Table VII-7: Summary of model evaluation. Criteria code: + = All requirements of the fulfilling the respective criterion were met. - =Requirements were not met. +/- = Several aspects were met. * =Criterion could not be validated. Numerical code for the models : 1 = ACC-HUMAN, 2 = FISH, 3 = FOODWEB, 4 = KABAM, 5 = BAF-QSAR, 6 = AQUAWEB, 7 = ECOFATE, 8 = RAMAS ECOTOXICOLOGY, 9 = BASS, 10 = TRIM.FATE, 11 = AQUATOX. Modified after Strauch 2012.



Model No. Criterion	01	02	03	04	05	06	07	08	09	10	11
Usefulness	-	-	-	-	-	-	-	-	-	-	+
Adaptability	-	-	-	-	-	-	+	*	+	+	+
Chemical properties	+/-	+/-	+/-	-	+/-	+/-	+	*	+	+	+
Data availability	-	-	-	+	+	+	-	*	*	+	+
Transparency	+	+	+	+	+	+	+	*	+	+	+
Uncertainty & sensitivity	-	-	-	-	-	-	-	+	-	+	+
Applicability	+/-	+/-	+/-	+/-	+/-	+	+/-	*	-	+	+

7.4 Model calibration

The AQUATOX simulation environment allows for the representation of very simple 'beaker situations' as well as very complex realistic ecosystem situations. As we decided to make our simulations representative for a tributary stretch longer than 40 km, a huge amount of information had to be queried and compiled. In the following chapters, the sources of information, the rationales and decisions taken during the calibration processes and the parameter values used are described in particular detail.

7.4.1 *Characteristics of water bodies - Site descriptor and Hydrodynamic modules*

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

(i) Physico-chemical parameters, remineralisation and climate

The nutrient contents and loadings were based on and adapted to the measurements of the MINIBAT sampling campaigns. The measurements of the MINIBAT project for the Daning - Wushan region have been published by Holbach et al. (2012). The dynamics of organic matter were not influenced by daily loadings or other external resources but up to partitioning processes of the internal biomass that was build and transformed. All variable values are summarized in Table VII-8. The rates of remineralisation were set to the default remineralisation record of the AQUATOX model suite (refer to Park & Clough 2010).

Zhang et al. (2010) revealed statistically significant differences between dry, flood and normal seasons (this was before the complete impounding of the TGR) in their long-time measurement series 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 from the years 2004 to 2007. 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 took this publication as a reference for a comparison if the simulation results met the range of 'desired output values' (model verification).

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 the City of Wushan versus surface water temperatures measured by the MINIBAT project (personal communication Andreas Holbach 2013).

Table VII-8: Initial values and und loadings of physico-chemical parameters for the base simulation of the model region at Daning River.

Variable	Initial condition	Daily loadings (from upstream segment)	Unit	Note
NO3	5	5	mg/L	equals total N; initial MINIBAT measurements 3-25 NO3-/L, mostly 4-6 mg Nitrate/L, information Holbach
Tot. Sol. P	0.35	0.3	mg/L	equals total P; initial manyfolds of dissolved phosphorous from Holbach et al. (2013) measurements at Wushan Lake
CO2	0.5		mg/L	arbitrarily chosen initial, no loadingup to remin
Oxygen	7.2	0	mg/L	measured at own sampling campaign, 2011-09-25 at 25°C water temperature
TSS	0	0	mg/L	up to processes in the model
R detr sed	0	0	g/m2 dry	
L detr sed	0	0	g/m2 dry	
R detr diss	2.944468	0	mg/L dry	organic matter, converted by the AQUATOX model originating from 2.12 mg organic carbon/L dry weight according to standard in the technical documentation (Park & Clough 2010); dissolved <-> particulate percentages 85% to 15%, labile <-> refractory
L detr diss	0.479332	0	mg/L dry	
R detr part	0.519612	0	mg/L dry	
L detr part	0.084588	0	mg/L dry	
Temp	14.8		deg. C	MINIBAT measurements at starting day of the simulation (1st of January), then modelled regression time series
Wind	2		m/s	estimated to assure surface mixis
Light	300		Ly/d	average light intensity in kWh/m^2 d was estimated from the map: http://www.wrsc.org/attach_paper/china-global-horizontal-solar-radiation-annual
pH	8		pH	lower values of MINIBAT measurements (Holbach et al. 2012)

(ii) Morphometry of and linkages between the water bodies

Generally, reservoirs and rivers in AQUATOX are extreme elliptic sinusoids (Neumann 1959). This is only if bathymetry equations are active. We assume that the cuboid system has vertical walls and thus a constant area as a function of depth. Consequently, water depth can be calculated using the coefficient of volume and surface area.

To model the hydrodynamic situation in our model region the dimensions of the water bodies of ten segments were taken from the model of the NUMOS project within the joint Yangtze project and linked in the AQUATOX environment. Areas and lengths have been measured by means of QGIS (Quantum GIS Development Team 2013).

The distance between Dachang Lake and Wushan Lake was divided into 123 cutlines, between which the flow velocities, water volume changes, discharges and water depths were recorded and converted into values for the 10 segments used in the AQUATOX simulation environment. The 10 segments were defined according to the sequence of broad, open and steep, narrow river sections.

Table VII-9: Dimensions of ten stream and reservoir segments of the model region at Daning River.

Site Name	Volume [m³] (annual mean)	Area [m²]	Maximum Depth [m]	Width [m] (calculated by volume/(length*width)	Maximum length [m] reach	Mean depth [m]
Segment_01_reservoir	144680000	3200000	94.92	612.1	2.8	84.42
Segment_02_stream	13610000	530000	91.29	84.2	2	80.79
Segment_03_reservoir	61170000	1400000	83.84	463.4	1.8	73.34
Segment_04_stream	4474300	240000	82.39	47.9	1.3	71.89
Segment_05_reservoir	141130000	2900000	78.42	519.5	4	67.92
Segment_06_stream	31384000	580000	71.84	119.0	4.3	61.34
Segment_07_reservoir	57613000	1600000	61.29	515.6	2.2	50.79
Segment_08_stream	25086000	794000	58.09	59.2	8.9	47.59
Segment_09_reservoir	195600000	2000000	45.58	402.9	13.8	35.18
Segment_10_stream	3831000	225000	32.01	74.6	2.3	22.33

Feedback links in AQUATOX allow the water to flow downstream as well as upstream. This is an important model capability as a backflow of water from the Yangtze to the tributary rivers is a common event in the TGR system, especially since the dam has been placed into operation. In theory, this could happen even at the same time but here we calibrated the flows against the modelled net flow per time step (obtained by the HEC-RAS model, U.S. Army Corps of Engineers 2001).

Figure VII-21 illustrates the structure of linked segments in our model. The geometry of the water bodies was largely simplified to cuboids.

For the ease of applying toxic substances, small tributaries were introduced that were linked only to the exposed segments. They contained a constant volume of 1000 m³ of water, a length of 1 km and very clear water (no detrital components, extinction coefficients were set to zero). These segments discharged each day 1000 m³ of water via a (one-directional) cascade link into the adjacent segment. The time-series of application events was provided in the toxicity section of AQUATOX as described by chapter VII7.4.3.

(i) 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. For calibration of the AQUATOX simulations, we used data of one year from 1st of January 2012 and the 31st of December 2012 (Figure VII-22). This year was in each of the simulation exercises the first year of simulation and the dynamic pattern of water volume changes was fixed and repeated deterministically each year of the simulation.

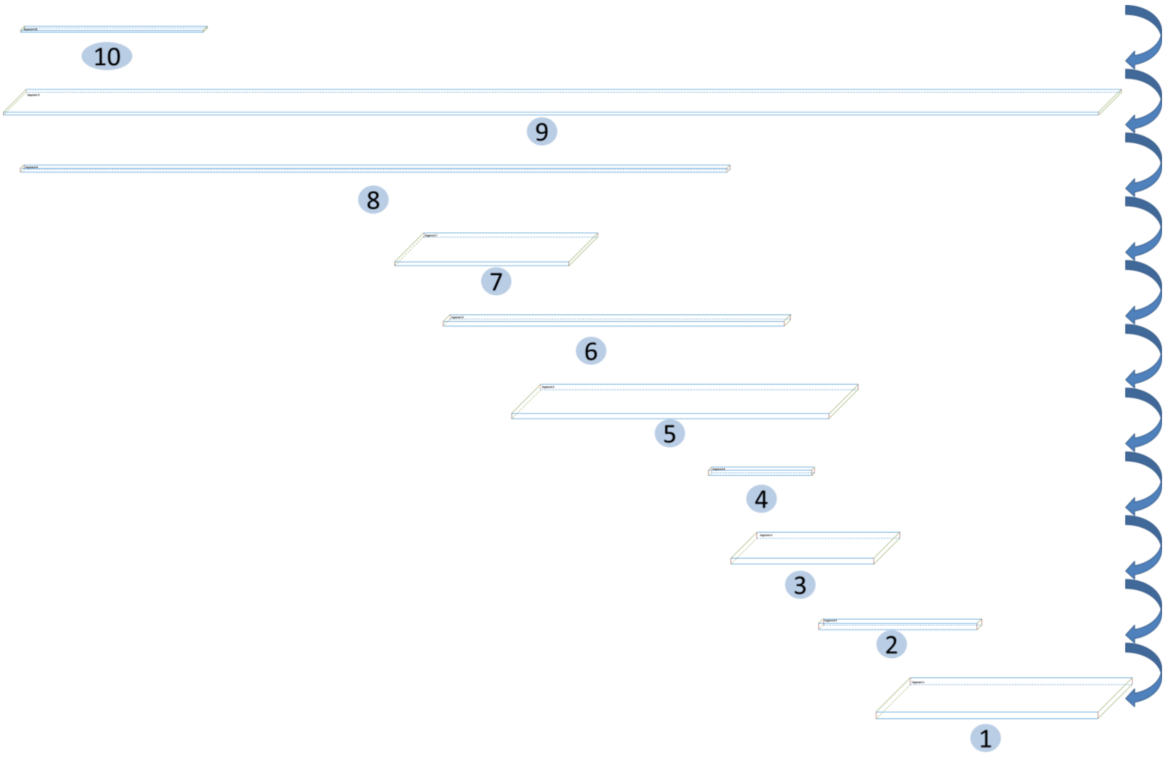


Figure VII-21: Overview over the linked segments in the model region and theirs dimensions true to scale. Arrows represent the normal flow direction of the water downstream.

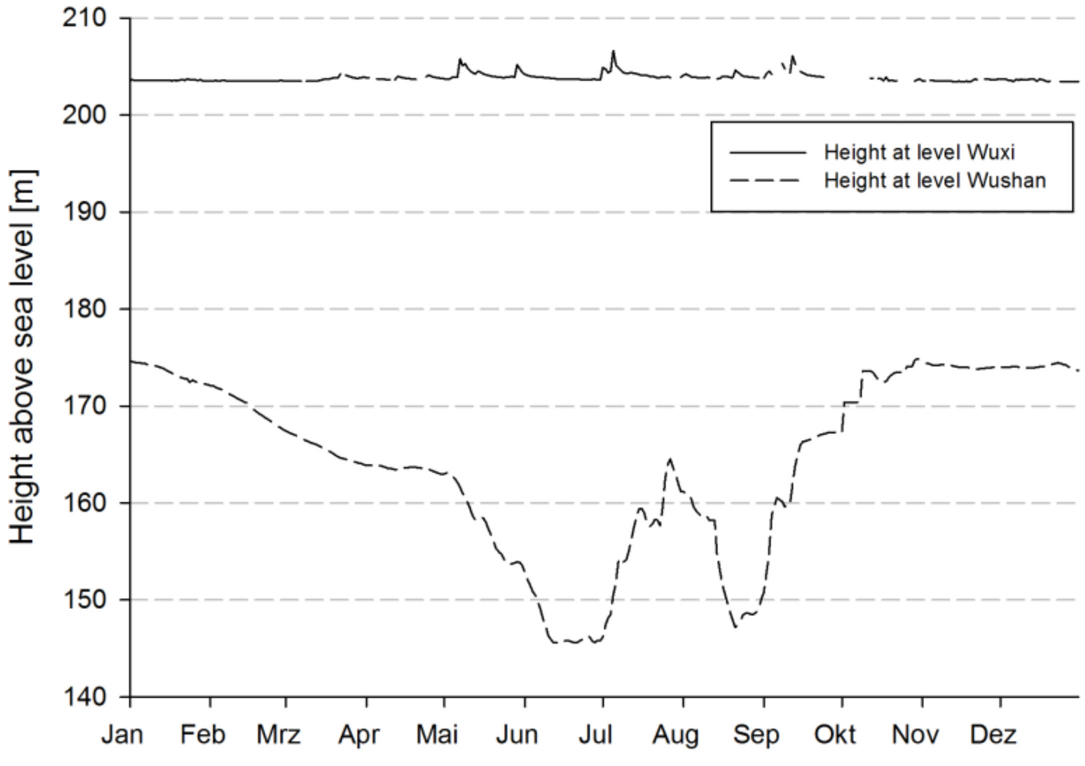


Figure VII-22: Boundary conditions for the hydrodynamic modelling by means of the one-dimensional model HEC-RAS.

Since simulations ran for longer periods of time than the calibrated time series, the slight lacks in the balance of water volume changes amplified with the duration of the simulation runs. A situation that was negligible in a one year study became very relevant in a 40-year simulation run. For this reason, gaps in the balance were counterbalanced by adding or subtracting a small amount of water at each time-step. The resulting patterns resemble very much the situation at the Wushan Lake with huge water fluctuations and the upstream sections with less dynamic water level changes (refer to Figure VII-22, Figure VII-23).

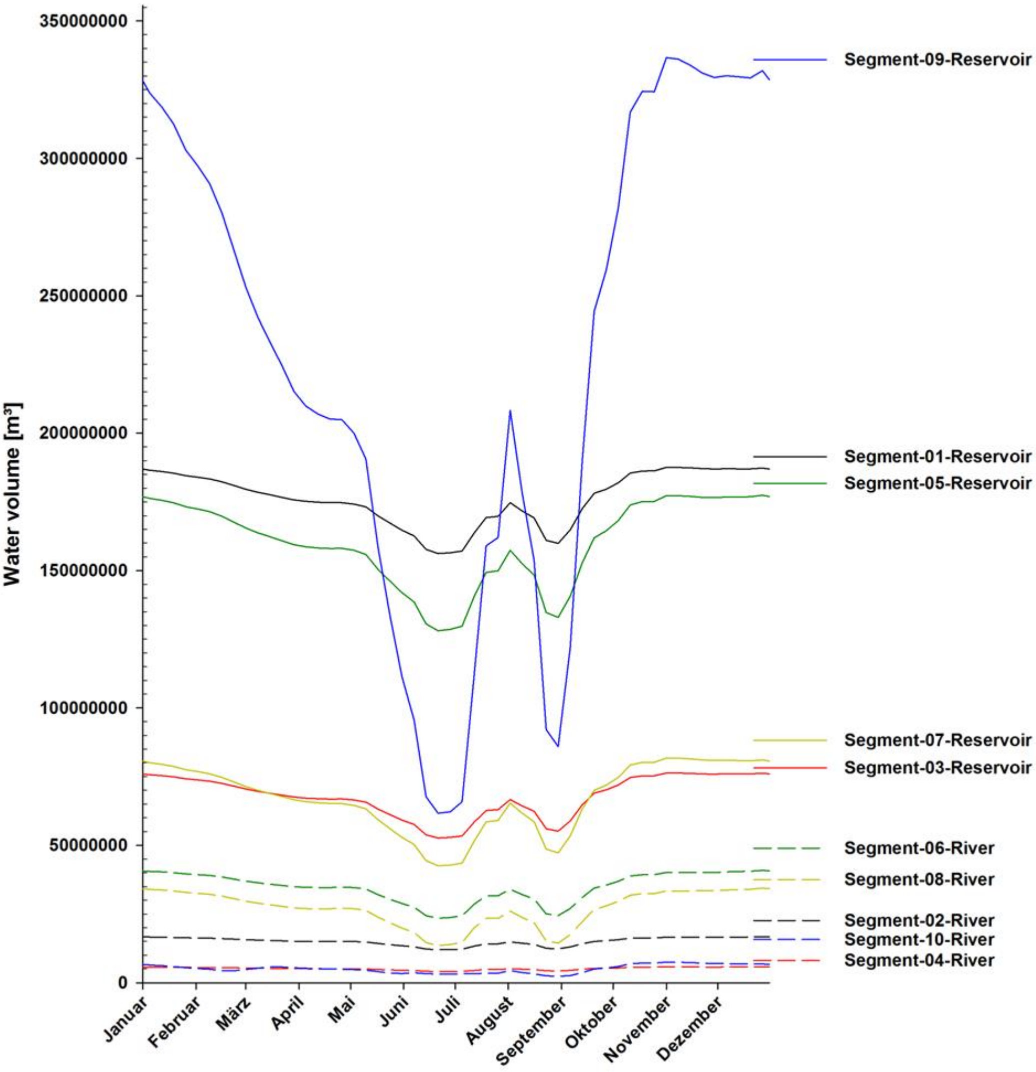


Figure VII-23: Changes in water volumes of the AQUATOX simulation at the model region 'Daning River'.

7.4.2 *Definition of pollution scenarios in the model region at Daning River*

The main scenarios of pollution 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 (Figure VII-24). 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 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.

(i) Definition of exposed segments

It was assumed that not all of the river and reservoir segments 1-10 had the same probability of being exposed to plant protection products, especially to the designated model substance Propanil. In order to define segments that receive 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 cover 'Globcover' of the European Space Agency (Leroy et al. 2006). All land-use types of a 300 m buffer zone around the 10 previously segments were analysed for its percentage area coverage of the total buffered fluctuation zone (GIS representation gives Figure VII-24). It was assumed that the category 'irrigated cropland' was most likely to consist of rice cultures and thus received relatively high amounts of herbicides, in this case represented by Propanil (exposure class 'red'). Further three categories of 'croplands' were found ('mosaic vegetation/croplands', 'rain fed croplands', 'mosaic croplands/vegetation') and considered to receive medium amounts of pesticides, i.e. herbicides due to their mosaic character if more than 30 % of the total area were covered by agricultural land (exposure class 'yellow'). Six of the land-use categories around the simulated reservoirs and river segments in the model region 'Daning area' were different combinations of shrub land, forests, grassland or artificial areas and were not used as indicators of pesticide use, the adjacent segment were set to zero exposure (exposure class 'green', for the detailed results and land-cover percentages see Table VII-10**)**.

GIS analysis of the land use in the adjacent areas to the water body of the TGR shows likely hotspots of pesticide use. Irrigated croplands were considered to be mainly rice paddies in the region and applied with the herbicide Propanil.

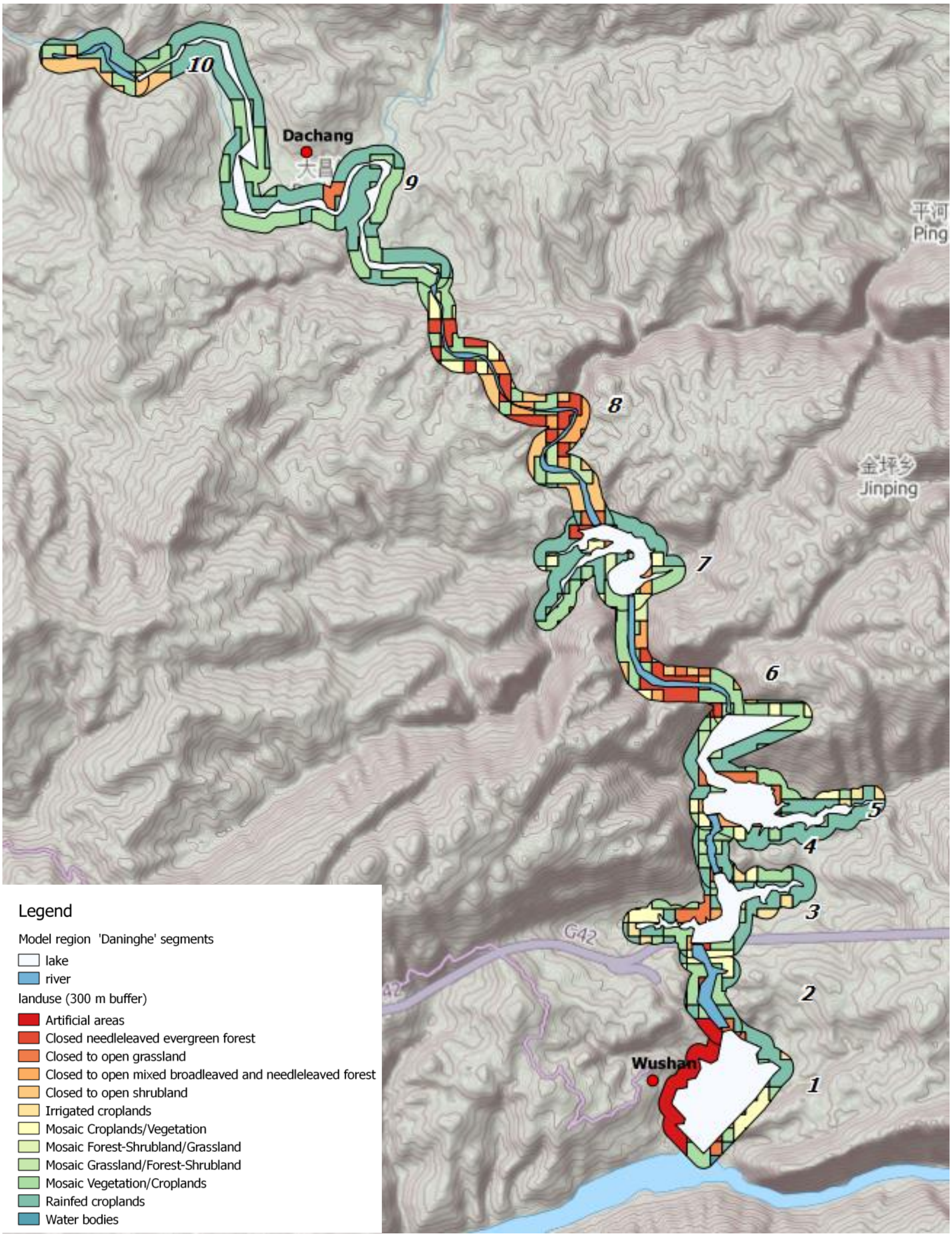


Figure VII-24: Land-use in a 300 m-buffer fluctuation zone around 10 river and reservoir segments.

(ii) Exposure patterns

Table VII-10: Analysis of land-use cover in a 300m buffer zone around the segments of the model region 'Daning River'. Red: Segments surrounded by irrigated croplands with high probability of Propanil exposure; yellow: medium exposed segments surrounded by 'other croplands'; green: zero exposed segments, no or few agricultural uses.

Segment **Percentage land-use cover**	1	2	3	4	5	6	7	8	9	10
Irrigated croplands	2%	5%	83%	0%	10%	0%	0%	0%	0%	0%
Mosaic Vegetation/Croplands	9%	1%	6%	5%	13%	3%	25%	14%	21%	2%
Rainfed croplands	5%	5%	9%	5%	23%	0%	10%	2%	36%	5%
Mosaic Croplands/Vegetation	1%	5%	15%	16%	25%	2%	5%	30%	0%	0%
Sum of non-irrigated croplands	15%	11%	31%	26%	61%	6%	40%	46%	57%	7%
Closed needleleaved evergreen forest	2%	3%	2%	0%	2%	11%	36%	43%	0%	0%
Closed to open grassland	17%	4%	20%	1%	14%	1%	25%	17%	3%	0%
Closed to open mixed broadleaved and needleleaved forest	3%	2%	7%	9%	15%	10%	13%	42%	0%	0%
Closed to open shrubland	0%	0%	0%	0%	0%	39%	3%	31%	7%	19%
Mosaic Forest-Shrubland/Grassland	0%	0%	0%	0%	0%	22%	78%	0%	0%	0%
Mosaic Grassland/Forest-Shrubland	0%	0%	0%	7%	41%	4%	0%	48%	0%	0%
Artificial areas	84%	16%	0%	0%	0%	0%	0%	0%	0%	0%

The model substance was added to each of the relevant segments in a time-series via small 'creek tributaries of 1000 m³ constant volume and 1000 m³ loaded inflow. The question of how much of the substance reaches the respective water bodies was deduced from the regulatory risk assessment of Propanil as rule-of-thumb values applied as worst-case PEC_{ini} of 220 µg/L, and correspondingly to the proposed degradation scheme below (Figure VII-25) 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. For the highly exposed segments 3 and 5, the basic loadings were assumed 10-fold higher than for medium exposed segments. This exposure regime was used for two two-week periods per year, because there was evidence that in this sub-tropical region two growing periods per year could be possible (in the lower reaches even three harvests have been reported (Encyclopaedia Britannica 2014). The application and consecutively run-off to the water bodies took place in spring from first to 14th of April and in autumn from first to 14th of September. It was assumed that the mode of application in Chinese rice cultures is similar to the intended uses undelaying the re-inclusion application in Europe that was finally not granted indeed (Ministry of Health Italy 2006). As for the demonstration of a 'safe use' in the standard risk assessment of Propanil, the substance 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 the pest species *Echinochloa crus-galli*.

There was no information available on degradation rates of TCAB under the conditions of real aquatic environments. In AQUATOX, the degradation of TCAB was set 0.025/d, which is 10-fold slower than for Propanil.

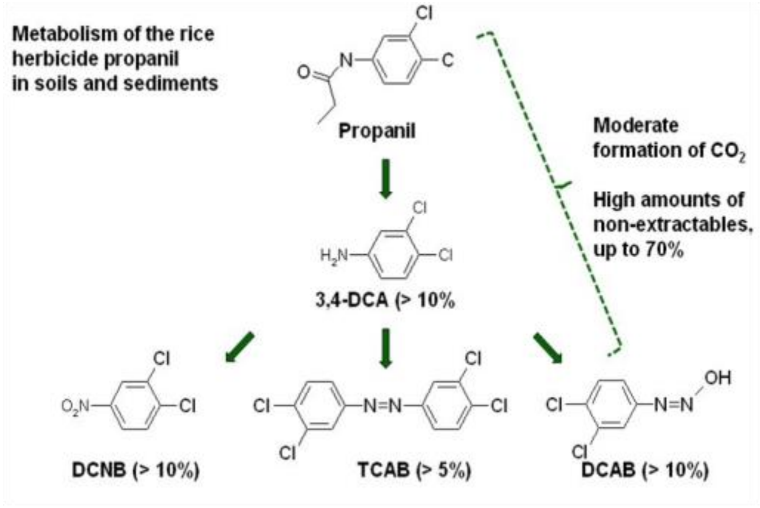


Figure VII-25: Proposed degradation scheme of Propanil.

The segments are connected by feed-back and feed-forward links to adjacent segments according to requirements of the AQUATOX simulation environment, i.e. the linkages between two well-mixed segments may be uni- or bidirectional (Park & Clough 2010). Hence, a dynamic stratification of water layers does not apply. For the relatively fast flowing tributary streams, stratification was not to be expected anyway. In a simulation, nutrients, biota and other state variables ‘pass’ from segment to segment through active migration, passive drift, diffusion, or bed-load.

Figure VII-26: Upper and lower tributary of the model region in the bioaccumulation module. Low water level situation (approx. 150 m) at Dachang lake (left) and Wushan Bay (right).

(iii) Chemical properties of Propanil, 3,4-DCA and TCAB

The chemical properties of the parent substance Propanil, its primary metabolite 3,4-Dichloroaniline (DCA) and the secondary metabolite 3,3’,4,4’-Tetrachloroazobenzene (TCAB) have been compiled from literature data (Table VII-11).

Table VII-11: Chemical properties of the model substances Propanil, DCA and TCAB.

ChemName	Propanil	DCA	TCAB
CAS Registry No	709-98-8	95-76-1	14047-09-7
MolWt	218.1	162.02	320
Solubility	0.095	0	0.04
Solubility Reference	BSS: g/L, DAR Propanil		BSS: Chemprop model
Henry	0.0004356	1.47E-05	4.95E-07
Henry Reference	BSS: DAR Propanil	25°C, PPDB	Scholz-Starke, Ottermanns et al. 2013
Pka	19.1	2.97	0
Pka Reference	BSS: DAR Propanil	starke Säure, PPDB	
VPress	0.000193	0	0
VPress Reference	BSS: DAR Propanil		
Octanol Water Coeff	2.29	2.69	5.84
Oct Water Reference		PPDB	Chemprop Model
Activation Energy	18000	18000	18000
A.E. Reference	default, BSS: important parameter for temperature adjustement of e.g. hydrolysis and other rates via Arrhenius equations	Lyman, Reehl, Rosenblatt, 1982	default, BSS: important parameter for temperature adjustement of e.g. hydrolysis and other rates via Arrhenius equations
Rate Anaerobic Degr.	0	0	0.025
Anaerobic Degr. Ref	BSS: assumed that aerobic rate covers anaerobic		BSS: same value as for aerobic degradtion, in case of lack of oxygen
Rate Aerobic Degr.	0.25	0	0.025
Aerobic Degr Ref	BSS: DT50 under aerobic aquatic conditions = 2 days (L1615, DAR Propanil), calc. as 50%/2days	Max. Rate of Aerobic Microbial Degradation	BSS: same as for Propanil, no measured values available, set 10fold smaller, because degradtion is for the substance not very likely
KUnCat	0	0	0
KUnCat Reference	BSHydrolysis constant calculated by pseudo-first order regression: Khyd=Kuncat+Kbasecat+Kacidcat); Aqueous hydrolysis DT50 (days) at 20oC and pH 7 (http://sitem.herts.ac.uk/aeru/iupac/545.htm) = 365 d		
KAcid	0	0	0
KAcid Reference	BSS: not used, because uncat. hydrolysis is assumed to cover the overall hydrolysis, Prop. was conisdered stable under the given conditions (L1615)		
KBase	0	0	0
KBase Reference			
Photolysis rate	0.01	0	0.0087
Photolysis Reference	BSS: DAR Propanil, L1615: DT50 52.1 days under spring light conditions. calc. as 50%/52.1		BSS: taken arbitrarily from Esfenvalerate and set 10fold smaller

7.4.3 *Toxic action of Propanil and its bioaccumulative metabolite TCAB - Ecotoxicity module*

The realistic representation of the effects of the model substances Propanil and TCAB required the model to include toxicity data for the feeding guilds included in our model (see below). Therefore, the literature was searched for standard toxicity data that could be used for the multi-guild groups ‘mussels’, ‘fish’, ‘zooplankters’, ‘macrophytes’ and ‘algae’. Because the suspected bioaccumulative and toxic metabolite TCAB has been scarcely investigated, a QSAR model had to be applied (UFZ 2012) and some rude assumptions on the toxicity of the compound had to be made (an overview gives Table VII-12).

Table VII-12: Plant and animal toxicity data for the herbicidal parent model substance Propanil and its secondary metabolite TCAB.

Test item	Test species	AQUATOX Toxicity Entry	Test system	Duration of exposure	Results	Reference
Propanil technical	*Cyprinodon variegatus*	Cyp var	Acute	96h	LC_{50}: 4.6 mg/L	Sousa (1990)
	Daphnia magna	Dap mag	Acute	48h	LC_{50}: 6.7 mg/L	Graney (1982)
	Lemna gibba	Lem gib	Acute	14d	EC_{50}: 0.11 mg/L	Giddings et al. (1990a), used as LC_{50} in AQUATOX
	Navicula pelliculosa	Nav pel	Acute	72h	EC_{50}: 0.025 mg/L	Giddings (1990b), used as LC_{50} in AQUATOX
	Physella acuta	Phy acu	not known	48h	LC_{50}: 8.8 mg/L	Kegley et al. (2014)
TCAB	*Pimephales promelas*	Cyp var	Acute	96h	LC_{50}: 0.029 mg/L	Chemprop QSAR Model (Scholz-Starke & Ottermanns et al. 2013)
	Daphnia magna	Dap mag	Acute	72h	LC_{50}: 0.048 mg/L	Own estimate by using the proportion of 140 fold higher toxicity beween fish tox of Propanil and TCAB derived from Chemprop
	Lemna gibba	Lem gib	Acute	72h	LC_{50}: 0.00079 mg/L	
	Navicula pelliculosa	Nav pel	Acute	72h	LC_{50}: 0.00017 mg/L	
	Physella acuta	Phy acu	Acute	48h	LC_{50}: 0.063 mg/L	

7.4.4 *Accumulation of Propanil within aquatic food webs - Biomagnification/bioaccumulation module*

(i) Toxicant bioconcentration and bioaccumulation in plants and animals

For the purposes of the research project at hand, the standard equations of AQUATOX were used to model toxicant uptake and egestion to/from plants and animals. For algae and macrophytes as well as for invertebrates and fish, 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. Time to reach equilibrium between the exposing phases and the organisms is taken into account, if necessary non-equilibrium kinetics is applied (Park & Clough 2010). The uptake rate *K1* for animals depends on both uptake via water phase and by feeding, thus the bioconcentration factor (BCF) becomes a bioaccumulation factor (BAF) accounting for food chain effects.

(ii) Biotransformation and Biodegradation of Propanil and TCAB

Most of the information on degradation of Propanil was gained by the EFSAs draft assessment report (DAR). 3,4-DCA and TCAB are just by- or intermediate products of pesticide production and there is no need for a comprehensive assessment because they are considered not to have pesticidal effects. Basic knowledge on the microbial degradation as half times under aerobic and anaerobic conditions as well as photolysis rates were necessary for the calibration of the model (see Ministry of Health Italy 2006).

- **Hydrolytic processes** were considered irrelevant at pH between 7-8 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 have been calculated with DT_{50} = 2 days equals 0.25/d (taken from DAR Propanil, Ministry of Health Italy 2006).
- The **photolysis rate** was estimated from an environmental DT_{50} by direct photolysis at the water surface indicated. It was reported 52.1 days (Ministry of Health Italy 2006), rate was calculated with 50%/52.1 days = 0.01/d.

7.4.5 *Biotic components of TGR ecosystems - Food web module*

(i) Trophic guilds and interactions

For the AQUATOX simulation environment, 14 trophic guilds were defined based on literature research on the most common and representative species in the TGR-region. The physiological characteristics of the species were based on standard species implemented in the internal AQUATOX databases and slightly modified to better meet the traits of sub-tropical plankton and fish species (Rings 2013). The food web structure is shown in Figure VII-27, trophic interactions between the guilds can be found in Table VII-13.

Primary producers were considered to contain stream and lake specialists; in particular the macrophytes prefer stagnant waters for the slower reproductions rates and lacking resistance to washout from a segment or the whole system. Many disappointing trials to include the macrophyte *Lemna spec.* into the system were quit when one of the developers of AQUATOX Jonathan Clough (warrenpinnacles.com) reported that *Lemna* couldn't grow appropriately at the moment. Instead *Myriophyllum* has been newly added.

Primary consumers (chironomids, bosminae, copepodae, daphnids, mussels) feed on labile and refractory particulate detritus, diatoms, green algae and bluegreen algae (Rings 2013).

Fish species were categorised according to their main feeding preferences and further denoted as 'feeding guilds' (Table VII-13).

- The **Black Carp** stands for a visual predator and was therefore assigned a 'game fish'. It exclusively feeds on zooplankton.

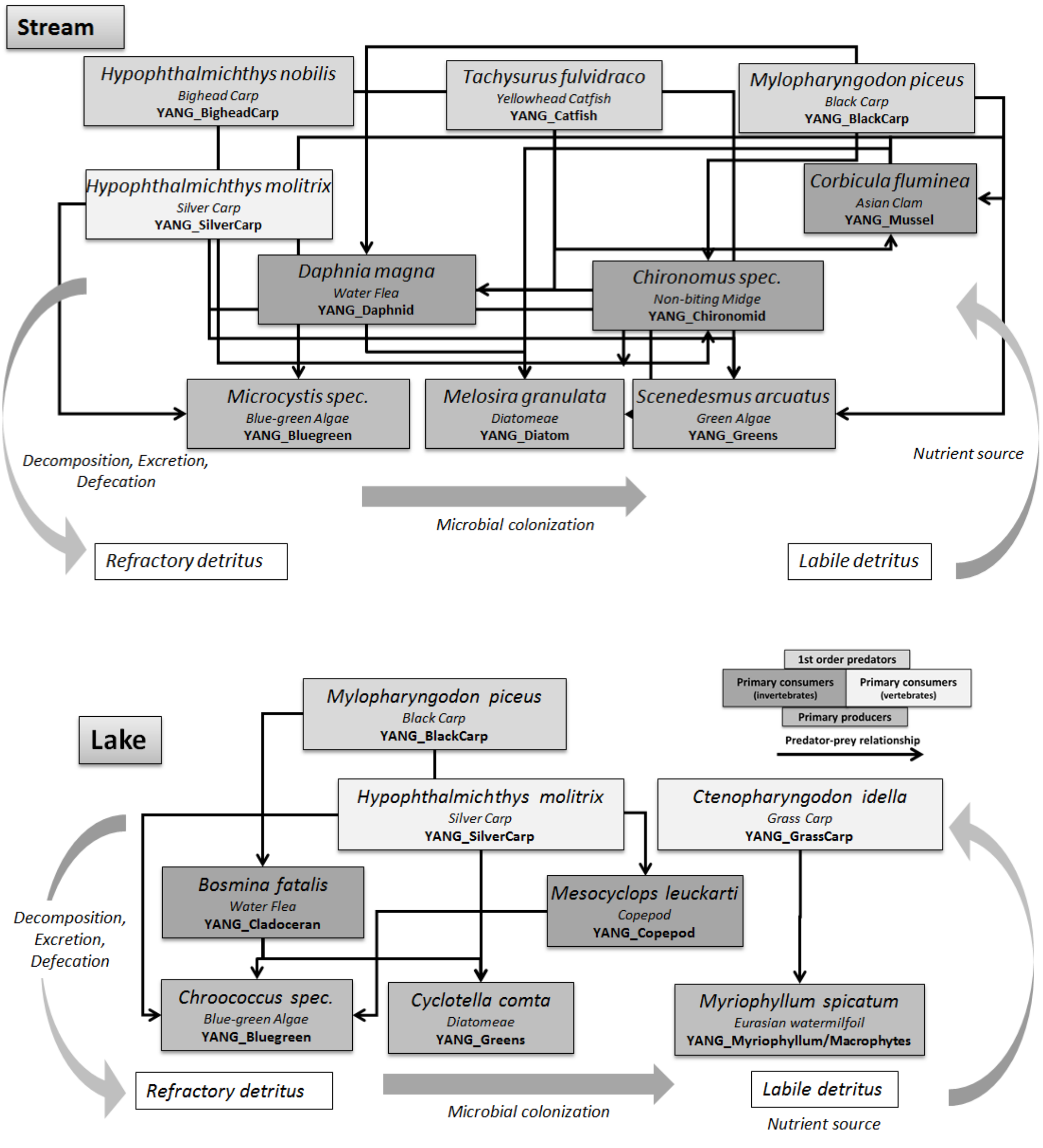


Figure VII-27: Interaction food webs

- The **Silver Carp** stands for an omnivorous fish, thus it feeds on sedimentary detritus and on both phyto- and zooplankton.
- The **Catfish** represents a species that is highly exposed to pollutants via the sediment and feeds on mussels, daphnids and detritus.
- The **Bighead Carp** feeds on phytoplankton only and is therefore strongly linked to primary production.
- The **Grass Carp** feeds nearly exclusively on macrophytes, here represented by *Myriophyllum*.

Table VII-13: Trophic interactions between guilds. Feeding preferences in percent of total energy budget of the respective organism, normalized to 100%.

	Y_Chironomid	Y_Bosmina	Y_Copepod	Y_Daphnia	Y_Mussel	Y_Catfish	Y_GrassCarp	Y_BlackCarp	Y_SilverCarp	Y_BigheadCarp
R detr sed	20.0%								11.1%	
L detr sed	20.0%					10.0%		8.3%	11.1%	12.5%
R detr part	15.0%	25.0%		45.5%			3.9%			
L detr part	15.0%	25.0%	25.0%	45.5%	25.0%		3.9%	8.3%		12.5%
Y_Diatom	10.0%		25.0%		25.0%				11.1%	15.0%
Y_Phyto Greens	10.0%	50.0%	25.0%		25.0%				11.1%	15.0%
Y_Blue-Greens	10.0%		25.0%	9.1%	25.0%				11.1%	15.0%
Y_Myriophyllum							88.2%			
Y_Chironomid							3.9%	16.7%	11.1%	15.0%
Y_Bosmina									11.1%	
Y_Copepod								16.7%	11.1%	
Y_Daphnia						45.0%		16.7%	11.1%	15.0%
Y_Mussel						45.0%		33.3%		
Y_Catfish										
Y_GrassCarp										
Y_BlackCarp										
Y_SilverCarp										
Y_BigheadCarp										

(ii) Initial densities, organism loadings and desired biomass

It was expected that the initial conditions of the AQUATOX simulation converged to an equilibrium of realistic densities of organisms after sufficient time. On a long term, a stable system would be established. Additional loadings of organisms (and nutrients as well) per time-step maintained the populations in case of nearly complete extinction (refuge), which could occur due to very high flow rates and dilution factors, and after adding toxic substances.

At the beginning of the levelling phase of 5 years (compare the following chapter 7.5.1(ii)), primary producers were initially added with densities of 100 mg/L, zooplankters were introduced with densities of 10 mg/L. Fish were added in abundances of 10 g dry weight/m^2 (differences between lake and stream segments lists Table VII-14). At each of the next time-steps, populations were increased by ten percent of the initial density of the respective taxon to balance losses for all implemented reasons (differentiated mortalities, washout).

Table VII-14: Initial densities and daily loadings in lake segments (right) and stream segments (left).

	STREAM segment			LAKE segment			
State Variable Name	Init. Cond.	Daily Loading	Multiple Loading Factor	Init. Cond.	Daily Loading	Multiple Loading Factor	Units
Y_Diatom	100	10	1	0	0	0	mg/L dry
Y_Phyto Greens	100	10	1	100	10	1	mg/L dry
Y_Blue-Greens	100	10	1	100	10	1	mg/L dry
Y_Myriophyllum	0	0	0	1	1	100	g/m2 dry
Y_Chironomid	1	0	1	0	0	0	g/m2 dry
Y_Bosmina	0	0	0	1	0	1	mg/L dry
Y_Copepod	0	0	0	1	0.1	1	mg/L dry
Y_Daphnia	1	0.1	1	0	0	0	mg/L dry
Y_Mussel	10	1	1	0	0	0	g/m2 dry
Y_Catfish	10	1	1	0	0	0	g/m2 dry
Y_GrassCarp	0	0	0	10	1	1	g/m2 dry
Y_BlackCarp	10	1	1	10	1	1	g/m2 dry
Y_SilverCarp	10	1	1	10	1	1	g/m2 dry
Y_BigheadCarp	10	1	1	0	0	0	g/m2 dry

Averaged over a simulation year, we aimed at realistic densities of organisms. Literature on Chinese rivers and lakes as well as experiences from temperate regions served as benchmarks for plausibility checks.

- **Chlorophyll-a** contents at the Daning River in the period just before the impoundment of TGR 2004-2007 were varied with the season between 1 und 23 mg Chlorophyll-a/L (Zhang et al. 2010).
- **Copepods**, in particular the species *Mesocyclops leuckarti* implemented in our simulations 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).

(iii) Migration of fish from segment to segment

A portion of 10 % of the populations of all 5 fish species were set to actively migrate once a year to the connected upstream and downstream segments. All other state variables (nutrients, pollutants, plankton organisms, and detritus) were subjected to passive drift in stream direction (wash-in and wash-out mechanisms).

7.5 Results and interpretation of simulation studies

Simulation studies after calibration of the model were conducted mainly for two reasons: Firstly, after calibrating numerous variables to the conditions at the model region at the Daning River, it had to be tested if the model output is stable over time and plausible (model verification). Long-term runs give information about the stability and the optimum compromise between the equilibration and run-time of the program. Secondly, the impact of very high dosages of nutrients (via loadings from upstream) was investigated because the

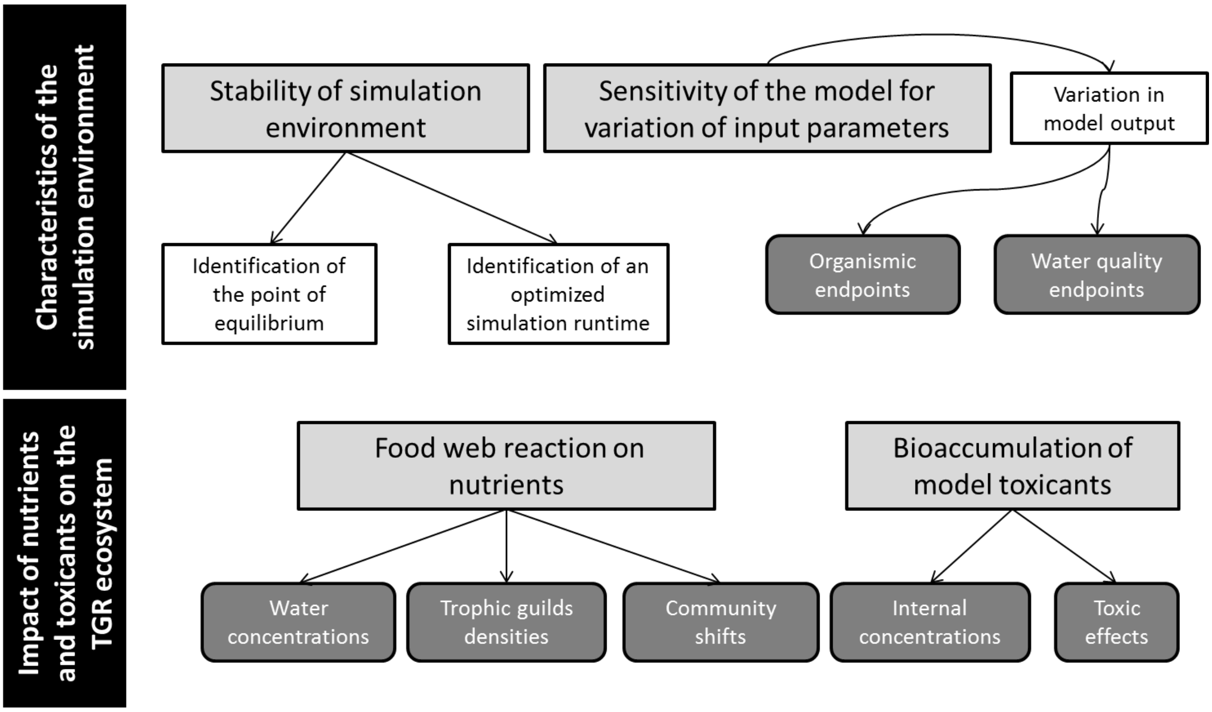


Figure VII-28: Flow chart of the data analysis of the simulation output

problem of algal blooms after the impounding of the TGD was identified as one of the most urging by the Chinese people, dealing with the assessment of TGR impacts on the environment and with drinking water supply. The flow chart of Figure VII-28 divides the two main parts of the simulation studies to ‘characterisation of the simulation environment’ and ‘impact of nutrients and toxicants on the TGR ecosystem’.

7.5.1 *Characteristics of the simulation environment*

(i) Fixed and alternating yearly patterns

The hydrodynamic situation, i.e. water volume and flow velocity changes over time. It alternates according to a fixed yearly pattern as described by section VII7.4.1(i) that is being repeated each year of simulation time. Organism densities vary over time depending on the changing environmental conditions originating from the initial densities that were chosen following the rationales described by section VII7.4.5.

(ii) Stability of the simulation environment and time to equilibration

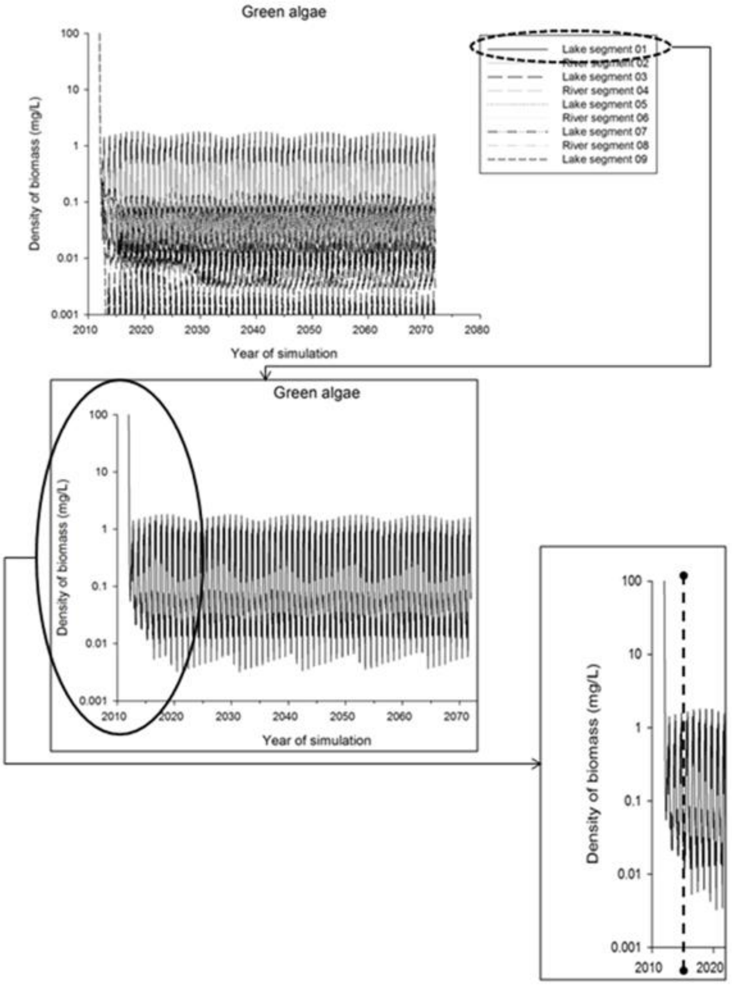


Figure VII-29: 60-year simulation run for phytoplankton, namely green algae (primary producers). Vertical dashed line marks designated the end of the levelling period. From then on, it was decided to analyse and show the results of simulation runs.

The simulation was considered to be nearly equilibrated if the densities of a trophic guild were not changing over orders of magnitude between the simulation years and if there was no directed trend to higher or lower abundances over longer periods of time. The concrete criteria after which period the system was considered sufficiently stable were chosen by means of expert judgement and pragmatism, and are explained and discussed in the following section.

The stability of the simulation environment was evaluated after a 60-year simulation run. The system showed stable populations for most of the species guilds for many simulation years after an initial period of equilibration. The system needed approximately five years to reach sufficient equilibrium, as shown by the vertical dashed line in example of Figure VII-29 for algae. Some feedings guilds needed up to 25 years for no significant changes to occur in the seasonal patterns. For fish, it could take up to 30 years to show completely stable patterns. Fish show significantly longer generation times than plants and life spans of about four years, so their population responded much slower (Figure VII-30). It was decided to run the simulations for 25 years, to assure a minimum stability of all populations and for taking into account that computing time should not last longer than the real-time.

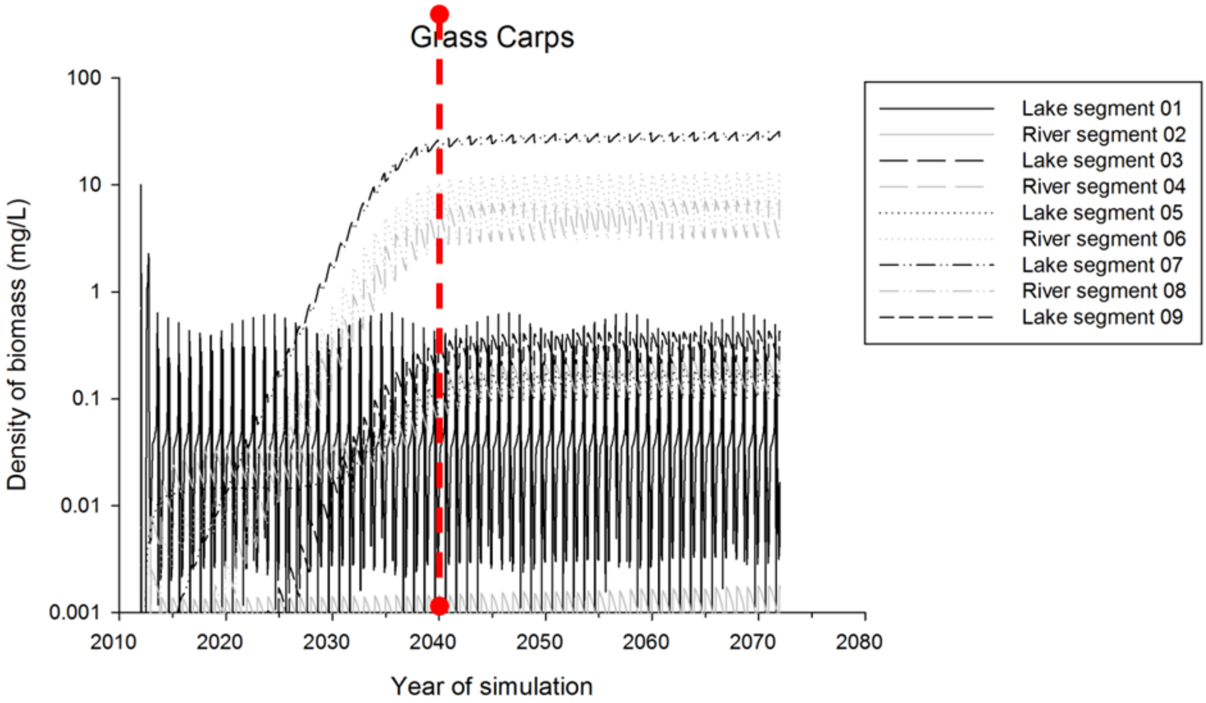


Figure VII-30: 60-year simulation run for fish, namely Grass Carps.

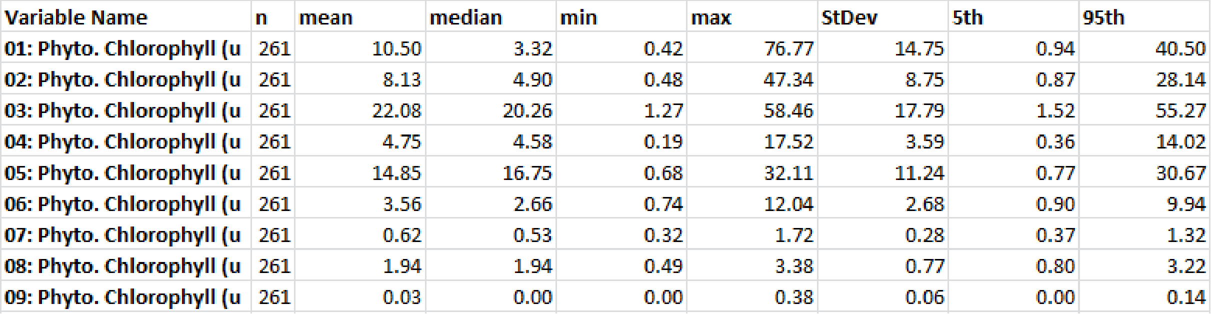
(iii) Plausibility of organism densities

There was only few data available that was published in English language, fitted more or less the region that was investigated (Daning River representing South Chinese rivers and lakes) and that delivered organism densities that could be converted to AQUATOX units. Because simulations started with 'free-flying' organisms densities framed by the resources available, the mean and equilibrium densities should be plausible, allowing for further refinement. Desired densities of algae, invertebrates and fish could only be estimated from the literature or oral communication and is discussed in the following by means of some examples.

Algae → Chlorophyll-a

In our simulations, total phytoplankton Chlorophyll-a concentrations varied between 0.03 and 22.08 µg/L, maximum values were between 0.38 and 76.77 µg/L. According to values that usually occur in temperate mesotrophic pond systems (unpublished data from aquatic mesocosm studies) obtained densities appear low but plausible Zhang et al. (2010) reported concentrations between 1 and 23 mg Chl-a/L, which we suspected to be an error due to decimal transposing.

Table VII-15: Chlorophyll-a concentrations of 9 lake and river segments at the Daning River model region. Values have been averaged over a 5-year simulation period after equilibration of the system.



Variable Name	n	mean	median	min	max	StDev	5th	95th
01: Phyto. Chlorophyll (u	261	10.50	3.32	0.42	76.77	14.75	0.94	40.50
02: Phyto. Chlorophyll (u	261	8.13	4.90	0.48	47.34	8.75	0.87	28.14
03: Phyto. Chlorophyll (u	261	22.08	20.26	1.27	58.46	17.79	1.52	55.27
04: Phyto. Chlorophyll (u	261	4.75	4.58	0.19	17.52	3.59	0.36	14.02
05: Phyto. Chlorophyll (u	261	14.85	16.75	0.68	32.11	11.24	0.77	30.67
06: Phyto. Chlorophyll (u	261	3.56	2.66	0.74	12.04	2.68	0.90	9.94
07: Phyto. Chlorophyll (u	261	0.62	0.53	0.32	1.72	0.28	0.37	1.32
08: Phyto. Chlorophyll (u	261	1.94	1.94	0.49	3.38	0.77	0.80	3.22
09: Phyto. Chlorophyll (u	261	0.03	0.00	0.00	0.38	0.06	0.00	0.14

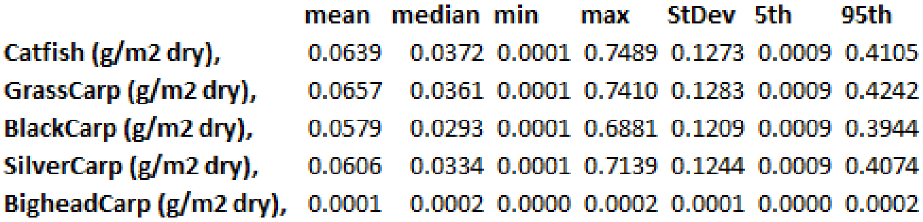
Copepods

Yao et al. 2008, chapter VII7.4.5(ii)) found up to 0.372 individuals of *Mesocyclops leuckarti* /L. Assuming that an individual copepod has a biomass of 6e-04 g=6e-01 mg wet weight a wet to dry conversion factor of 5 was applied as a default in the model, and the average density of 5.4e-03 mg dry weight/L was measured in segment 01 in the five-year reference period, Individuals/L = 5.4-03 mg*5/(6e-01 mg) = 4.5e-02 Individuals per Litre (Calculation: Ind=wet*5/dry=5.4e-03*5/6*e-01=4.5e-02=0.045 Ind/L). Further assuming, that Yao et al. had to expect lower densities in the Yangtze main stream than we had to expect in the Wushan Lake, the densities of invertebrates in our simulations were considered quite plausible.

Fish

Mean densities of the five fish species guilds in the 'densely populated' segment 01 for a considered equilibrated 5-year period (year 9-14 after simulation start) are shown in Table VII-16. The densities per square meter are quite low. 1 g dry weight/m² was added at each time step resulting in a loading of e.g. 18 % per time step for the grass carp, offsetting the losses due to low oxygen supply that occurred from time to time.

Table VII-16: Mean densities of five fish guilds in the simulation exercises (standard run, segment 01, five year period 9-14).



	mean	median	min	max	StDev	5th	95th
Catfish (g/m2 dry),	0.0639	0.0372	0.0001	0.7489	0.1273	0.0009	0.4105
GrassCarp (g/m2 dry),	0.0657	0.0361	0.0001	0.7410	0.1283	0.0009	0.4242
BlackCarp (g/m2 dry),	0.0579	0.0293	0.0001	0.6881	0.1209	0.0009	0.3944
SilverCarp (g/m2 dry),	0.0606	0.0334	0.0001	0.7139	0.1244	0.0009	0.4074
BigheadCarp (g/m2 dry),	0.0001	0.0002	0.0000	0.0002	0.0001	0.0000	0.0002

The common carps and catfish were observed to increase after the TGD was built (Yi et al. 2010), many other species extinct. There is not much information on the natural density of fish in reservoir ecosystems. The annual reports on the ecological monitoring of TGR gives catches of fish in tons per year and total reservoir area, e.g. 3329 t in 2009, of this 119 t was

Yellow Catfish (MEP 2010). The reservoir covers finally an area of 1082 km², which would mean that about 3 g fish biomass per square meter has been removed by fishing. In artificial ponds the yearly stocking with juvenile grass carp of 800 g wet weight is between 150 and 500 individuals/ha. This would equal 800 g wet weight / wet-to-dry conversion factor of 5 = 160 g dry weight / 10000 m² = 0.016 g/m². This is at least in the range of the densities simulated and consequently the simulation results are considered plausible.

(iv) Sensitivity analysis of the model

The main question for sensitivity analysis was how varying nutrient loads and water concentrations of toxic model substances influence the resulting water concentrations of the respective nutrients and the densities of all feeding guilds in the system. For this purpose, control and perturbed simulations with different sets of response variables investigated have been run. We concentrated on the last segment 01, the Wushan Lake, because most parameter values concentrate in this segment due to the given main mass flow direction.

Each of the seven variable values that were considered most relevant for the equilibrium state of the system, which were the average epilimnic temperature, average light intensity, CO_2 load, mean depth, NO3 load, and total soluble P load, were varied by 33 % increase or decrease. Forty-two variables that describe the nutritional and detrimental status and the densities of the different feeding guilds were chosen as the model output. The simulation was run for 15 years and parameter values were averaged over the last 365 days.

The analysis shows that variation of the phosphorous loads caused changes in the P-content in the water column in the same direction, as expected. Other variables than P-loading were not affecting the P-concentration in the water phase, which is a plausible and intentional finding (see Figure VII-31 above). Also plausible is the observed relative change of green algae biomass. Since the P-content is very high, the growth of algae is not limited by this nutrient and cannot be further stimulated by higher loadings of P. If the loadings are reduced though, then competition for this resource could lead to better growth of green compared to e.g. bluegreen algae (see Figure VII-31 below). A decreased water depth causes a larger photic zone and thus promotes growth.

7.5.2 *Shifts of food web structure due to varying amounts of growth limiting nutrients*

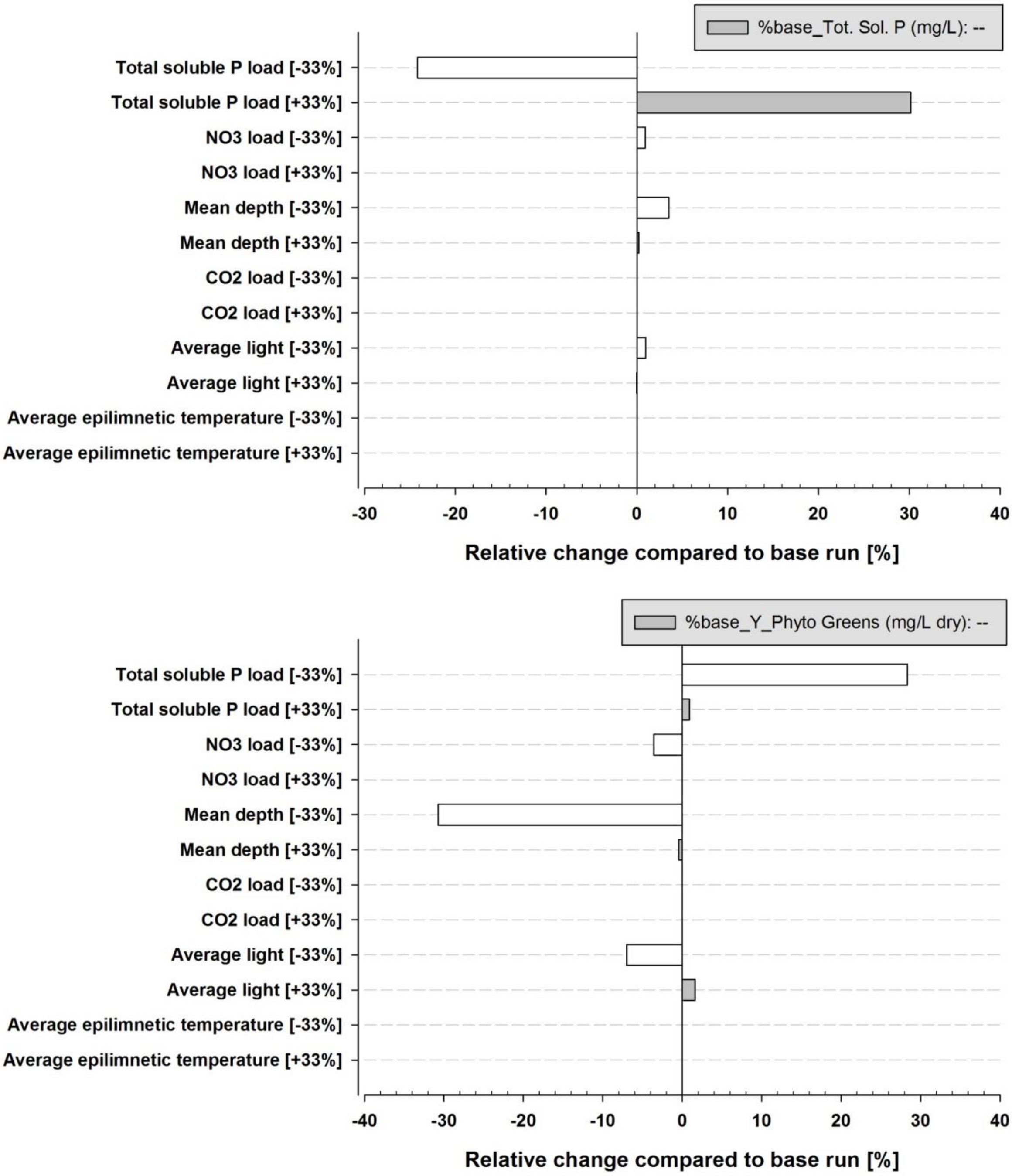


Figure VII-31: Sensitivity analysis of a 33 % change of the parameter values as they affect the measurement endpoints (here exemplified: biomass of green algae and the water concentration of total soluble phosphate).

(i) - Rationales of the analysis

The use of fertilizers 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 phosphorous was simulated.

It was assumed that at least one of these essential nutrients would be the limiting factor for the growth of the primary producers, such as green and blue-green algae, as well as diatoms and macrophytes (as implemented in the AQUATOX model by Park & Clough 2010 or compiled in standard ecology textbooks, e.g. Lampert & Sommer 1999). It was expected from basic ecological and physiological reasoning that due to several processes of nutrient consumption the patterns for both the effects of N- and P-variation would be evident for water concentrations and guild densities. For the primary producers direct effects were assumed, whereas the succeeding trophic levels were expected to show indirect effects depending on varying nutrient supply.

In China nowadays, the excessive use of water and fertilizers in rice cultures very often leads to ineffective conversion into biomass and further surface runoff from rice paddies into the adjacent water bodies can occur (Liang et al. 2013).

In our simulations the daily loads were varied with factors of 0.5, 1, 5, 10, 50-fold for nitrogen, for phosphorous and the combination of nitrogen and phosphorous, 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 enter the water bodies strongly depend on the size and transport capacity of the upstream segments. Here, concentrations of ammonia and phosphorous, as well as the densities of one guild of primary producers (green algae), primary consumers (daphnids), a plant feeding fish (grass carp) and a predatory fish (black carps) are shown in the following.

(ii) Results & Discussion

(a) Water concentrations of nutrients

Ammonia and total phosphorous concentrations in the water column did not show clear dose-dependent differences as an effect of N-variation (Figure VII-32, Figure VII-33). However, clear dose-dependent differences in phosphate water concentrations were detected after P-variation. The results of the combined concordant variation of N and P loads per time step of the simulation did not show any emergent effects that were not explainable as from the variation (i.e. concentration) of one nutritional component alone.

The patterns of water concentrations of the nutrients could be partially explained by the basic physiological characteristics of the phytoplankton organisms implemented in the model. As the output of the AQUATOX model showed, diatom algae were predominantly limited by the phosphorous concentration during a simulation year. On the other hand, green algae (Figure VII-34) have been limited rather by the nitrogen (ammonia) concentration in the water phase (output variable ‘fraction limited by…’ in AQUATOX). In late October, there was a drop in phosphorous concentrations due to a peak in diatom biomass during that time.

(b) Patterns of guild`s densities

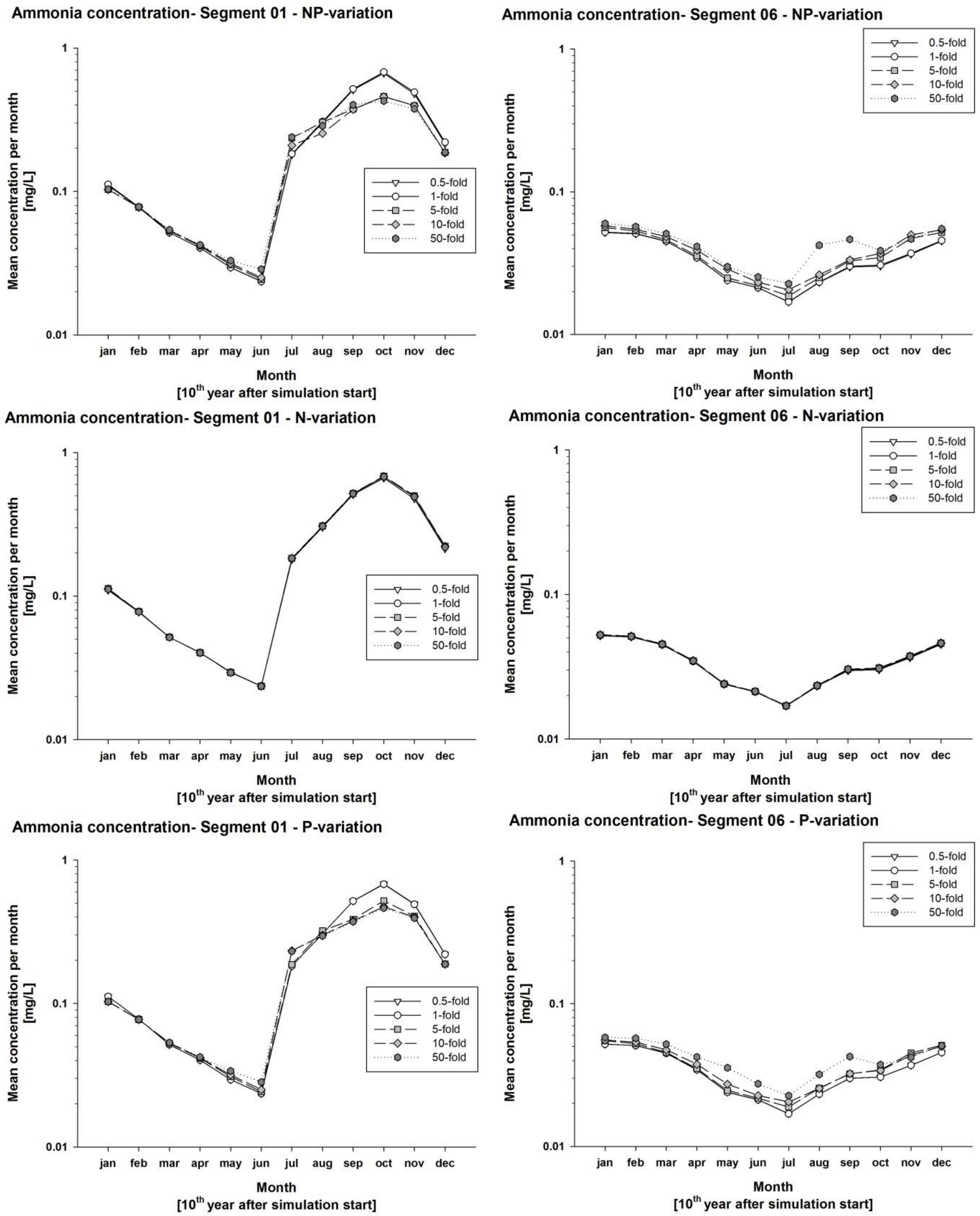
As a consequence of the differences in concentrations of total phosphate, densities of green algae varied dose-related in the lake segment 01 as well as in the example stream segment 06. The growth of most trophic levels (trophic guilds) highly depended on the phosphorous contents whereas the variation in nitrogen contents impacted the densities less. As an example, the population dynamics of green algae is shown in Figure VII-34. This finding could not completely be explained by the fraction of the total populations that were limited by the respective nutrients, 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 phosphorous concentrations (approx. 30% fraction limited for both groups). For blue-green algae, the limitation was similar with 70% nitrogen limitation and about 40% phosphorous limitation. This is because the system is severely P-oversaturated.

Blue-greens usually have a competition advantage in N-limitation or O_2 deficiency situations. This fact is represented in this model by the calibrated physiology in which the blue-greens have a P-half saturation rate of 0.03 mg/L and N-half saturation rate of 0.4 mg/L, whereas greens need 0.05 mg/L and 0.006 mg/L N-half saturation for half-saturation of growth rates.

The interpretation of the mere nutrient limitation was not sufficient to explain the complete picture of the population dynamics that depended on the nutrient variation. The patterns of primary producers densities over a representative year (here: year 15 after simulation start) emerged partially from complex interactions within the model that could not be ascribed to simple monocausal reasons.

The invertebrates e.g. daphnids that feed on the primary producers follow roughly the patterns predetermined by the phytoplankton organisms and thus reveal a relation to the nutrient contents in the water column as well. Since the daphnids as abstracted as a guild feeding on green, blue-green and diatom algae and detritus to the same amounts, the resulting pattern is influenced by complex biotic and abiotic factors. Following data analyses could dissect the single factors that influence the densities of organisms in more details because the AQUATOX simulation environment delivers a vast compilation of variables and formation or reduction rates.

For the herbivorous grass carp and the predatory black carp the simulation showed that densities depended on nutrient concentrations. Grass carps did not occur in stream segments (Figure VII-36 and Figure VII-37). For that reason a minimum number of individuals occurred in segment 06, most likely only supplied by migration of 1% of the upstream population from segment 07 and downstream migration from 05 but no stable population could be maintained.



Ammonia concentration- Segment 01 - NP-variation

Ammonia concentration- Segment 06 - NP-variation

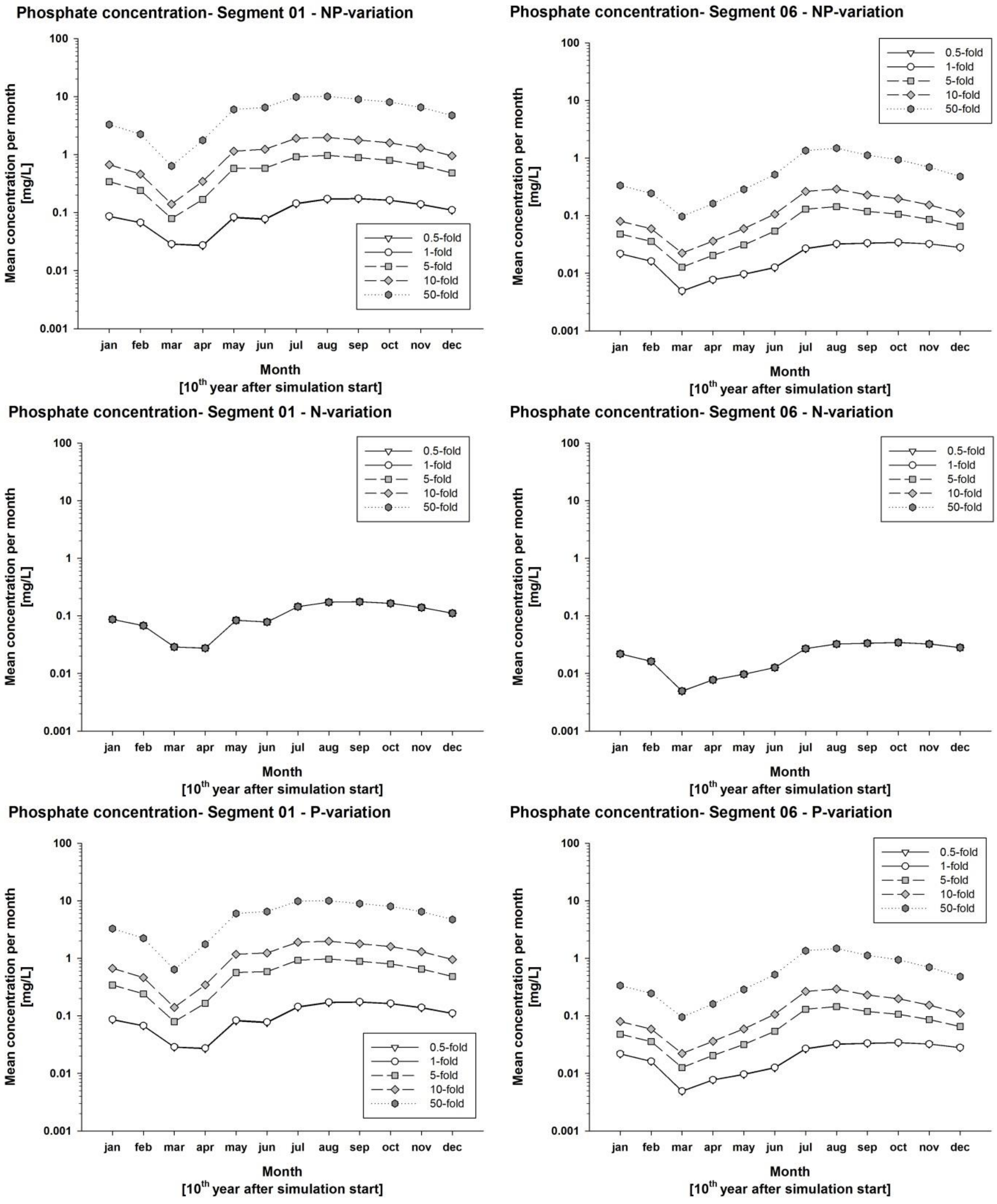
Ammonia concentration- Segment 01 - N-variation

Ammonia concentration- Segment 06 - N-variation

Ammonia concentration- Segment 01 - P-variation

Ammonia concentration- Segment 06 - P-variation

Figure VII-32: Ammonia concentrations after variation of phosphorous, nitrate and both phosphorous and nitrate loads from 0.5 to 50 fold of 0.3 mg P/L constant loading from upstream segments.



Phosphate concentration- Segment 01 - NP-variation

Phosphate concentration- Segment 06 - NP-variation

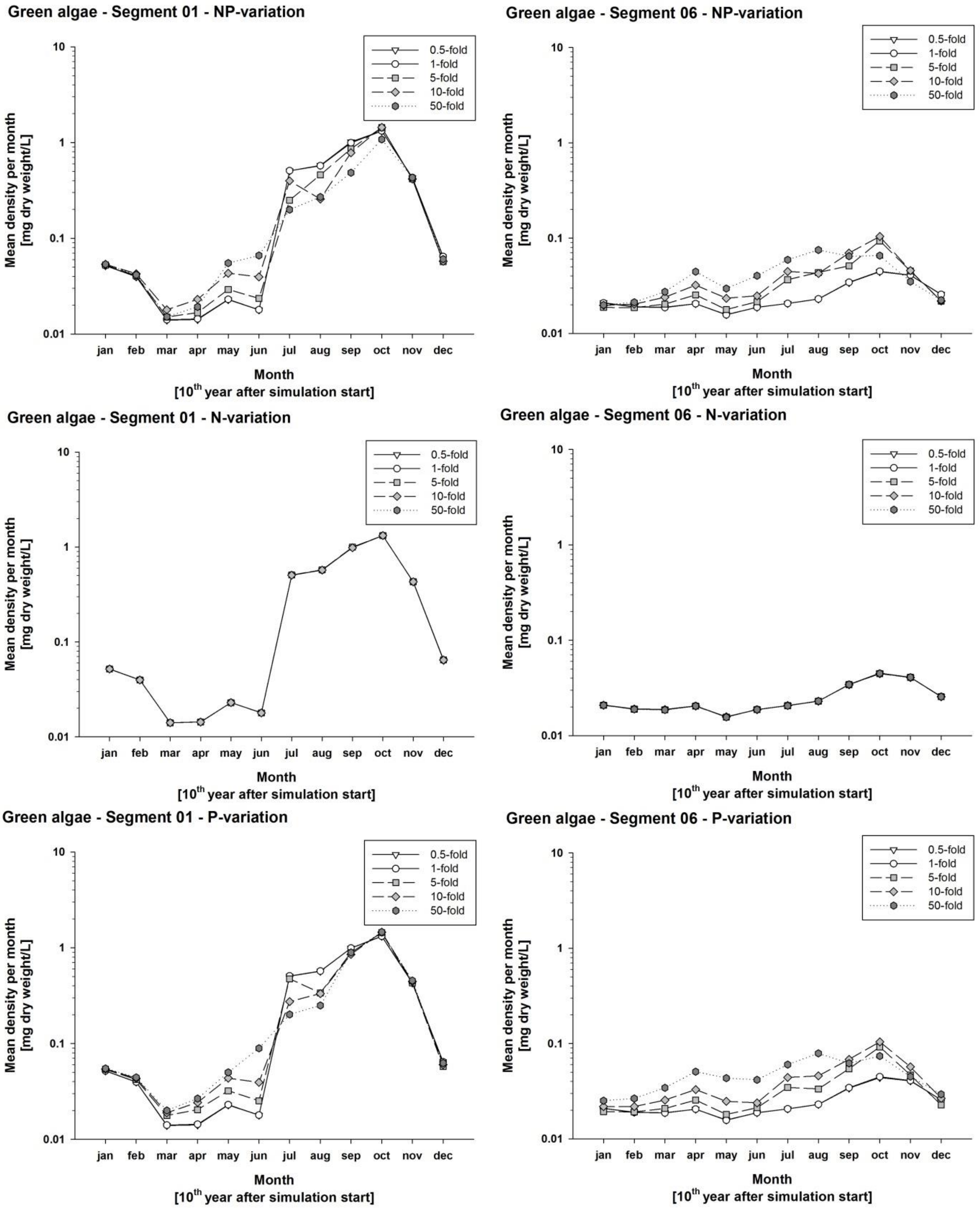
Phosphate concentration- Segment 01 - N-variation

Phosphate concentration- Segment 06 - N-variation

Phosphate concentration- Segment 01 - P-variation

Phosphate concentration- Segment 06 - P-variation

Figure VII-33: Phosphate concentrations after variation of phosphorous, nitrate and both phosphorous and nitrate loads from 0.5 to 50 fold of 5 mg Nitrate/L for segments 1 and 6.



Green algae - Segment 01 - NP-variation

Green algae - Segment 06 - NP-variation

Green algae - Segment 01 - N-variation

Green algae - Segment 06 - N-variation

Green algae - Segment 01 - P-variation

Green algae - Segment 06 - P-variation

Figure VII-34: Average densities of green algae (as biomass in mg/L) per month 10 years after start of the simulations.

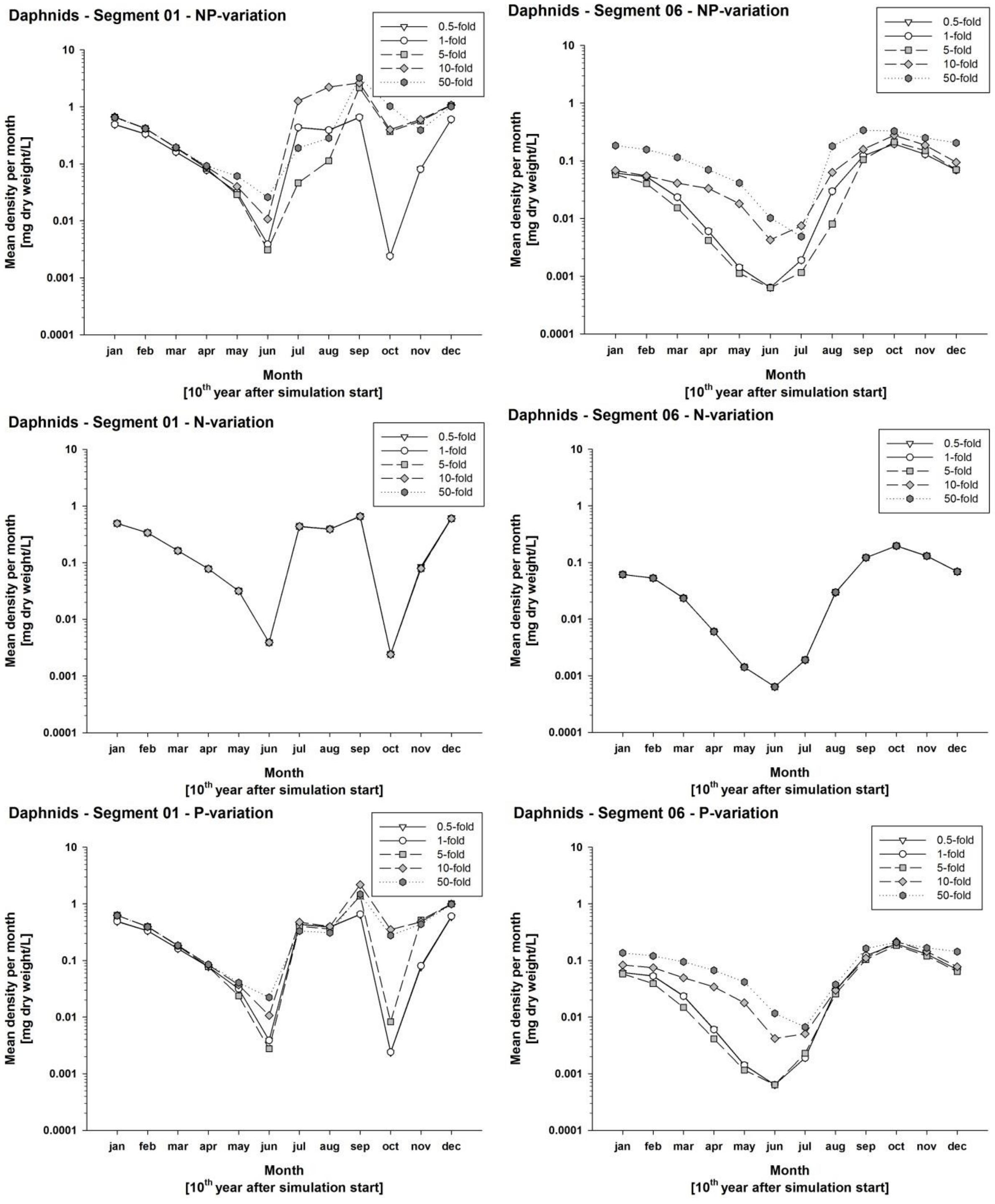


Figure VII-35: Average densities of daphnids (as biomass in mg/L) per month 10 years after start of the simulations.

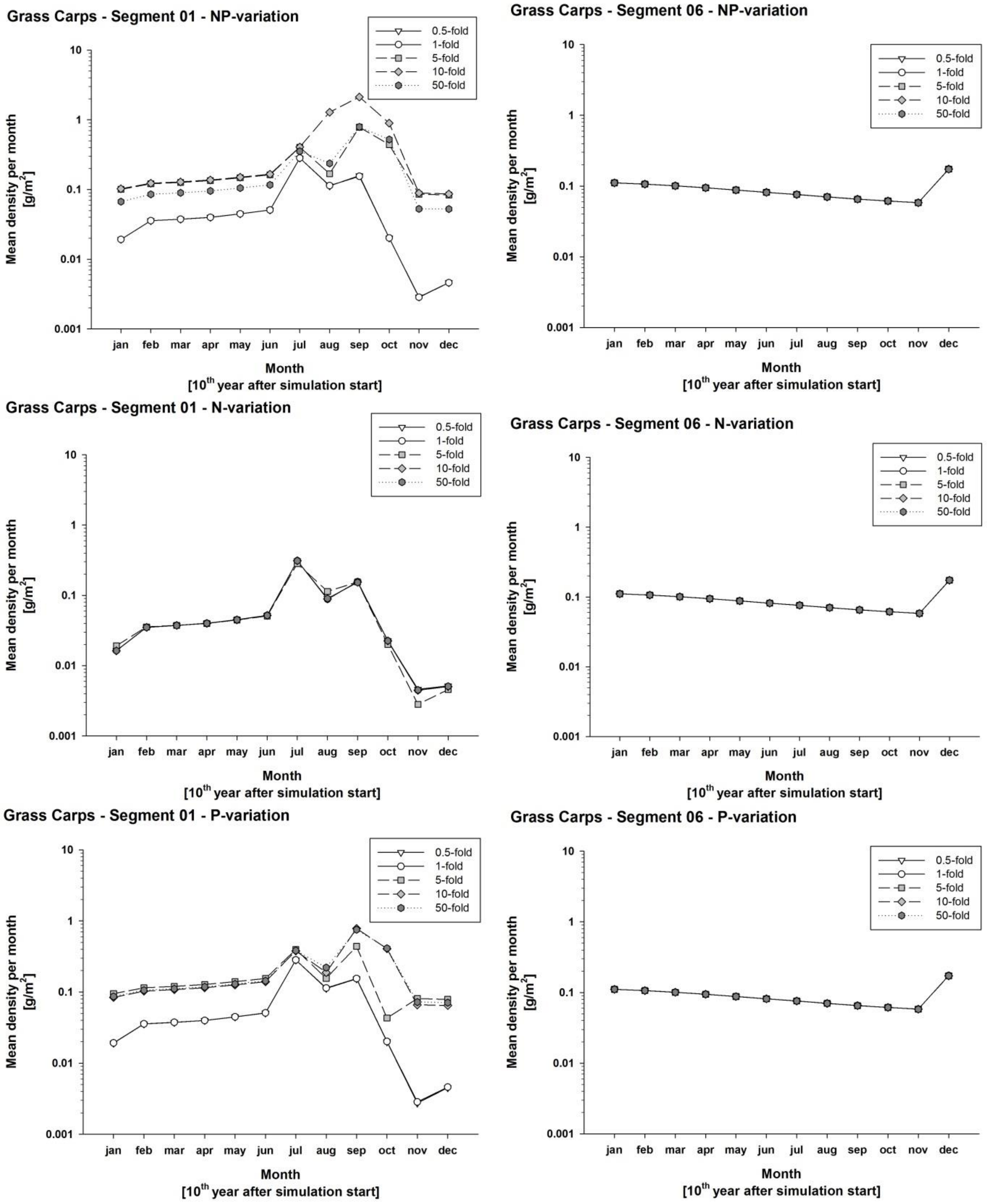


Figure VII-36: Average densities of grass carps (as biomass in g/m²) per month 10 years after start of the simulations.

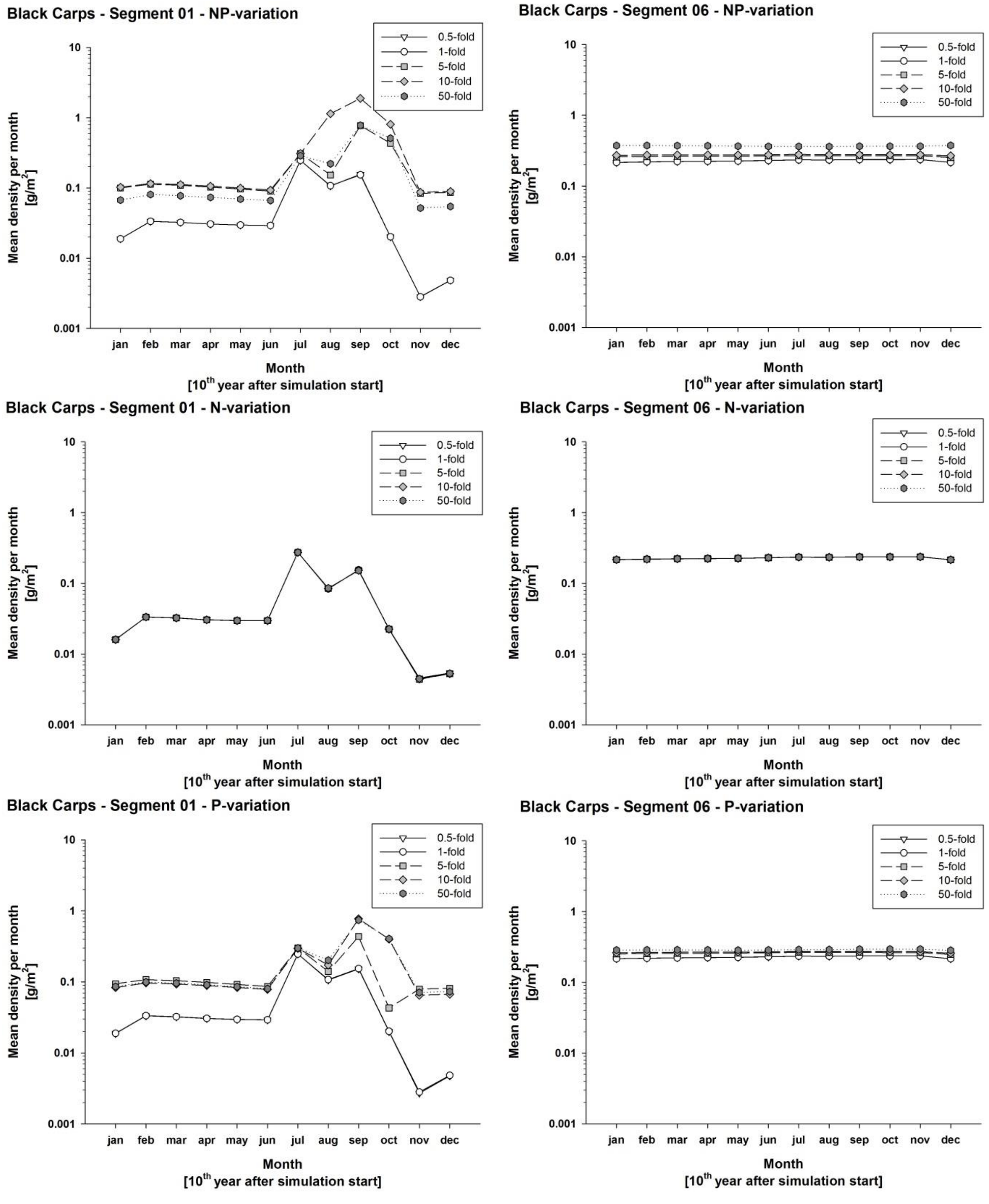
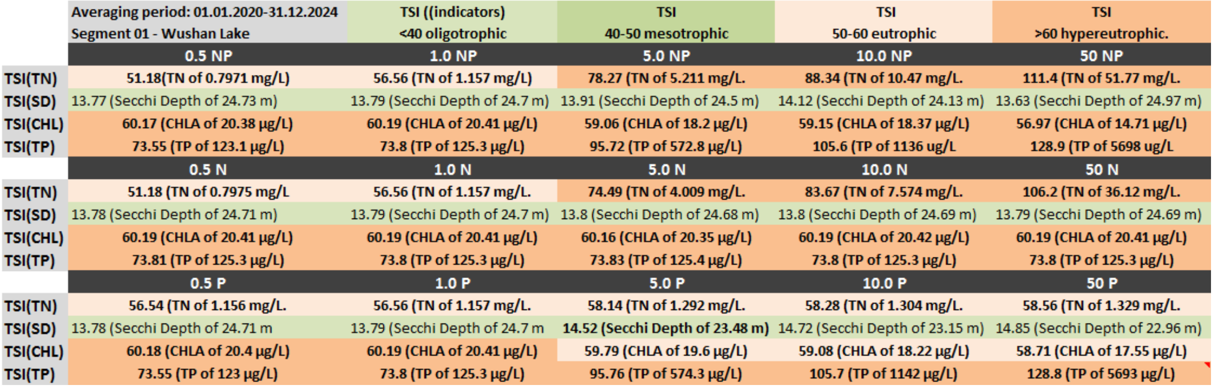


Figure VII-37: Average densities of black carps (as biomass in g/m²) per month 10 years after start of the simulations.

Summing up the analysis of the impact of different nutrient loads on the trophic guilds included in the AQUATOX simulation, it can be concluded that the system reaches a new level of trophic status only by adding huge amounts of nutrients. Due to high flow rates resulting in high dilution rates of nutrients the system is well buffered towards a massive introduction of nutrients. A significant increase of agricultural activity in the upstream areas of the Daning River could have minor impact on the communities of the aquatic organisms. However, the longer the free-flowing section, the less turbulent the water towards stagnant conditions and the longer the residence time of the water is, the more defined is the impact of nutrients in the TGD ecosystem. It has been shown by other authors that large scale algal blooms under the hydrodynamic preconditions of a relatively fast flowing tributary river 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 occur in spring, followed by a period of dominance of green algae in summer and in late summer the possibility of blue-green algae blooms is given (Schaumburg 1992). In the simulated ecosystem at the Daning River under sub-tropical conditions, the peaks of the guilds of diatoms, green 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 in the rainy season, they sampled in August. In April, during the dry season, densities were relatively lower. They concluded from their results that the decreased flow velocity led to the occurrence of algal blooms rather than a higher nutritional status.

A trophic classification of stagnant waters, for example of large flooded gravel pits in the ‘German system’ (compare LAWA 2003), takes several abiotic and biotic factors into account. A rude classification into five classes, oligotrophic, mesotrophic, eutrophic, polytrophic and hypertrophic can be achieved by the criteria ‘chlorophyll-a content, Secchi depth, total phosphorous (TP) in spring and TP in summer. Fortunately, the AQUATOX program provides trophic state indices based on the classification by the US Environmental Protection Agency (see Table VII-17, EPA 2000), which is almost the same but includes the water concentration of nitrogen instead of distinguishing between spring and summer TP. It is assumed applicable to lakes and reservoirs and should be used with care for the stream sections of the simulations and is therefore used for section 01 only. The analysis showed that the trophic state of the model regions last segment has been eutrophic to hyper-eutrophic anyway in the reference simulation 1-fold, even before increasing the loadings. This was the case for all segments up to the Dachang Lake. In 2009, up to 43 % of the primary tributaries of the TGD have been found eutrophic by the Chinese monitoring program accompanying the construction of the TGD (MEP 2010). It can be concluded that even massive extension of agriculture, which is unlikely because of the morphology of the adjacent hills of 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). The Secchi depth is the only measure that indicated an oligotrophic state of the reservoir, which seems to be very unlikely. The AQUATOX algorithms calculate the Secchi depth from the overall extinction, composed from phytoplankton, water and particulate and dissolved organic matter (POM, DOM). In our simulation, very small amounts of organic matter were added. It was up to genesis from biomass and thus staid 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 an average Secchi depth of about 40 cm has to be expected. Consequently, the Secchi measures have not been considered for further interpretation.

Table VII-17: Trophic State Indices (EPA 2000) for the last segment 01 of the model region before the confluence with the Yangtze River. The nutrient loadings had been varied systematically to look for dose-related shifts of the trophic level.



	Averaging period: 01.01.2020-31.12.2024 Segment 01 - Wushan Lake	TSI ((indicators) <40 oligotrophic	TSI 40-50 mesotrophic	TSI 50-60 eutrophic	TSI >60 hypereutrophic.
	0.5 NP	**1.0 NP**	**5.0 NP**	**10.0 NP**	**50 NP**
TSI(TN)	51.18(TN of 0.7971 mg/L)	56.56 (TN of 1.157 mg/L)	78.27 (TN of 5.211 mg/L.	88.34 (TN of 10.47 mg/L.	111.4 (TN of 51.77 mg/L.
TSI(SD)	13.77 (Secchi Depth of 24.73 m)	13.79 (Secchi Depth of 24.7 m)	13.91 (Secchi Depth of 24.5 m)	14.12 (Secchi Depth of 24.13 m)	13.63 (Secchi Depth of 24.97 m)
TSI(CHL)	60.17 (CHLA of 20.38 µg/L)	60.19 (CHLA of 20.41 µg/L)	59.06 (CHLA of 18.2 µg/L)	59.15 (CHLA of 18.37 µg/L)	56.97 (CHLA of 14.71 µg/L)
TSI(TP)	73.55 (TP of 123.1 µg/L)	73.8 (TP of 125.3 µg/L)	95.72 (TP of 572.8 µg/L)	105.6 (TP of 1136 ug/L	128.9 (TP of 5698 ug/L
	0.5 N	**1.0 N**	**5.0 N**	**10.0 N**	**50 N**
TSI(TN)	51.18 (TN of 0.7975 mg/L	56.56 (TN of 1.157 mg/L.	74.49 (TN of 4.009 mg/L.	83.67 (TN of 7.574 mg/L.	106.2 (TN of 36.12 mg/L.
TSI(SD)	13.78 (Secchi Depth of 24.71 m)	13.79 (Secchi Depth of 24.7 m)	13.8 (Secchi Depth of 24.68 m)	13.8 (Secchi Depth of 24.69 m)	13.79 (Secchi Depth of 24.69 m)
TSI(CHL)	60.19 (CHLA of 20.41 µg/L)	60.19 (CHLA of 20.41 µg/L)	60.16 (CHLA of 20.35 µg/L)	60.19 (CHLA of 20.42 µg/L)	60.19 (CHLA of 20.41 µg/L)
TSI(TP)	73.81 (TP of 125.3 µg/L)	73.8 (TP of 125.3 µg/L)	73.83 (TP of 125.4 µg/L)	73.8 (TP of 125.3 µg/L)	73.8 (TP of 125.3 µg/L)
	0.5 P	**1.0 P**	**5.0 P**	**10.0 P**	**50 P**
TSI(TN)	56.54 (TN of 1.156 mg/L.	56.56 (TN of 1.157 mg/L.	58.14 (TN of 1.292 mg/L.	58.28 (TN of 1.304 mg/L.	58.56 (TN of 1.329 mg/L.
TSI(SD)	13.78 (Secchi Depth of 24.71 m	13.79 (Secchi Depth of 24.7 m	**14.52 (Secchi Depth of 23.48 m)**	14.72 (Secchi Depth of 23.15 m)	14.85 (Secchi Depth of 22.96 m)
TSI(CHL)	60.18 (CHLA of 20.4 µg/L)	60.19 (CHLA of 20.41 µg/L)	59.79 (CHLA of 19.6 µg/L)	59.08 (CHLA of 18.22 µg/L)	58.71 (CHLA of 17.55 µg/L)
TSI(TP)	73.55 (TP of 123 µg/L)	73.8 (TP of 125.3 µg/L)	95.76 (TP of 574.3 µg/L)	105.7 (TP of 1142 µg/L)	128.8 (TP of 5693 µg/L)

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 is 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 & Clough 2010). Consequently, total ammonia concentrations were well below toxic thresholds.

7.5.3 *Bioaccumulation of model pollutants within the aquatic food webs*

(i) Rationales of the analysis

In the following, it was focused on the suspected bioaccumulative secondary metabolite TCAB, but the bioaccumulation behaviour of Propanil has also been modelled. The mechanism of downstream transport is assumed to be similar for DCA, Propanil and TCAB; however only TCAB should accumulate to toxic internal concentrations. To check that the model assumptions of AQUATOX work out, the behaviour of both substances has been simulated and the resulting concentrations have been compared.

Several questions arose from the perspective of an environmental risk assessment that could be addressed by simulation studies using the model herbicide Propanil and especially its secondary metabolite TCAB.

Is 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 is known to be not accumulative due to log KOW-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. For Propanil and especially TCAB, no literature data was available.

Are the water concentrations and the internal concentrations within the modelled organisms in 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. The ecotoxicologically important metabolite 3,4-DCA is known to be bound to the sediment and thus sediment-dwelling or feeding organisms (here: catfish) could be exposed to relatively high amounts. Similar assumptions were drawn for TCAB from the chemical properties of the substance.

The simulation ran for 25 years from 2012-2036. Results are shown for the middle period of 5 yrs. (2020-2024) after levelling of the system (Figure 38).

(ii) Results & Discussion

The model substances DCA, Propanil and TCAB were transported very fast to the last downstream segment of the model region before the confluence with Yangtze River (Wushan Lake, segment 01). The relatively highest water concentrations of nutrients and pollutants accumulated in the same place. This was mainly due to the fact that 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 exercises where the model substance TCAB was added to the water phase are shown for the Wushan Lake segment no. 01.

(a) Water concentrations Propanil and TCAB

The highest water concentrations of both Propanil and TCAB were modelled to occur after the second application period in mid-September in the downstream Wushan Lake segment with 0.01-0.06 µg TCAB/L.

(b) Internal concentrations TCAB

All of the modelled organisms (trophic guilds) accumulated TCAB within their tissues. From the guilds occurring in the lake segments of the simulations, catfish showed the highest mean concentrations of 40 mg/kg within the five year period evaluated (2020-2024). The primary producers showed mean concentrations of 300 µg/kg wet weight. Zooplankters and other fish like the carps showed internal concentrations between 650 and 22.000 µg/kg wet weights. Those very high peak concentrations could be questioned realistic. An earlier application of the AQUATOX model showed for the ‘Coralville reservoir’ standard study, that a peak concentration of 0.465 µg/L after applying 10 kg of the pesticide Dieldrin in a terrorist attack resulted in maximum internal concentration in shad of about 1 mg/kg wet weight

(Rashleigh 2007). Dieldrin has, comparable to TCAB, a very high Octanol-Water partition coefficient of 5 (TCAB 5.84). The variable values regarding the concentrations in water after short-time application and the internal concentrations within the organisms in our simulation seem to be plausible for very bioaccumulative chemicals. A considerable amount of TCAB was fixed for a certain time in refractory and labile detritus fractions, in particular in particulate and sediment fractions. All of the fish guilds feed partly on detritus, and thus an additional uptake path is given beyond direct uptake via the water phase or biomagnification via other organisms.

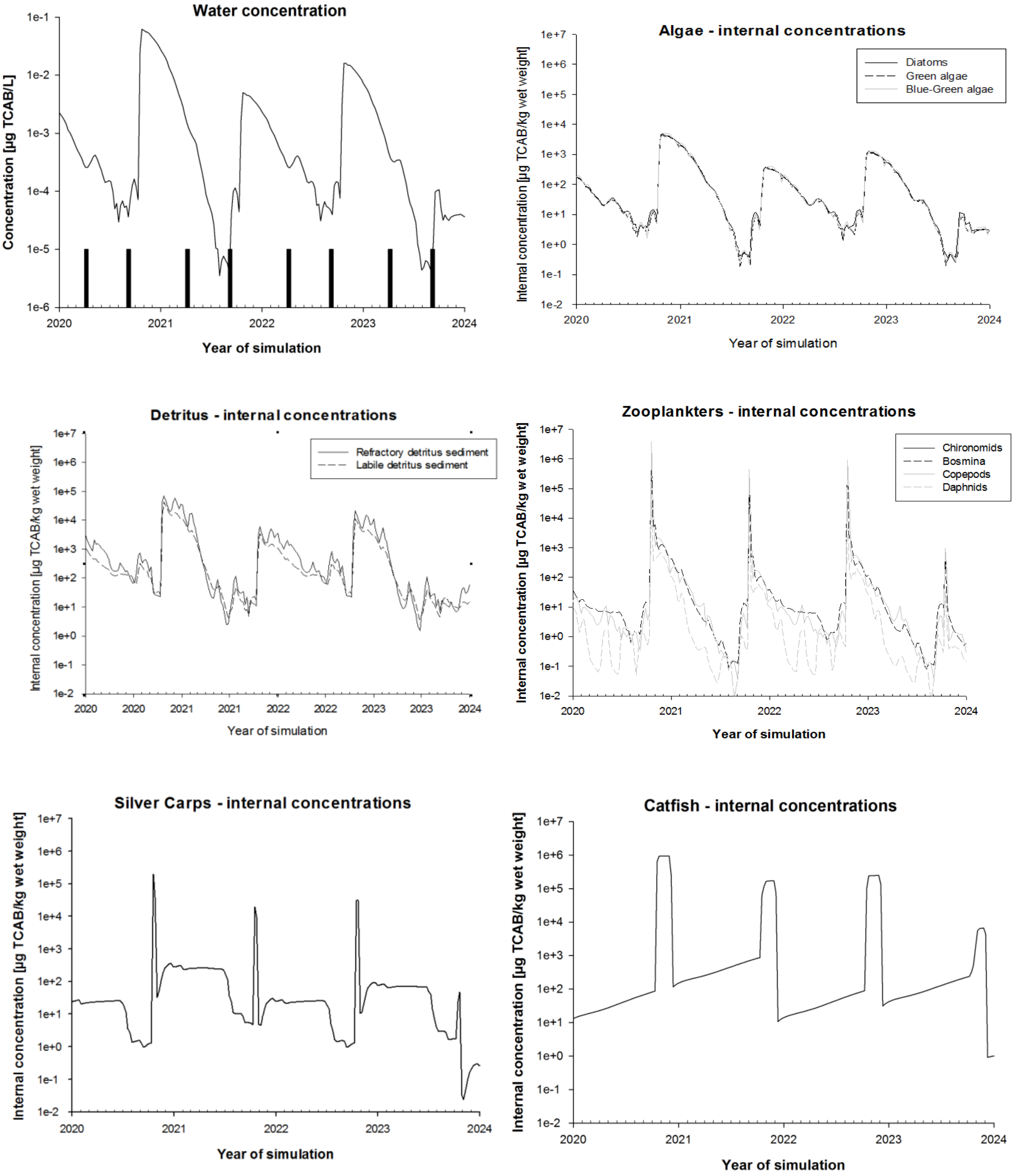


Figure VII-38: Water and internal concentrations of TCAB in species-guilds at segment 01 of the model region at the Daning River.

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

(c) Toxic Effects

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. for 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.

Altogether it can be seen that TCAB accumulates along the food chains in the TGR environment. Nevertheless, no clear food chain effect, no strong biomagnification can be deduced from the results for silver carps that have a broad spectrum of food items.

For the interpretation of the results it is important to know that bioaccumulation within the AQUATOX model in large fish is determined by gill uptake and dietary uptake, while the elimination from the organisms' tissues can be expressed as functions of excretion and biotransformation processes (Park & Clough 2010).

7.6 Summary and conclusions module bioaccumulation-Outlook to Environmental Risk Assessment

Model development and adjustment

The simulation environment provided by the AQUATOX software has been a powerful tool and an excellent starting point for the adaptation to the specific situation at a tributary reach of the Yangtze River. The estimates of many parameters needed for the adjustment of the model could be rather taken from the literature or formulated as generic assumptions. The modelling approach proved to be useful to understand some basic principles of such a tributary system that was strongly influenced by the TGR water level fluctuations. It was very 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 data has been under lock and key. However, the adjustment of the simulation environment led to widely plausible results, in terms of orders of magnitude of organism densities and the dynamics of the system.

It can be concluded that our integrated approach can be used for a huge variety of research questions in the future, beyond basic 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.

Bioaccumulation of model Pesticides

As we have shown by the analysis of land-use patterns, an exposure to plant protection products, in particular rice herbicides, can be expected for the model region at the confluence of Daning and Yangtze rivers.

The aquatic food web of the TGR-model contains several interconnected trophic levels. Together with high the $\log K_{OW}$ of the suspect metabolite TCAB a significant biomagnification of this secondary metabolite was expected. Basically, this expectation has been confirmed by the simulation studies shown and discussed here. In particular, stagnant downstream sections of tributaries like the Daning River exhibit comparably high risk of accumulating pesticides from upstream sources. We recommend managing the upstream catchment areas or more comprehensively the whole catchment area regarding sustainable pesticide use. This can be achieved e.g. by the introduction of the principles of Integrated Pest Management, that is 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 at al. 2014) often exceeding the recommended concentration levels (Floehr & Xiao et al. 2013).

Nutrients

Under adverse site conditions, like stagnating flowing-sections, nutrients showed a profound, non-linear influence on the model outcome. We demonstrated this influence on populations and communities of feeding guilds in virtual dose-response simulation experiments. Even high nutrient loads have been shown to result in only slight impacts on densities of organisms of all trophic levels. The system seems saturated due to high nutrient concentrations, so that e.g. phosphate is 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 is eutrophic, but the risk for large scale algal blooms affecting the drinking water quality even in the Wushan Lake is small because of the high flow velocities and discharge rates to the Yangtze River.

Outlook Risk assessment

The simulation of the situation at the downstream Daning River allows for the deduction of internal concentrations within fish as the main animal protein source of the local population. Informed on the maximum residue levels in food items and the maximum daily intake rates of the respective model substances Propanil, 3,4-DCA and TCAB, human risk assessment is possible in principle using our adjusted AQUATOX model. Nevertheless, at the moment further adjustment of model assumptions is necessary before realistic human risk assessment can be done. Due to a lack of sufficient data for the environmental risk assessment and the toxicology of this active substance and its main metabolite 3,4-DCA, Propanil was not approved for the use in the European Union (European Commission 2011, EFSA 2013)) Thus, despite the suitability of our modelling approach, there is substantial lack of information to do a proper risk assessment of Propanil at the moment.

8 Ecotoxicity of sediments and biomarker analysis for toxic stress

8.1 Embedding in overall problem

Due to a number of factors, the newly created ecosystem of the Three Gorges Reservoir faces several challenges, e.g. increasing pollution. As a consequence of the impoundment, which was completed in October 2010, 13 cities, 140 towns and over 1,300 villages have been submerged in addition to more than 1,600 factories and abandoned mines. They bear the potential to release remaining contamination into the reservoir. Beyond, more than a 1.24 million people had to be resettled and found new homes along the river, concentrating on the major cities - like Chongqing with more than 29 million citizens in 2011 - , which also due to general urbanization continue to grow. This will trigger an increasing amount of wastewater in the urbanized regions along the Yangtze River. The elevation of the water level in the TGR region also improved the navigation of large container ships between Sandouping and Chongqing, and thus became an essential factor for the economic development of this region. Besides the increased traffic, the growing industry will entail new and increasing discharge of pollutants. Another factor is that the construction of the dam reduced the flow velocity of the river for about one magnitude, changing this section of the Yangtze River from river-like to lake-like. This has a serious influence on the dilution of the pollutants that enter the water body, and also an impact on the sedimentation rate of suspended particles. A large variety of organic pollutants, like PAHs, PCBs and numerous pesticides, tend to bind to particulate matter that is suspended in the water and will form sediment. The sediment functions as a sink for these contaminants from which they can again be remobilized (Brinkmann et al. 2010). The Yangtze River is one of the largest sediment carriers in the world. Before the construction of the TGD the annual sediment load was 320 Mt/yr (1993-2002) (Mt = 10^6 tons), measured at Datong, the tidal limit of the Yangtze River (Yang et al. 2007). The TGD represents an obstacle for the natural sediment transport, but operates sluice gates to flush down the sediment that settles down in front of it. However, since the operation of the dam annually 151 Mt of sediment have been trapped in the TGR (2003-2005), which accounts for about 64% of the sediment entering the TGR from upstream (Yang et al. 2007). Furthermore, periodical changes of about 30 m in water level cause flooding events and thereby a relocation of contaminated water, particulate matter and sediment onto agriculturally used areas along the reservoirs shore.

8.2 Objective (areas of concern, pattern, problematic substances)

Although a large number of studies have been performed along the Yangtze River, the TGR section remains a black box, little illuminated only by a couple of studies mainly focusing on the chemical analysis of pollutants in the compartments water and sediment (Hollert et al. 2000, Floehr et al. 2013). Thus, it is reasonable to ask (a) what is the current pollution status of this newly created ecosystem, which is a source of food and water for millions of people, (b) are there any hotspot areas and (c) how large is the impact of the tributaries on the Yangtze mainstream. Furthermore has to be asked (c) in what way is the local fauna, e.g., fish species, affected and (c) which would be the responsible priority pollutants?

8.3 Method

In order to assess if ecotoxicological effects be related to adverse effects in fish from the field, sediment samples and fish were analysed using a weight-of-evidence (WOE) approach with several lines of evidence as previously addressed by Chapman & Hollert (2006). The sediment and fish samples have been taken at 4 major tributaries (Jialing River – Chongqing, Long River – Fengdu, Pengxi River – Yunyang, Daning River - Wushan) in addition to an artificial lake in the TGR drainage basin (Hanfeng Lake - Kaixian) and a reference site (Baijiaxi River/Pengxi River Wetland Nature Reserve). The sediment has been sampled at each site in the Yangtze mainstream upstream (MSUT) and downstream (MSDT) of the tributary as well as in the tributary itself. The sediment has been extracted with acetone-hexane (1:1), and the extracts have been further analysed.

Table VII-18: Overview on sampling campaigns in module 'Ecotoxicology'

Period	Sampling	Area	Locations (Figure VII-39)
16.09. - 30.09.2011	Sediment	Chongqing Fengdu Yunyang Wushan Kaixian	CNG Up, CNG Down, JL River FEN Up, FEN Down, LN River YUN Up, YUN Down, PX River WU Up, WU Down, DN River HF Lake, BJX River
26.04. -14.05.2012	Fish	Chongqing Fengdu Yunyang Wushan Kaixian	TGR mainstream TGR mainstream TGR mainstream TGR mainstream Hanfeng Lake, Baijiaxi River
23.04. -09.05.2013	Sediment & Fish	Chongqing Kaixian	YAN Up, YAN Mid, YAN Down, JIA Up, JIA Mid, JIA Down, TGR Up, TGR Down HAN A, HAN B, HAN C, HAN D

Briefly, (i) a comprehensive battery of acute (Growth Inhibition Test with *Desmodesmus subspicatus*, Acute Immobilisation Test with Daphnia magna and the Fish Embryo Toxicity

Test with *Danio rerio*) and mechanism-specific bioassays (EROD Assay, Ames Fluctuation Assay and Yeast Estrogen Screen) have been applied to characterize the ecotoxicological hazard potential of the sediment in addition to (ii) the analysis of selected organic pollutants (PAHs, PCBs, pesticides, flame retardants, etc.) with GC-MS. (iii) Biochemical investigations and the micronucleus assay with erythrocytes have been applied at the model fish species *Pelteobagrus vachellii*, a bagrid catfish, representing in situ parameters.

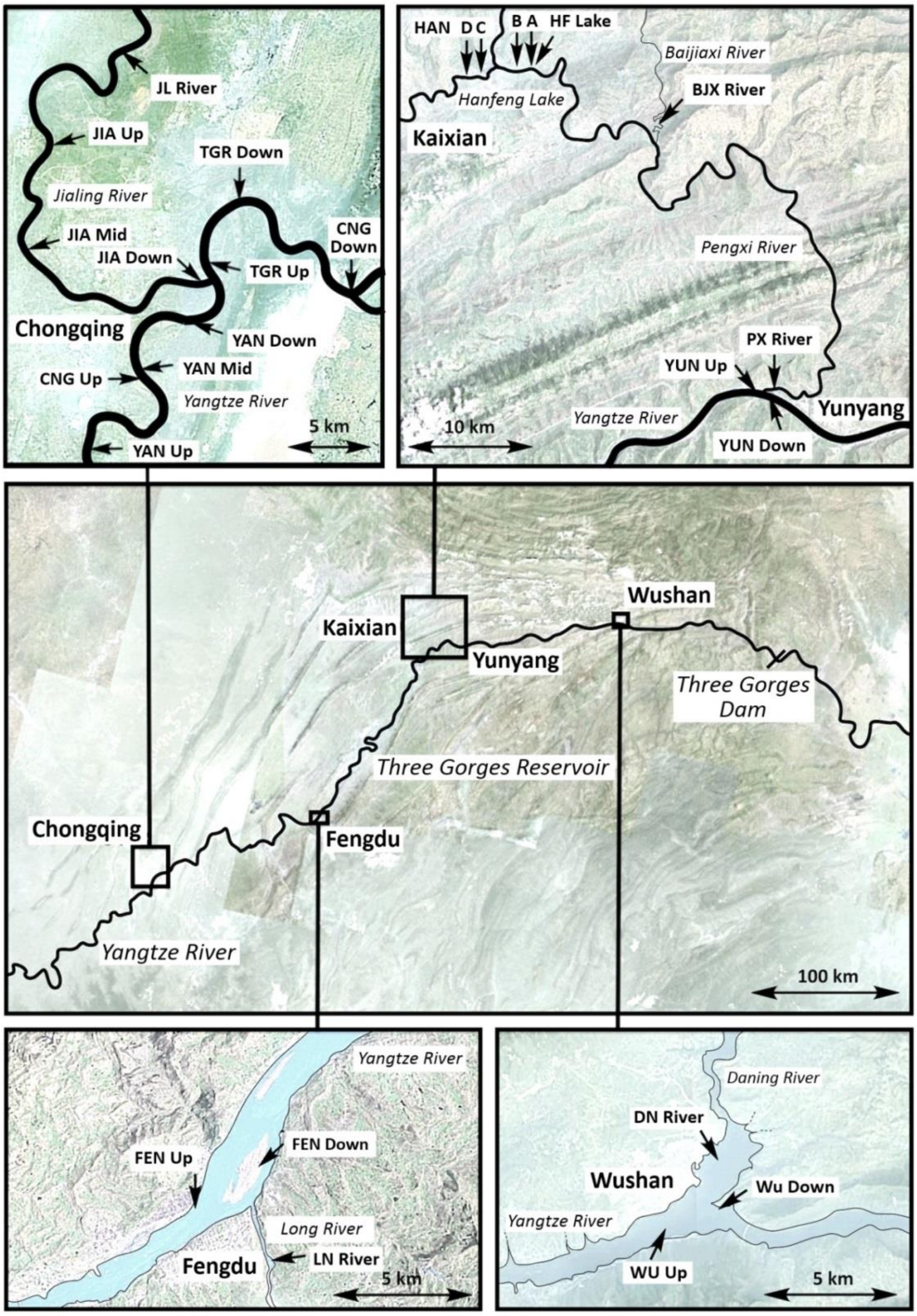


Figure VII-39: Overview map of sediment sampling sites at Yangtze River and tributaries (modified satellite pictures by Google Earth).

8.4 Ecotoxicological evaluation of sediments at selected sites

During the first sampling campaign, sediment has been taken at major tributaries along the Yangtze River in regular distances to evaluate the selected areas in order to (a) identify potential hot spot areas and (b) understand the impact of the tributaries on the Yangtze River mainstream.

8.4.1 *Acute Toxicity*

(i) Growth Inhibition Test with Desmodesmus subspicatus

This assay was performed according to OECD guideline 201 (OECD 2011) with sediment extracts and aims at the endpoint growth inhibition of the selected test species *Desmodesmus subspicatus.* The results displayed no significant effects. (data not shown).

(ii) Acute Immobilisation Test with Daphnia magna

This test was performed according to the guideline OECD 202 (OECD 2004) with sediment extracts and aims at the endpoint immobilisation/lethality of the test species Daphnia magna. As an additional aim the assay has been modified in order prolong the test duration from 48h to 96h, as suggested by Dabrunz et al. (2011) to see if an extended exposure reveals significant differences in immobilisation/lethality. The results show that in most cases no EC50 could be determined, because the effect of the samples on the daphnia was too low. EC50 values could be calculated for the mainstream downstream of Chongqing (CNG Down) (47 mg SEQ/ml), Long River (20 mg SEQ/ml), Daning River (19 mg SEQ/ml), Hanfeng Lake (209 mg SEQ/ml) and Baijiaxi River (131 mg SEQ/ml) after an exposure for 48 h (data not shown). After an exposure for 96 h the impact increased on the same samples, displayed by a decreased EC50, CNG Down (7 mg SEQ/ml), Long River (11 mg SEQ/ml), Daning River (15 mg SEQ/ml), Hanfeng Lake (12 mg SEQ/ml) and Baijiaxi River (36 mg SEQ/ml), and in addition to that Jialing River (120 mg SEQ/ml) (data not shown). Besides the identification of the above mentioned effects it was considered reasonable to prolong the Acute Immobilisation Test in order to approach the situation in the field reflected by an extended exposure time.

(iii) Fish Embryo Toxicity Test (FET) and Sediment Contact Assay (SCA) with Danio rerio

Both assays aim at the endpoints lethality and sublethal effects in embryos and larvae of the test species *Danio rerio*. Both assays have been performed over duration of 96 h, where the fish eggs have been exposed to freeze dried sediment in the SCA, to reveal the bioavailable toxicity, and to sediment extracts in the FET, to analyse the maximum toxic potential of the sediments. In the SCA all samples showed effects on the fish eggs only in range of the negative control (0-10% effect) (data not shown). In the FET lethality could only be detected for the samples Long River (EC50 50 mg SEQ/ml) and Hanfeng Lake (EC50 30 mg SEQ/ml).

The toxicity of the sediment extracts displayed by the sublethal effects ranged from medium to low. The pattern of toxicity was in 3 out 4 sites at the mainstream: upstream > tributary > downstream. The tributaries did not seem to add their toxicity to those from upstream. The sample with the highest impact was Hanfeng Lake (EC50 9.79 mg SEQ/ml).

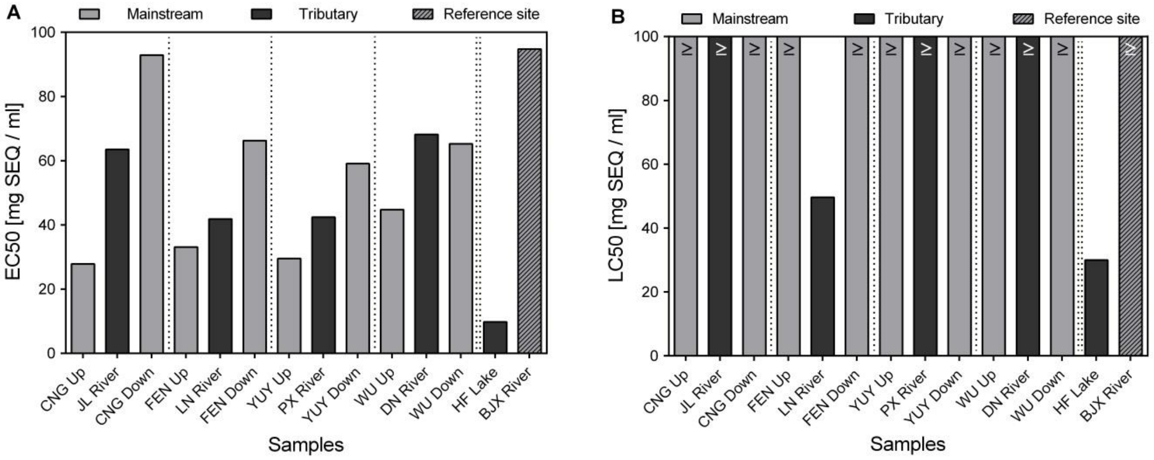


Figure VII-40: EC_{50} (mg SEQ/ml) values for sublethal effects (A) and lethality (B) of embryos and larvae of *Danio rerio* after the exposure with sediment extracts for 96 h; Sampling campaign September 2011; Legend: SEQ = Sediment Equivalent; ≥ = EC50 ≥ 100 mg SEQ/ml (maximum test concentration); CNG = Chongqing, FEN = Fengdu, YUY = Yunyang, WU = Wushan, JL = Jialing, LN = Long, PX = Pengxi, DN = Daning, HF = Hanfeng (part of Pengxi River), BJX = Baijiaxi (part of Pengxi River Wetland Nature Reserve).

8.4.2 *Mechanism-specific toxicity*

(i) AMES Fluctuation Assay with Salmonella typhimurium

Sediment extracts have been analysed in the AMES Fluctuation Assay, aiming at the endpoint mutagenicity, with the bacteria strains *Salmonella typhimurium* TA98 (frameshift mutagen indicator) and TA100 (baseshift mutagen indicator) with and without bioactivating liver enzymes (S9-mix). Only the mainstream downstream sample at Yunyang (YUN Down) showed a significant effect (NOEC 200 mg SEQ/mL) at strain TA100 with S9-mix, whereas no sample displayed a significant effect at the same strain without S9-mix (data not shown). For strain TA98 only the mainstream downstream sample at Chongqing (CNG Down) revealed a significant effect without S9-mix (NOEC 200 mg SEQ/mL) (data not shown). The most samples showed mutagenic impacts with strain TA98 and S9-mix Figure VII-41 indicating the presence of promutagenic substances that induce frameshift mutations. The most significant samples were JL River, FEN Down, WU Up and WU Down (NOEC 25 mg SEQ/ml), followed by CNG Up and YUN Down (NOEC 50 mg SEQ/ml) and CNG Down, LN River, YUN Up and PX River (200 mg SEQ/ml). For better comparison with other sites the maximum induction factor (IFmax) was calculated, a theoretical value that describes the effect strength. These results showed that with exception of the sampling site of Chongqing the upstream mainstream samples had a lower mutagenic potential than the downstream samples. The mutagenicity of the tributary samples differed in their potential compared to the mainstream. Furthermore, the samples Jialing River (IFmax 7.2), Long River (IFmax 3.4), FEN Down (IFmax 7.7), YUY Down (IFmax 4.6), Daning River (IFmax 3.9) and WU Down (IFmax

6.34) Hanfeng Lake (IFmax 3.4) displayed a maximum induction factor (IFmax) larger than 3.3, which indicates a potential threat for fish populations (Keiter et al. 2009).

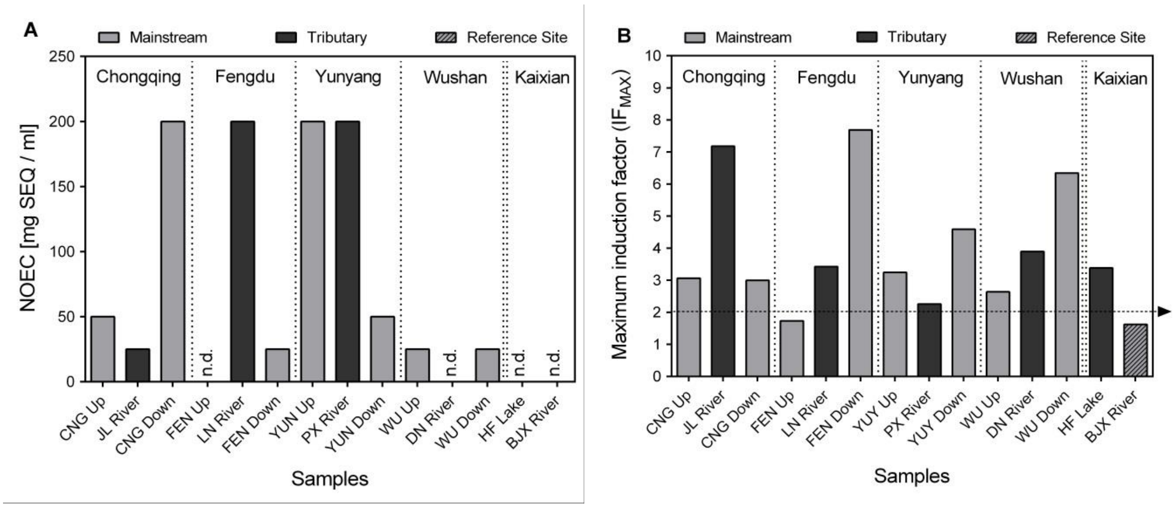


Figure VII-41: (A) No observed effect concentration (NOEC) and (B) maximum induction factors (IFmax) from the exposure of the *Salmonella typhimurium* TA98 strain (+ S9-mix) with sediment extracts; Sampling campaign September 2011; Legend: SEQ = Sediment Equivalent; n.d. = not determinable; CNG = Chongqing, FEN = Fengdu, YUY = Yunyang, WU = Wushan, JL = Jialing, LN = Long, PX = Pengxi, DN = Daning, HF = Hanfeng (part of Pengxi River), BJX = Baijiaxi (part of Pengxi River Wetland Nature Reserve).

(ii) YES Assay with Saccharomyces cerevisiae

The Yeast Estrogen Screen, aiming at the endpoint endocrine (estrogenic) activity by binding the estrogen receptor, with the genetically modified yeast *Saccharomyces cerevisiae* by Routledge & Sumpter (1996) was performed with sediment extracts in a modified version according to Schultis & Metzger (2004) using Lyticase. For none of the samples a dose-response curve could be determined, because estrogenic activity was too low and cytotoxicity was induced in the upper concentration range. A comparison of the estradiol equivalents (EEQs) at a concentration of 25 mg SEQ/ml shows a maximum of 7 ± 2 ng EEQ/L in the sample from the Pengxi River (data not shown). The upstream mainstream samples had a higher estrogenic potential than the downstream samples. The estrogenicity of the tributary samples differed in their potential compared to the mainstream.

(iii) EROD Assay with RTL-W1 cells

The Ethoxyresorufin-O-deethylase (EROD) Assay with rainbow trout liver cells (RTL-W1) aims at the endpoint dioxin-like activity by the activation of the arylhydrocarbon receptor. The results show that the toxicity of the sediment extracts can be classified as low to medium according to Keiter et al. (2009). The pattern of toxicity is in 3 out of 4 sites at the mainstream similar to the fish egg assay: upstream > tributary > downstream. The most toxic samples were the mainstream upstream sample at Yunyang (YUN Up) (BioTEQ EC25 1161 ± 326 pg TCDD/ g sediment) and Hanfeng Lake (BioTEQ EC25 1063 ± 253 pg TCDD/ g sediment) (Figure VII-42).

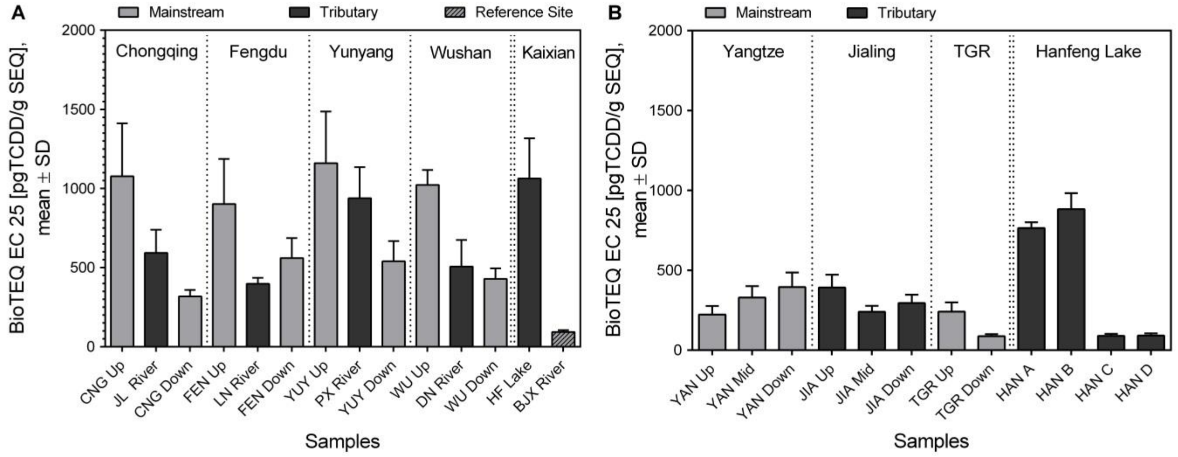


Figure VII-42: BioTEQ 25 (pg TCDD/g sediment) values from the exposure of RTL-W1 cells with sediment extracts; Sampling campaign (A) September 2011 and (B) May 2011; Legend: SEQ = Sediment Equivalent; CNG = Chongqing, FEN = Fengdu, YUY = Yunyang, WU = Wushan, JL = Jialing, LN = Long, PX = Pengxi, DN = Daning, HF = Hanfeng (part of Pengxi River), BJX = Baijiaxi (part of Pengxi River Wetland Nature Reserve).

8.4.3 *Chemical analysis of organic toxicants in sediments*

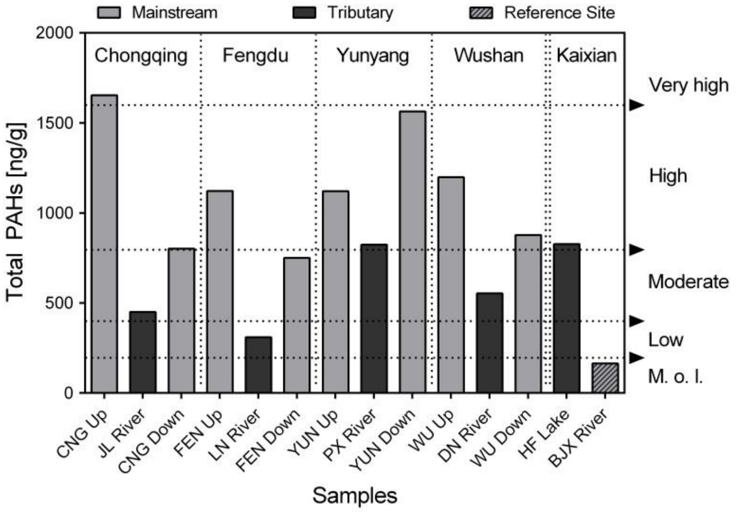


Figure VII-43: Total PAH content (ng/g sediment) in sediment extracts; Sampling campaign September 2011; Legend: Arrows = Threshold values according to ICRP (2009); Legend: CNG = Chongqing, FEN = Fengdu, YUY = Yunyang, WU = Wushan, JL = Jialing, LN = Long, PX = Pengxi, DN = Daning, HF = Hanfeng (part of Pengxi River), BJX = Baijiaxi (part of Pengxi River Wetland Nature Reserve).

The sediment extracts have been analysed by co-workers of the project partner IWW in Mühlheim for 54 organic contaminants using a gas chromatography–mass spectrometry (GCMS). The analysed compounds were: 16 Polycyclic Aromatic Hydrocarbons (PAHs), 6 Polychlorinated Biphenyls (PCBs), 12 insecticides, 5 herbicides, 15 other toxic and bioaccumulative substances, flame retardants and byproducts from chemical production. The detection limit was 10 ng/g sediment. Out of all substances only PAHs could be measured, which ranged in most cases from a low (> 400 - 800 ng PAHtotal/g sediment) to moderate (> 800 - 1,600 ng PAHtotal /g sediment) content (ICRP 2009). Only the mainstream upstream sample at Chongqing (CNG Up) can be classified as highly contaminated (1653 ng/g sediment), whereas the total PAH burden of Long River (310 ng PAHtotal/g sediment) and Baijiaxi River (165 ng PAHtotal/g sediment) ranged in the maximum objective load (≤ 400 ng/g sediment) (ICRP 2009).

The samples with the highest total PAH burden were all upstream mainstream samples at the sites Chongqing (CNG Up) (1653 ng/g sediment), Fengdu (FEN Up) (1122 ng/g sediment), Yunyang (YUN Up) (1121 ng/g sediment) and Wushan (WU Up) (1198 ng/g sediment) as well as the downstream mainstream sample at Yunyang (YUN Down) (1563 ng/g sediment).

The dominating compounds (> 750 ng/g sediment) were fluoranthene, phenanthrene, chrysene, pyrene, benzo[b]fluoranthene and benzo[g,h,i]perylene. Whereas acenaphthylene, acenaphthene, fluorene, anthracene, benzo[k]fluoranthene and dibenz[a,h]anthracene belonged to the substances that could be measured in a lower range (< 750 ng/g sediment; > 10 ng/g sediment).

8.5 Ecotoxicological evaluation of effects on a model fish species (Pelteobagrus vachellii)

In order to supplement the sediment toxicity data gained from the first sampling, in a second campaign fish have been taken at the same sites (Table VII-18) and investigated with respect to several biomarkers to determine any toxicological impacts on the fish. Based on the information of the first and second campaign a third campaign has been initiated to more closely examine two identified areas of concern – Chongqing and Kaixian.

8.5.1 *Micronucleus Assay with erythrocytes of Pelteobagrus vachellii*

The formation of micronuclei in erythrocytes of the model fish species *Pelteobagrus vachellii* indicates genotoxic effects on the fish. For the sampling campaign May 2012 by comparison of the micronucleus frequency between the different sampling sites none of the mainstream sites at Chongqing, Fengdu, Yunyang and Wushan showed any significant differences to the reference site Baijiaxi River(0,200 ± 0,158 ‰). Only samples from Hanfeng Lake at Kaixian (0,400 ± 0,175 ‰) revealed a significant difference (Mann-Whitney-U-Test, $p < 0.05$). This could be confirmed by the sampling campaign in May 2013 where an even stronger significant genotoxic impact (Mann-Whitney-U-Test, $p < 0.01$) was identified in the fish from the same lake (1,450 ± 2,040 ‰). In addition, the fish from Chongqing (2,250 ± 2,073 ‰) from the same year displayed a highly significant genotoxic influence (Mann-Whitney-U-Test, $p < 0.01$) (Figure VII-45). Both indicate a serious impact on the fish in these areas.

Figure VII-44: Model fish species *Pelteobagrus vachellii.*

8.5.2 *Histological alterations in tissues of P. vachellii*

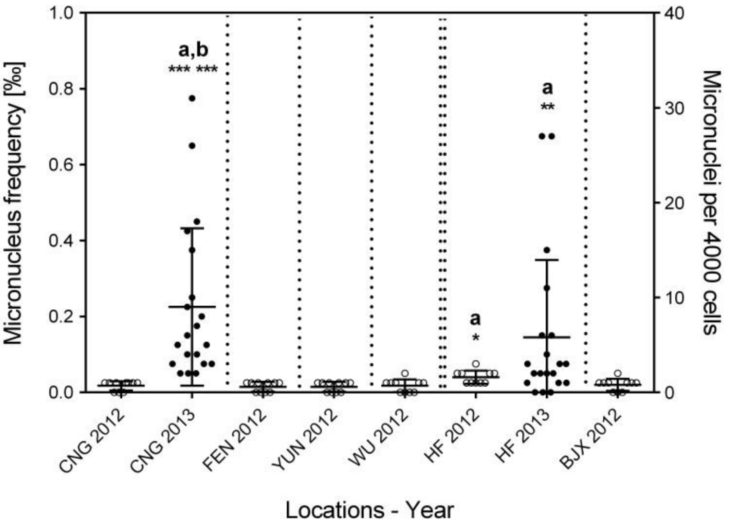


Figure VII-45: Micronucleus frequency [‰] in erythrocytes of P. vachellii; Legend: CNG = Chongqing, FEN = Fengdu, YUY = Yunyang, WU = Wushan, HF = Kaixian, Hanfeng Lake (part of Pengxi River), BJX = Kaixian, Baijiaxi River (part of Pengxi River Wetland Nature Reserve); 2012 = Sampling campaign May 2012 (n = 10); 2013 = Sampling campaign May 2013 (n = 20); Data were statistically analysed with Mann-Whitney U test; a = significant difference compared to reference site BJX 2012; b = significant difference compared to same site in 2012; * = $p < 0.05$; ** = $p < 0.01$; *** = $p < 0.001$.

Liver and kidney samples from fish catched in May 2012 have been closely examined for histological alterations (cooperation with Prof. Helmut Segner, University of Berne). Regarding the kidney tissues particularly the infiltration of macrophages and giant cells (Chongqing, Fengdu, Wushan), the multifocal accumulation of macrophages (Yunyang, Wushan), the degeneration of melano-macrophage aggregates (Chongqing), as well as the deposition of crystals (Chongqing) could be observed. However, integrated over the whole catch of fish (n = 10) none of the mentioned criteria was significant in its grade of manifestation compared to the reference site Baijiaxi River (ANOVA on ranks; multiple comparison; followed by Dunn's test; $p < 0.05$). Still, these criteria can be related to inflammation reactions and as response to foreign matters in the tissues, e.g. parasites. In Chongqing 30 %, as well as Fengdu 10 % and Wushan 10 % of the catch were afflicted by the trematode *Isoparochis hypselobagri* (Figure VII-46), which settled in the swim bladder, on the kidney and digestive tract. The appearance of the trematodes also closely correlated with the occurrence of infiltration of macrophages, the degeneration of melano-macrophage aggregates and the deposition of crystals in the livers of fish from Chongqing. Furthermore, lymphoid tissue around the biliary tract (Fengdu, Yunyang, Hanfeng Lake, Baijiaxi River) and its proliferation (Yunyang, Hanfeng Lake, Baijiaxi River), as well as the karyopyknosis and degeneration of hepatocytes (Baijiaxi River) could be observed in the liver tissues. These primarily account for inflammation reactions. Here also, integrated over the whole catch of fish (n = 10) none of the mentioned criteria was significant in its grade of manifestation compared to the reference site Baijiaxi River (ANOVA on ranks; multiple comparison; followed by Dunn's test; $p < 0.05$). Though not significant the observed effects can indicate negative environmental impacts, as pollution can suppress the immune system of fish, thus increasing the chance for parasites to enter and settle in the host.

Figure VII-46: (A) Model fish species *Pelteobagrus vachelli* afflicted with (B) trematode *Isoparochis hypselobagri* displaying the typical symptom of intestines covered in dark mucus.

8.5.3 *PAH metabolites in bile of P. vachellii*

During the sampling campaign in May 2012 bile fluid was sampled from each fish from all sites in order to determine the content of PAH metabolites (cooperation with the Johann Heinrich von Thünen Institute in Hamburg, Dr. Ulrike Kammann). Due to the small available volumes the samples (n = 10) had to be pooled into three replicates per site. The results showed that the concentration of 1-Hydroxypyrene per bile volume were comparable to those in German rivers. However, differences between the sampling sites in terms of the bile colour could be detected, indicating also a difference in the nutrition conditions (data not shown). Whereas the fish from Chongqing, Fengdu, Yunyang and Hanfeng Lake were comparable to the reference site Baijiaxi River, the fish from Wushan showed the best nutrition status, but also the highest content of PAH metabolites. Meaning, that they were either exposed to particularly high concentrations of PAHs or were catched in an extreme situation. In comparison, the fish from Baijiaxi and Yunyang displayed the lowest contamination with PAHs.

8.5.4 *Intermodular Experiment*

In order to investigate the impact of the model pesticide Propanil and its metabolites on fish embryos of *Danio rerio* under simulated conditions (compare chapter 'Fate' VII6) a parallel setup was run to the main fate experiment. The aim was to show the effects of bioavailable compounds on the fish embryos. Whereas the fate setup was run with radioactive labelled Propanil, the ecotoxicology setup was run with unlabelled Propanil under the same conditions with three replicates and controls per dedicated sampling timepoint. Meaning, after 30 days the spiked soil was also submerged with water and at day 33, 42, 50 and 60 days per replicate and control 20 fish eggs were placed on the submerged soil and incubated for 96 h at 26°C. However, at no sampling timepoints a significant difference to the corresponding negative controls could be observed.

8.5.5 *Identification of areas of concern*

The Hanfeng Lake at Kaixian as well as the Yangtze and Jialing River at Chongqing could be identified as potential areas of concern based on the performed bioassays and biomarker studies in the first and second sampling campaign. Both areas resemble regions that rely strongly on their corresponding water bodies.

Therefore, the third sampling campaign has been undertaken to concentrate on these areas and to resample sediments in a closer grid to identify potential transitions in toxicity in these water bodies. The combined sampling of a higher number of fish should help to put the correlation of potential toxic impacts on a broader basis. Whereas the sediment toxicity was only in a low to medium level, the genotoxic effects manifested in the erythrocytes of *Pelteobagrus vachellii* from the Hanfeng Lake and the TGR at Chongqing also indicate a potential ecological threat. A toxicity reduction evaluation is recommended in these areas.

Overall only low to medium toxicity could be discovered, which stands in contrast to the expectations. However, it is reasonable to assume that this observation is based on the strong dilution capacity of the Yangtze River. Its mean water discharge at Yichang (13,700 m^3/s) (Yang et al. 2007) is more than 6 times greater compared to this of the Rhine River (2,200m^3/s) (Huisman et al. 2000). But this also implicates that at the same contamination levels in both rivers, the 6-fold amount of toxic substances would still enter the receiving water body, depending on the hydrological conditions in this case the East China Sea. Dilution is not the solution for a pollution problem, because contaminants that enter the system at one point do not disappear, they are deposited somewhere else and accumulate - especially persistent pollutants, like the here identified main sediment contaminants, the PAHs. One may argue that the Three Gorges Dam is a barrier for suspended particulate matter and sediment that settles in front of the dam. However, the installed sluice gates transport these sediments through the dam and thus influence the areas downstream.

The bioassays aiming at acute toxicity revealed only little impact. Especially the Sediment Contact Assay, which demonstrated the impact of the bioavailable fractions on the fish eggs and larvae the showed that the animals were not affected when exposed over a short exposure period of 96 h.

Detached from the total level of toxicity, regular patterns could be discovered. In most cases (FET_{effect}, EROD, YES) the upstream mainstream sample showed a higher ecotoxicological potential than the downstream samples of the same site, which also correlates with the chemical analysis. In addition these potentials increased from the downstream sample of one site to the upstream sample of the next major tributary further downstream (e.g., CNG Down to FEN Up), indicating an addition of toxicity between those areas. It has also to be noted that the tributaries did not add their toxic potential to the upstream potential, which should result in a combined potential downstream. However, this was not the case. It is suggested that due to the backwater pressure from the mainstream the water of the tributaries takes a long time to be incorporated into the mainstream (Holbach et al. 2013), meaning that this hydrological trap influences the sedimentation of the suspended particles, which eventually settle down in this conversion zone.

8.5.6 *Identification of problematic compounds*

The chemical analysis identified only PAHs out of 54 possible substances as present in the sediment extracts. The total PAH content was in a low to moderate range (maximum 1653 ng/g sediment; sample CNG Up). The dominating compounds (> 750 ng/g sediment) were fluoranthene, phenanthrene, chrysene, pyrene, benzo[b]fluoranthene and benzo[g,h,i]perylene. The pattern of total PAH content (Upstream > Downstream) correlates with the results from the EROD assay with RTL-W1 cells, with exception of sample YUN Down. It has to be considered that besides the Total PAH content also the individual induction efficiency of each PAH has an influence on the EROD induction (Bosfeld et al. 2002). YUN Down possessed a comparably high percentage of chrysene (50 %) which is a strong inducer of EROD activity (Bosfeld et al. 2002).

8.5.7 *Recommendations for pursuing monitoring (evaluation of the applied concept)*

The applied concept has been proven as a useful method to monitor the TGR region. The results demonstrated that it is crucial to integrate the media water, sediment and biota in order to get a holistic picture. An evaluation of the area based only on chemical analysis resembles not the realistic status. The selection of bioassays was based on the criteria feasibility, cost effectiveness and significance. In this context, all assays can be further recommended. However, the FET based on the DIN EN ISO 15088 guideline (DIN 2009) and the adopted SCA (Hollert et al. 2003) have proven to be particularly efficient tools for acute toxicity testing. Especially due to the FETs correlation to the conventional acute fish test OECD testing guideline 203 (OECD 1992, Lammer et al 2009). The prolonged testing period from 48 h to 96 h was also considered elementary, because the chorion, which still surrounds the embryo after 48 h but not anymore after 96 h, seems to function as a specific barrier for toxicants (Henn und Braunbeck 2011, Strähle et al. 2012). The AMES Assay, depicting mutagenicity, as well as the EROD assay, depicting arylhydrocarbon receptor mediated dioxin-like activity, can particularly recommended for further monitoring covering mechanism specific effects. Based on our review (Floehr et al. 2013) mutagenicity was of prior interest, whereas dioxin-like activity was hardly investigated, which was surprising as the identified priority pollutants PAHs interact with the arylhydrocarbon receptor.

Due to its high ecological relevance further *in situ* testing is also strongly recommended. The model fish species *Pelteobagrus vachellii* shows several positive criteria: (a) ubiquitous distribution along the TGR (b) in sufficient numbers as a (c) bottom feeder and thus close interaction with the media sediment and water. Sampling of blood for the micronucleus assay with erythrocytes, depicting genotoxicity, is a quick and simple procedure. The sampling of bile and subsequent analysis of PAH metabolites in context of the project was not considered efficient due to the small bile volumes in the sampled individuals of the model fish species. Whereas the histological investigations delivered interesting results, but requested educated staff with long-time experience. Summarizing, a combination of chemical analysis, *in vitro* and *in vivo* testing, especially supported by *in situ* investigations is considered crucial for an integrative monitoring of the region.

8.6 Summary of ecotoxicological results

Summarizing it can be stated that the detected toxicity only ranged from a low to moderate level, and is in most cases comparable to the status of German rivers. Two areas of concern could be identified: the Hanfeng Lake at Kaixian and the Jialing-Yangtze River system at Chongqing. Significant genotoxic effects in erythrocytes of *Pelteobagrus vachellii* could be detected in both areas. A toxicity reduction evaluation is highly recommended in both regions. Among 54 investigated substances - PAHs, PCBs, pesticides, other toxic and bioaccumulative substances, flame retardants and by-products from chemical production - only PAHs could be identified above a detection limit of 10 ng/L. Furthermore, by comparison of the individual toxicities of the sampling sites it seemed that the tributaries did not add their toxicity to the corresponding upstream samples of the Yangtze mainstream, resulting in a combined toxicity downstream. A reason could be that the backwater pressure of the mainstream is so high that the flow velocity of the tributaries is reduced to a minimum in the conversion zone, resulting in a sedimentation of the suspended particulate matter carried by the tributary, creating a 'hydrological trap' (Holbach et al. 2013). It could also be observed that the toxicity of the downstream samples of one sampling site increased to the next site further downstream, indicating an input of toxicants between these areas. Although the overall toxicity was at a low to moderate level the overall magnitude of the water system has to be taken into account. The mean water discharge at Yichang (13,700 m^3/s) (Yang et al. 2007) is more than 6 times greater compared to this of the Rhine River (2,200m^3/s) (Huisman et al. 2000). But this also implicates that at the same contamination levels in both rivers, the 6-fold amount of toxic substances would still enter the receiving water body. Dilution is not the solution for a pollution problem, because contaminants that enter the system at one point do not disappear, they are deposited somewhere else and accumulate - especially persistent pollutants, like the here identified main sediment contaminants, the PAHs. One may argue that the Three Gorges Dam is a barrier for suspended particulate matter and sediment that settles in front of the dam. However, the installed sluice gates transport these sediments through the dam and thus influence the areas downstream.

9 Overall conclusion - Summary of results of the MICROTOX research project

9.1 Basic hypotheses and objectives

The main objective of the MICROTOX project has been to generate ideas on the impact of the construction and the operation of the Three Gorges Dam on the processes of transformation, bioaccumulation and –magnification as well as on the toxicity of organic micropollutants in sediments, soils and waters on the best possible scientific basis. It was presumed that the long periods of flooding would lead to remobilisation processes and thus to a higher pollution of the main streams and its tributaries compared to the situation before the dam was fully operating. In the fate part of the MICROTOX project, it was investigated whether the metabolism of common pesticidal compounds would lead to toxic metabolites and how environmental conditions (fluctuating water levels) would influence the fate of pesticides. The objective of the ecotoxicological part of the MICROTOX project was to assess (i) possible links between molecular/biochemical responses and ecologically relevant effects, and (ii) if ecotoxicological effects might be related to adverse effects in fish from the field. Sediment samples and fish were collected at different locations in the Three Gorges Reservoir as well as its catchment area and analysed using a weight-of-evidence (WOE) approach with several lines of evidence. Both, sediment and fish samples have been taken at major cities as well as feeder rivers and their estuaries along the Yangtze Three Gorges Reservoir in order to characterize the state of contamination and the potential risk for human and wildlife. The monitoring strategy should help to observe the water body's quality and to serve as a basis to initiate if necessary counteractive measures.

The sub-project 'bioaccumulation' aimed at a deeper understanding of the processes that determine the bioaccumulation of organic pollutants, mainly pesticides, within aquatic food chains focusing on the tributary rivers. For this purpose, we simulated quantitatively the internal concentrations of chosen model pollutants in ecologically and economically important fish species, under the influence of pollution scenarios representative for worst-case situations at the TGR, using the ecosystem model 'AQUATOX'. We analysed different agricultural land use patterns and nutrient loads under the fluctuating water level regime caused by the mode of operation of the dam. The concept of this integrated modelling procedure required input data from various scientific disciplines such as ecotoxicology, environmental analysis, ecology and hydrology.

9.2 Interconnections and mutual benefits between the three parts of the MICROTOX project

In the run-up, many interconnecting aspects between the three parts of the MICROTOX project were identified. It turned out to be very difficult to fulfil the specific requirements of e.g. the model calibration by data that was collected for different purposes. However, the combination of experimental work, monitoring and simulations, which also means a combination of retrospective and prospective angles, allowed for deeper insights in the mechanisms of ecotoxicity than the single modules ever could.

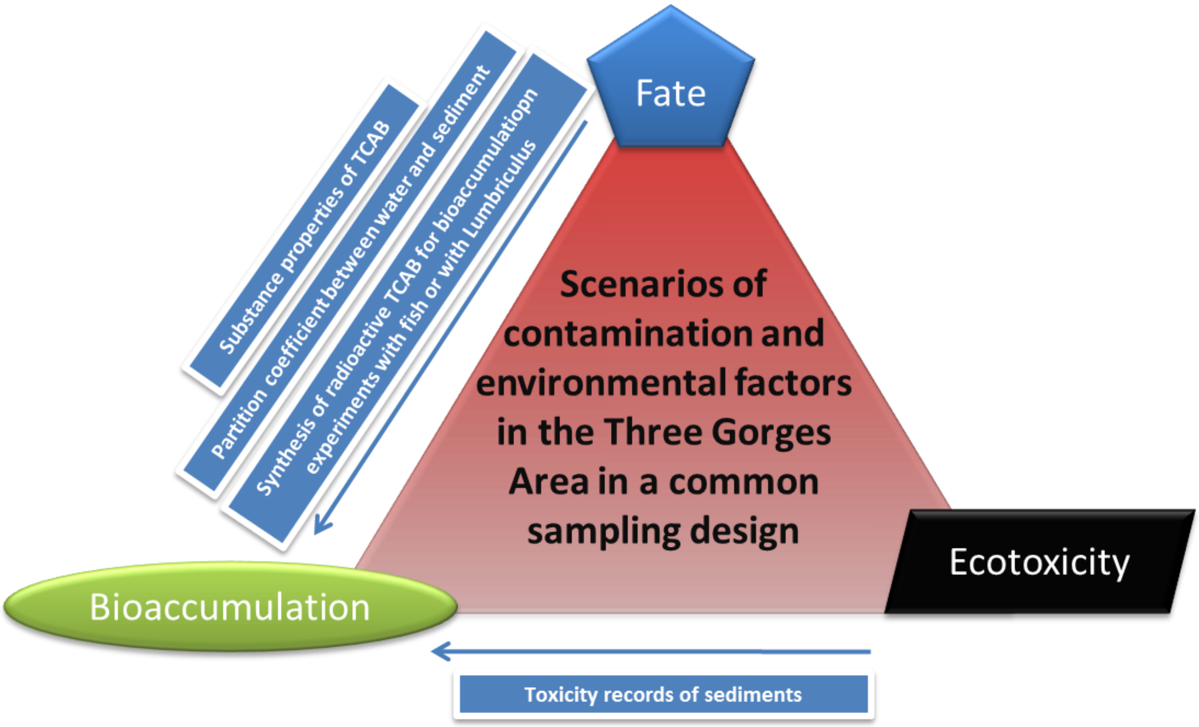


Figure VII-47: Interactions and interfaces of data exchange between the three project modules 'fate of model substances', modelling of bioaccumulation' and 'ecotoxicity of sediments and biomarkers' of the MICROTOX project.

Experiments using sediment extracts delivered acute and mechanism-specific toxicity measures that were well-suited for comparative assessments but had a qualitative, black-box character.

In follow-up experiments (PhD thesis Hongxia Xiao, MSc Thesis of Yan Yan) with the model substances Propanil and its metabolites 3,4-DCA and TCAB standard toxicity values have been acquired (results not subject of this report) that could be used for the calibration of particularly the AQUATOX model for the widely undescribed metabolite TCAB. The methodology for testing the ecotoxicological impact of parent and metabolized pesticidal compounds has been developed by the MICROTOX project and is ready to use in the future.

In order to avoid the black box character of testing sediment eluates, it was planned to conduct a handover experiment from the water-sediment-systems spiked with Propanil from the fate module to a fish egg assay in the Ecotox module (see chapter 8).

Calibrated ecosystem model available

The simulation environment provided by the AQUATOX software has been a powerful tool and an excellent starting point for the adaptation to the specific situation at a tributary reach of the Yangtze River. The estimates of many parameters needed for the adjustment of the model could be rather taken from the literature or formulated as generic assumptions. The modelling approach proved to be useful to understand some basic principles of such a tributary system that was strongly influenced by the TGR water level fluctuations. It was very 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 data has been under lock and key. However, the adjustment of the simulation environment led to widely plausible results, in terms of orders of magnitude of organism densities and the dynamics of the system.

Relevance of the model substance

The relevance of the model substance chosen in this project was high. At the time of the start of the project, it was intensely used in China and the re-evaluation process for the inclusion in annex I of the European pesticide legislation was running. Nowadays, Propanil is still used in China, although in some regions other pesticides have been introduced as substitutes. As we assumed, in the risk assessment of the European Union the active substance turned out to be problematic in the meantime and was not granted for use in European rice cultures (European Commission 2011, EFSA 2011, 2013). In particular, no sufficient data on the degradation in soils and water-sediment-systems, furthermore, data on consumer toxicity of metabolites were available and there was a high risk to birds, mammals, aquatic organisms and non-target arthropods.

Identification of most relevant pollutants

For the TGR-region, it can be concluded from a thorough literature survey within the MICROTOX project (Floehr & Xiao et al. 2013) and from measurements of RWTH Aachen University and our cooperation partners within the Joint Hydro-projects, that PAHs can be identified as priority pollutants at TGR. Most of the measurements that point to PAHs come from water and sediment samples, for fish tissues this finding was not confirmed.

Out of 54 investigated organic substances only PAHs could be detected in the sediments. PCBs, herbicides, insecticides, flame retardants, by-products from chemical production and other toxic and bioaccumulative substances were below the detection limit of 10 ng/g sediment. Among the PAHs Fluoranthene, Phenanthrene, Chrysene, Pyrene, Benzo[b]fluoranthene und Benzo[g,h,i]perylene were the dominant substances. The total PAH content was low to moderate. The comparison of the total PAH content of each sampling site displayed the following order: MSUT > MSDT > tributary. The samples from the Hanfeng Lake at Kaixian showed the highest total PAH content (827 ng/g sediment).

Biotests elucidate the biological effectiveness of the complex environmental samples; however, the substances responsible for the effects are remaining unclear. One approach to identify the substances causing adverse effects in the biotests is the effect-directed analysis (EDA). As an additional line of evidence MSc Hongxia Xiao (CSC stipendium until end of the year 2015) is using EDA with open column and HPLC fractionation to identify the toxic substances. Up to now several moderate polar PAHs have been identified to cause the majority of the AhR-mediated (=Dioxin-like) activities. However, for mutagenicity and endocrine effects also more polar fractions are of relevance. In ongoing follow-up investigations the polar fractions are characterized by Hongxia Xiao using a more sophisticated Effect-directed fractionation approach for polar compounds (co-operation with the Helmholtz-Zentrum for Environmental Research, Leipzig, Dr. Brack).

9.4 *Identification of effects*

9.4.1 *Effect assessment of sediment (in vitro and in vivo)*

The sediments induced a moderate to strong mutagenicity in the Ames Fluctuation Assay. The Yangtze mainstream downstream the tributary (MSDT) revealed higher activity than the Yangtze mainstream upstream the tributary (MSUT). Furthermore, the samples Jialing River, Long River, FEN Down, YUY Down, Daning River, WU Down and Hanfeng Lake displayed a maximum induction factor larger than 3.3, which indicates a potential threat for fish populations (Keiter et al. 2009). The sediments caused a low to moderate dioxin-like activity in the EROD assay as well as low to moderate sublethal effects in the Fish Embryo Toxicity Test. Here the MSUT revealed higher activity than the MSDT. The tributaries did not seem to add their activity to the MSUT activity. Overall the samples from the Hanfeng Lake at Kaixian appeared to be most active.

9.4.2 *Adverse effects in aquatic organisms (in situ studies) / areas of concern*

The Hanfeng Lake at Kaixian as well as the Yangtze and Jialing River at Chongqing could be identified as potential areas of concern based on the performed bioassays and biomarker studies. Both areas resemble a region that relies on their corresponding water bodies. The genotoxic effects manifested in the erythrocytes of *P. vachellii* from the Hanfeng Lake also indicate a potential ecological threat. A toxicity reduction evaluation is recommended.

9.5 *Characterisation of the environmental risks*

The toxic metabolite 3,4-DCA is rapidly formed when Propanil is degraded in water sediment systems. 3,4-DCA as a priority pollutant is also formed by several other pesticides with related substructures. The fate of DCA is subsequently dominated by formation of non-extractable residues (NER). Low amounts of potentially toxic follow-up metabolites of DCA were formed, most important tetrachloroazobenzene (TCAB). The toxicity of this potentially mutagenic substance will be studied in separate experiments. TCAB is also formed in low amounts by degradation of Propanil (< 5% of the applied Propanil amount). TCAB has – like DCA – a high affinity to sorb to the sediment, but itself shows a low tendency to form NER, i.e., it is easily extracted from sediments by organic-aqueous solvent mixtures. Studies with fluctuating water regimes – incubation of Propanil in 'dry' sediment, followed by submersion with a water phase – showed that part of the residues (Propanil and DCA) were remobilized from the sediment to the water phase.

In summary, Propanil as widely used herbicide in rice cultures in Asian countries forms critical metabolites: besides the well-known DCA the follow-up product TCAB is present in the sediments for which very limited data on fate and ecotoxicity are available.

The simulation of the situation at the downstream Daning River allows for the deduction of internal concentrations within fish as the main animal protein source of the local population. Informed on the maximum residue levels in food items and the maximum daily intake rates of the respective model substances Propanil, 3,4-DCA and TCAB, human risk assessment is possible in principle using our adjusted AQUATOX model. Nevertheless, at the moment further adjustment of model assumptions is necessary before realistic human risk assessment can be done. Due to a lack of sufficient data for the environmental risk assessment and the toxicology of this active substance and its main metabolite 3,4-DCA, Propanil was not approved for the use in the European Union (European Commission 2011, EFSA 2013) Thus, despite the suitability of our modelling approach, there is substantial lack of information to do a proper risk assessment of Propanil at the moment.

In contrast to the expectations only little evidence of serious pollution could be detected. The general activity of the sediment samples as well as their PAH burden was low to moderate, with exception of their mutagenic potential. However, the genotoxic impact on the model fish species *P. vachellii*, which has a frequent contact with sediment, was significant at the artificial Hanfeng Lake and Chongqing (only second sampling campaign) compared to the reference site. Both indicate a serious impact on the fish in these areas. A toxicity reduction evaluation of the Hanfeng Lake area is highly recommended.

The moderate to low toxicity levels can most likely be explained by strong dilution due to a high mass transport of water and sediment in the Yangtze River. To summarize, it can be stated that dilution reduces the ecotoxicological risk in the Yangtze River, but does not eliminate it. Keeping in mind an approximately 14 times greater water discharge compared to the major European River Rhine, the absolute pollution mass transfer of the Yangtze River may be of severe concern for the environmental quality of its estuary and the East China Sea (Floehr & Xiao et al. 2012, Liu et al 2014).

9.6 Impact of TGD on the environment in the region

It´s in the nature of retrospective monitoring, that more the current or immediately past status quo of a system than its future state is described. It was considered necessary for a proper description of the impact of the TGD that the monitoring would start earlier in advance the start of the normal operation mode of the dam. Due to the highly dynamic situation, even in terms of sediment transport and allocation, it was difficult to grasp the rushing changes directly after impounding compared. The situation before the impounding was most probably no more reflected at all by the sediment cores that could be taken during the MICROTOX project. Despite considerable efforts to get monitoring data of cooperating Chinese institutions, it was not possible because of the politically sensitive TGD-area.

Under adverse site conditions, like stagnating flowing-sections, nutrients showed a profound, non-linear influence on the model outcome. We demonstrated this influence on populations and communities of feeding guilds in virtual dose-response simulation experiments. Even high nutrient loads have been shown to result in only slight impacts on densities of organisms of all trophic levels. The system seems saturated due to high nutrient concentrations, so that e.g. phosphate is 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 is eutrophic, but the risk for large scale algal blooms affecting the drinking water quality even in the Wushan Lake is small because of the high flow velocities and discharge rates to the Yangtze River.

Integrative monitoring strategy

An integrative monitoring combines the methodologies and measurements of in-situ biomarkers in relevant organisms (here: catfish), laboratory toxicity experiments with sediment extracts and the chemical analysis of water, sediment and organism samples, preferably in an effect directed analysis approach. In fact, we propose a combination of an extended TRIAD approach complemented by ecosystem modelling exercises to better understand the mechanisms of transport and metabolism in an upscaled sense to identify a couple of priority pollutants of genuine relevance. For example, the ranking between the sampling sites regarding the environmental risks as indicated by the biomarker experiments did not match completely conclusions suggested by the ecotoxicological risk indicators. Obviously, the migrating fish were exposed to highly contaminated sediments somewhere else than in immediate vicinity of the sampling sites.

As we have shown by the analysis of land-use patterns, an exposure to plant protection products, in particular rice herbicides, can be expected for the model region at the confluence of Daning and Yangtze rivers.

The aquatic food web of the TGR-model contains 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. Basically, this expectation has been confirmed by the simulation studies shown and discussed here. In particular, stagnant downstream sections of tributaries like the Daning River exhibit comparably high risk of accumulating pesticides from upstream sources. We recommend managing the upstream catchment areas or more comprehensively the whole catchment area regarding sustainable pesticide use. This can be achieved e.g. by the introduction of the principles of Integrated

Pest Management (IPM) that is already applied by 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 at al. 2014) often exceeding the acceptable concentration levels (Floehr & Xiao et al. 2013).

9.8 Outlook to future applications and utilization of the findings of the MICROTOX project

Discharge of industrial and urban wastewaters, along with the application of fertilizers, pesticides, and herbicides in farming, have negative impacts on the water quality. These impacts include release of heavy metals and persistent organic pollutants as PAHs, together with re-mobilization of polluted sediments. Due to its pollution, the Yangtze River was rated by the World Wildlife Fund as being amongst the top 10 rivers at risk in the world.

The increasing worldwide contamination of freshwater systems with thousands of industrial and natural chemical compounds is one of the key environmental problems of the twenty-first century and global challenges. Considering this alarming situation, which are addressed in the Yangtze cooperation projects and workshops, the following lessons can be learned: (a) to understand the complex environment of the Three Gorges Reservoir and to develop research strategies a long standing and sustainable cooperation is needed; (b) basic research is needed for the development of conceptual strategies and technical solutions considering the multidimensional environmental problems in this region; (c) joint forces supported by bi- and multilateral, international research programs are needed; (d) research programs to support fundamental research are often too short-lived to derive reliable results and sustainable solutions. (e) For this reason, it is necessary that basic and applied research sponsors combine their forces and create specific calls in the funding bodies that address basic and applied research in environmental sciences.

We can conclude that our integrated approach can be used for a huge variety of research questions in the future, beyond basic 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.

A further development of the research questions addressed in the project at hand towards more applied approaches has already been started and deals with the testing of native, flood-tolerant and pollutant degrading plants. Also, the toxicity and bioavailability of the detected follow-up metabolite TCAB needs to be investigated.

It is planned to implement a toxicodynamic-toxicokinetic sub-module into the AQUATOX model. For this purpose, fat contents of a very relevant fish species (catfish) will be delivered by our project partners that will put us into the position to calibrate the TK-TD model by using this and further information on this species.

10 Publications (project results)

Here, we list the contributions of the projects participants to national and international conferences (poster and oral presentations) and in peer-reviewed journals (accepted, under review, in preparation).

Prof. Dr. Henner Hollert as a guest editor was responsible for the publication of a special issue of the high-ranked Environmental Science & Pollution Research (ESPR).

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 KW, Subklew G, Tiehm A, Temoka C, Wang J, Westrich B, Wilken RD, Wolf A, Xiang X, Yuan Y (2011) The Yangtze-Hydro Project: a Chinese - German environmental program. Environmental Science and Pollution Research 19: 1341-1344

Floehr T, Hollert H, Kouril S, Ottermanns R, Roß-Nickoll M, Schäffer A, Schmidt B, Scholz-Starke B, Strauch K, Yuan X, Zhang P (2012) Transformation, Bioaccumulation and Toxicity of Organic Micropollutants in the Yangtze Three Gorges reservoir. Oral presentation at the workshop 'Processes in the Yangtze River System - 10th Anniversary of Sino-German Cooperation'. September 22-23, Shanghai, China.

Floehr T, Scholz-Starke B, Li B, Wu L, Hou J, Yuan X, Yin D, Hollert H (2011) Effects of micropollutants in the Yangtze River - MICROTOX Poster presentation, abstract in: Küppers S, Subklew G, Wilken RD (eds.) (2011) Processes in the Yangtze River System-Experiences and Perspectives. Schriften des Forschungszentrums Jülich Reihe Energie & Umwelt /Energy & Environment Band / Volume 123 ISSN 1866-1793 ISBN 978-3-89336-744-3

Floehr T, Scholz-Starke B, Xiao H, Koch J, Wu L, Hou J, Wolf A, Yuan X, Roß-Nickoll M, Schäffer A, Hollert H (2014) A glimpse in the black box -Ecotoxicological impacts on the Yangtze Three Gorges Reservoir, China Oral presentation, at the SETAC Europe 24th Annual Meeting 11-15 May 2014, Basel, Switzerland.

Floehr T, Scholz-Starke B, Xiao H, Paxmann B, Gutnik S, Kübel W, Zielke H, Hollert H (2014) RWTH-Forscher am Yangtze-Dreischluchtenreservoir / RWTH Researchers at Yangtze Three Gorges Dam http://www.youtube.com/watch?v=FIwJsXS0AvY

Floehr T, Scholz-Starke B, Zoschke A, Wolf A, Bergmann A, Erger C, Li B, Wu L, Hou J, Yuan X, Yin D, Roß-Nickoll M, Schäffer A, Hollert H (2012) Toxicity of Organic Micropollutants in the Yangtze Three Gorges Reservoir - MICROTOX Poster presentation at the SETAC Europe 22th Annual Meeting/ 6th SETAC World Congress 20-24 May 2012, Berlin, Germany

Floehr T, Scholz-Starke B, Zoschke A, Wolf A, Bergmann A, Erger C, Li B, Wu L, Hou J, Yuan X, Roß-Nickoll M, Schäffer A, Hollert H (2012) Ecotoxicological effects of sediment bound and water born pollutants in the Three Gorges Reservoir. Oral presentation at

the workshop 'Processes in the Yangtze River System - 10th Anniversary of Sino-German Cooperation', September 22-23, Shanghai, China.

Floehr T, Scholz-Starke B, Zoschke A, Wolf A, Bergmann A, Erger C, Li B, Wu L, Hou J, Yuan X, Roß-Nickoll M, Schäffer A, Hollert H (2013) Ecotoxicological effects of sediment bound and water born pollutants in the Three Gorges Reservoir Oral presentation, Seminar Dr. Wu, 7th May 2013, Tongji University, Shanghai, China, Invited speaker

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 literature review on the ecotoxicological status of the Yangtze River region. Environmental Science and Pollution Research 20: 6934-6971. DOI 10.1007/s11356-013-1666-1.

Floehr T, Xiao H, Yuan X, Wu L, Hou J, Scholz-Starke B, Ross-Nickoll M, Schaeffer A & Hollert H (2013) Ecotoxicological effects in the newly created ecosystem of the Yangtze Three Gorges Reservoir, China Oral presentation, SURF Seminar Dr. Müller, 28th October 2013, EAWAG Kastanienbaum/Lucerne, Switzerland, Invited speaker

Holbach A, Floehr T, Kranzioch I, Wolf A (2013) Dilution of pollution? Processes affecting the water quality in the river-style Three Gorges Reservoir. Environmental Science and Pollution Research. DOI 10.1007/s11356-012-1252-y

Hollert H, Roß-Nickoll M, Schäffer A (2013) Umweltforschung und Technikfolgenabschätzung - Der Dreischluchtenstaudamm am Yangtze in China RWTH Themen 2/2013: 22-25

Paxmann A, Brendt J, Floehr T, Scholz-Starke B, Xiao H, Paxmann B, Gutnik S, Kübel W, Zielke H, Hollert H (2014) RWTH-Forscher am Yangtze-Dreischluchtenreservoir / RWTH Researchers at Yangtze Three Gorges Dam http://www.youtube.com/watch?v=FIwJsXS0AvY

Roß-Nickoll M, Floehr T, Hollert H, Ottermanns R, Schaeffer A, Schmidt B, Rings U, Yuan Y, Westrich B, Hu W, Holbach A, Norra S, Scholz-Starke B (2012) Simulating the potential biomagnification of organic pollutants in aquatic food webs in the TGR ecosystem. Oral presentation at the workshop 'Processes in the Yangtze River System - 10th Anniversary of Sino-German Cooperation'. September 22-23, Shanghai, China.

Schaeffer A, Floehr T, Hollert H, Ottermanns R, Ross-Nickoll M, Schmidt B, Scholz-Starke B, Strauch K, Yuan Y (2011) Transformation, Bioaccumulation and Toxicity of Organic Micropollutants in the Yangtze Three Gorges reservoir Oral presentation, Sino-German Workshop 'Workshop on Interactions in the Water System -- in the Frame of the Sino-German Yangtze-Project' 27.3.-2.4.2011, Shanghai, China

Schäffer A, Hollert H, Roß-Nickoll M, Floehr T (2010) MICROTOX: Transformation, Bioakkumulation und Toxizität organischer Mikroschadstoffe im Reservoir des Drei-Schluchten-Damms Poster presentation, Kick-off meeting Yangtze-HYDRO projects, Mülheim a.d. Ruhr, 10.09.2010

Schäffer A, Hollert H, Roß-Nickoll M, Floehr T (2010) MICROTOX: Transformation, Bioaccumulation and Toxicity of organic micro pollutants in the Yangtze Three Gorges reservoir Poster presentation, First joint meeting of total Yangtze Project network at KIT (Karlsruhe), 30.11.2010

Scholz-Starke B, Chen Z, Floehr T, Hollert H, Hou J, Li B, Ottermanns R, Roß-Nickoll M, Schmidt B, Strauch K, Wu L, Yin D, Yuan Y, Yuan X, Zoschke A, Schäffer A (2012) Consequences of the Three Gorges Dam in China - Conceptual approaches to study the fate, bioaccumulation and effects of organic micropollutants in aquatic food webs and sediments of the Yangtze Oral presentation at the SETAC Europe 22th Annual Meeting/ 6th SETAC World Congress 20-24 May 2012, Berlin, Germany

Scholz-Starke B, Chen Z, Floehr T, Hollert H, Keiter S, Ottermanns R, Roß-Nickoll M, Schäffer A, Wolf A, Yuan Y (2012) Research at the Three Gorges Reservoir - Examples of recent and future German-Chinese joint projects. Oral presentation. Symposium at the Chongqing University, China. 13 June 2012.

Scholz-Starke B, Floehr T, Hollert H, Huo J, Li B, Ottermanns R, Schäffer A, Strauch K, Wu L, Yin D, Yuan Y, Roß-Nickoll M (2012) Modeling the potential biomagnification of organic pollutants in aquatic food webs of the new Three Gorges Reservoir ecosystem at the Yangtze River Poster presentation at the SETAC Europe 22th Annual Meeting/ 6th SETAC World Congress 20-24 May 2012, Berlin, Germany

Scholz-Starke B, Ottermanns R, Floehr T, Holbach A, Hollert H, Bo L, Rings U, Schaeffer A, Wei H, Yuan X, Ross-Nickoll M (2014) Simulation of the environmental situation of the tributary ecosystem Daning River in the Yangtze Three Gorges Area Poster presentation, at the SETAC Europe 24th Annual Meeting 11-15 May 2014, Basel, Switzerland.

Scholz-Starke B, Ottermanns R, Rings U, Floehr T, Hollert H, Hou J, Li B, Wu Ll, 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. Environmental Science & Pollution Research 20: 7009-7026. DOI 10.1007/s11356-013-1504-5.

Scholz-Starke B, Ottermanns R, Strauch K, Floehr T, Li B, Wu L, Hou J, Yuan X, Yin D, Roß-Nickoll M (2011) Bioaccumulation of micropollutants in the Yangtze River - MICROTOX. Poster, abstract in: Küppers S, Subklew G, Wilken RD (eds.) (2011) Processes in the Yangtze River System-Experiences and Perspectives. Schriften des Forschungszentrums Jülich Reihe Energie & Umwelt /Energy & Environment Band / Volume 123 ISSN 1866-1793 ISBN 978-3-89336-744-3

Scholz-Starke B, Yuan Y, Floehr T, Strauch K, Heister S, Chen Z, Li B, Wu L, Hou J, Yuan X, Yin D, Ottermanns R, Schmidt B, Roß-Nickoll M, Hollert H, Schäffer A (2011) Conceptual approach and first results of the MICROTOX project: Fate, effects and bioaccumulation of model pollutants in the Yangtze river Oral presentation, abstract in: Küppers S, Subklew G, Wilken RD (eds.) (2011) Processes in the Yangtze River System-Experiences and Perspectives. Schriften des Forschungszentrums Jülich Reihe Energie & Umwelt /Energy & Environment Band / Volume 123 ISSN 1866-1793 ISBN 978-3-89336-744-3

Yuan Y, Heister S, Schäffer A, Schmidt B (2012) Fate of pesticides and metabolites in the Yangtze River. Poster presentation at the SETAC Europe 22th Annual Meeting/ 6th SETAC World Congress 20-24 May 2012, Berlin, Germany.

Yuan Y, Schäffer A, Schmidt B, Ciecielski K (2011) Fate of model pollutants in the Yangtze River- MICROTOX Poster, abstract in: Küppers S, Subklew G, Wilken RD (eds.) Processes in the Yangtze River System-Experiences and Perspectives. Schriften des Forschungszentrums Jülich Reihe Energie & Umwelt /Energy & Environment Band / Volume 123 ISSN 1866-1793 ISBN 978-3-89336-744-3

Yuan Y, Schäffer A, Schmidt B, Ciecielski K (2012) Fate of pesticides and metabolites in the Yangtze River. Poster presentation at the SETAC Europe 22th Annual Meeting/ 6th SETAC World Congress 20-24 May 2012, Berlin, Germany

Yuan Y, Zhang P, Schmidt B, Romich M, Scholz-Starke B, Hollert H, Ross-Nickoll M, Schaeffer A (2014) Fate of rice herbicide Propanil and its metabolite 3, 4-Dichloroaniline in water-sediment systems from rice paddy with and without flooding simulation Oral

presentation, at the SETAC Europe 24th Annual Meeting 11-15 May 2014, Basel, Switzerland.

A number of master, diploma and PhD theses have been conducted and finished within the MICROTOX project.

Floehr T (In preparation) Toxicity of organic micropollutants in the Yangtze Three Gorges Reservoir, China. PhD thesis at the Institute for Environmental Research, RWTH Aachen University.

Heister S (2013) Synthese und mikrobieller Abbau von 14C-3,3`,4,4`-Tetrachlorazobenzol im Sediment-Wasser-System. Diploma thesis at the Institute for Environmental Research, RWTH Aachen University. Supervised by Ye Yuan. pp. 43.

Hennig M (2013) Verhalten und Metabolismus von 14C-Propanil in nicht landwirtschaftlich genutzten Böden aus der Wasserpegel-Fluktuationszone des Yangtze Drei-Schluchten-Reservoirs Master thesis at the Institute for Environmental Research, RWTH Aachen University. Supervised by Ye Yuan. pp. 104.

Koch J (2012) Bewertung des mutagenen Potentials von Sedimenten des Drei-Schluchten-Reservoirs und seiner Zuflüsse. - Assessment of the mutagenic potential of sediments of the Three Gorges Reservoir and its feeder rivers. Bachelor thesis at the Institute for Environmental Research, RWTH Aachen University. Supervised by Tilman Floehr. pp. 54.

Könemann S (2013) Bestimmung der akuten Toxizität von Sedimenten des Yangtze Drei-Schluchten-Reservoirs, China gegenüber Daphnia magna Straus. - Assessment of the acute toxicity of sediments from the Three Gorges Reservoir, China on Daphnia magna Straus. Bachelor thesis at the Institute for Environmental Research, RWTH Aachen University. Supervised by Tilman Floehr. pp. 54.

Rings U (2013) Anpassung des komplexen Ökosystemmodells AQUATOX zur Simulation von aquatischen Nahrungsnetzen am Drei-Schluchten-Stausee in China. Master thesis at the Institute for Environmental Research, RWTH Aachen University. Supervised by Björn Scholz-Starke. pp. 106.

Strauch K (2012) Evaluation von Bioakkumulationsmodellen für verschiedene Schadstoffszenarien in der Region des Drei-Schluchten-Staudamms in China - Evaluation of bioaccumulation models for different contamination scenarios in the Three Gorges Dam region in China. Diploma thesis at the Institute for Environmental Research, RWTH Aachen University. Supervised by Björn Scholz-Starke. pp. 90.

Yuan Y (In preparation) Fate, degradation and use patterns of important rice herbicides in the Three Gorges Reservoir region, China. PhD thesis at the Institute for Environmental Research, RWTH Aachen University.

Zhang P (2013) Schicksal von 14C-markiertem 3,4-Dichloroanilin in einem Wasser-Sediment System. Master thesis at the Institute for Environmental Research, RWTH Aachen University. Supervised by Ye Yuan. pp. 97.

Zoschke A (2012) Untersuchung der chemischen Belastungssituation im Drei-Schluchten-Stausee, China – Abschätzung des Gefahrenpotentials für lokale Fischarten anhand von Bioassays und Feldstudien. Diploma thesis at the Institute for Environmental Research, RWTH Aachen University. Supervised by Tilman Floehr. pp. 107.

11 References

Ahlf W, Hollert H, Neumann-Hensel H, Ricking M (2002) A Guidance for the Assessment and Evaluation of Sediment Quality: A German Approach Based on Ecotoxicological and Chemical Measurements. JSS - Journal of Soils and Sediments 2: 37-42.

Alef K, Kleiner D (1989) Rapid and sensitive determination of microbial activity in soils and in soil aggregates by dimethylsulfoxide reduction. Biol. Fertil. Soils. 8, 349-355.

Argent RM (2004) An overview of model integration for environmental applications - components, frameworks and semantics. Modeling & Software 19: 219-234

Bosveld ATC, De Bie PAF, Van den Brink NW, Jongepier H, Klomp AV (2002) In vitro EROD induction equivalency factors for the 10 PAHs generally monitored in risk assessment studies in The Netherlands. Chemosphere 49: 75-83

Brinkmann M, Hudjetz S, Cofalla C, Roger S, Kammann U, Giesy J, Hecker M, Wiseman S, Zhang X, Wölz J, Schüttrumpf H & Hollert H. (2010) A combined hydraulic and toxicological approach to assess re-suspended sediments during simulated flood events. Part I-multiple biomarkers in rainbow trout. JSS 10:1347-1361

Chapman PM, Hollert H. (2006) Should the sediment quality triad become a tetrad, a pentad, or possibly even a hexad? JSS - Journal of Soils and Sediments 6:4-8.

Chen GS, White PA (2004) The mutagenic hazards of aquatic sediments: a review. Mutation Research-Reviews in Mutation Research 567: 151-225.

Dabrunz A, Duester L, Prasse C, Seitz F, Rosenfeldt R, Schilde C, Schaumann GE, Schulz R (2011) Biological surface coating and molting inhibition as mechanisms of TiO2 nanoparticle toxicity in Daphnia magna. PloS one, 6(5):e20112.

DIN EN ISO (2009) Water quality–Determination of the acute toxicity of waste water to zebrafish eggs (Danio rerio) ISO, E. N. 15088: 2008–(ISO 15088: 2007). German version: DIN EN ISO, 2009, 15088. Jg.

Echeverría M, Wellman M, Park R, Clough J (2003) Evaluation of AQUATOX for Ecological Risk Assessments in the U.S. EPA Office of Pesticide Programs. SETAC NA 24th Annual Meeting in North America, Austin, Texas

EFSA - European Food Safety Authority (2011) Conclusion on the peer review of the pesticide risk assessment of the active substance propanil. EFSA Journal 2011;9(3):2085. [63 pp.]. doi:10.2903/j.efsa.2011.2085

EFSA - European Food Safety Authority (2013) Reasoned opinion on the review of the existing maximum residue levels (MRLs) EFSA Journal 2013;11(6): 3280

Encyclopaedia Britannica (2014) Yangtze River. Encyclopædia Britannica Online. Encyclopædia Britannica Inc., 2014. Web. 27 Jun. 2014 <http://www.britannica.com/Ebchecked/topic/651857/Yangtze-River/48046/Agriculture>.

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, Ottermanns R, Roß-Nickoll M, Schäffer A & Hollert H (2013) Solution by dilution? - A review on the pollution status of the Yangtze River. Environ Sci Poll Res 20:6934-6971.

Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. Chemical Engineering Journal 156:2-10

Förstner U (2002) Sediments and the European Water Framework Directive. JSS - Journal of Soils and Sediments 2: 54.

Fu J, Mai B, Sheng G, Zhang G, Wang X, Peng P, Xiao X, Ran R, Cheng F, Peng X, Wang Z, Tang UW (2003) Persistent organic pollutants in environment of the Pearl river Delta, China: an overview. Chemosphere 52: 1411-1422.

Fuhr F, Opho H, Burauel P, Wanner U, Haider K (1998) Modification of the definition of bound residues. In: Pesticide Bound Residues in Soil (Report of a Workshop, September 3±4, 1996). Ed. State Commission for the Assessment of Chemicals used in Agriculture. Report No. 2. Publ., Wiley-VCH, DFG.

Gevao B, Semple KT, Jones KC (2000) Bound pesticide residues in soils: a review. Environmental Pollution, 108(1), 3-14.

Giddings JM, Bayne MCR, Mao J (1990b) Propanil - Toxicity to the freshwater diatom Navicula pelliculosa. SLI Report No. 90-3-3254. Performed by Springborn Laboratories, Inc., Wareham, Massachussetts. Submitted by the Propanil Task Force. EPA MRID No. 417775-01.

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

Graney R (1982) The Acute Toxicity of STAM Technical to the Daphnia magnaStraussTitle 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)Source

Grimm V, Ashauer R, Forbes V, Hommen U, Preuss TG, Schmidt A, van den Brink P, Wogram J, Thorbek P (2009) CREAM: a European project on mechanistic effect models for ecological risk assessment of chemicals. Environ Sci Poll Res16(6): 614-617.

Grube A, Donaldson D, Kiely T, Wu L (2011) Pesticides industry sales and usage. Environmental Protection Agency, US.

Heim K, Schuphan I, Schmidt B (1994) Behavior of [14C]?4?nitrophenol and [14C]?3, 4?dichloroaniline in lab sediment?water systems. 1. Metabolic fate and partitioning of radioactivity. Environmental toxicology and chemistry, 13(6), 879-888.

Henderson KL, Belden JB, Coats JR (2007) Mass balance of metolachlor in a grassed phytoremediation system. Environmental Science and Technology 41: 4084-4089

Hisschemöller M, Tol RSJ, Vellinga P (2001) The relevance of participatory approaches in integrated environmental assessment. Integrated Assessment 2:57-72

Holbach A, Norra S, Wang L, Yuan Y, Hu W, Zheng B, Bi Y (2014) Three Gorges Reservoir: density pump amplification of pollutant transport into tributaries. Environ. Sci. Technol., Just Accepted Manuscript o Publication Date (Web): 18 Jun 2014; Downloaded from http://pubs.acs.org on June 21, 2014

Holbach A, Wang L, Chen H, Hu W, Schleicher N, Zheng B, Norra (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 DOI 10.1007/s11356-012-1373-3 (online first)

Hollert H, Dürr M, Erdinger L, Braunbeck T (2000) Cytotoxicity of settling particulate matter (SPM) and sediments of the Neckar river (Germany) during a winter flood. Environ Toxicol and Chem 19: 528-534.

Hollert H, Ernst M, Seiler TB, Wölz J, Braunbeck T, Kosmehl T, Keiter S, Grund S, Ahlf W, Erdinger L, Dürr M (2009) Strategien zur Sedimentbewertung - ein Überblick. Umweltwissenschaften und Schadstoff-Forschung 21: 160-176.

Hollert H, Haag I, Dürr M, Wetterauer B, Holtey-Weber R, Kern U, Westrich B, Färber H, Erdinger L, Braunbeck T (2003) Untersuchungen zum ökotoxikologischen Schädigungspotenzial und Erosionsrisiko von kontaminierten Sedimenten in staugeregelten Flüssen Umweltwissenschaften und Schadstoff-Forschung 15: 5-12

Hollert H, Heise S, Keiter S, Heininger P, Förstner U (2007b) Wasserrahmenrichtlinie - Fortschritte und Defizite. UWSF - Z Umweltchem Ökotox 19: 58-70.

Hollert H, Seiler TB, Blaha L, Young AL (2007a) Multiple stressors for the environment: Present and future challenges and perspectives. Environmental Science and Pollution Research 14: 272

Hommen U, Poethke HJ, Dülmer U, Ratte HT (1993) Simulation-models to predict ecolo-gical risk of toxins in fresh-water systems. J Marine Sci 50: 337-347.

Hommen U, Ratte HT (1997) Vom Labor ins Freiland - Modelle zur Effektabschätzung. Z Umweltchem Ökotox 9: 267-272.

Huisman P, De Jong J, Wieriks K (2000) Transboundary cooperation in shared river basins: experiences from the Rhine, Meuse and North Sea. Water Policy 2:83 - 97

ICPR - International Commission for the Protection of the Rhine). (2009) Sediment management plan-Rhine Summary Report No. 175. ICPR, Koblenz. Available at http://www.iksr.org/fileadmin/user_upload/Dokumente_en/Reports/Bericht_175e.pdf

Imhoff J, Clough J, Park R, Stoddard A (2004) Evalutation of chemical bioaccumulation models of aquatic ecosystems (Final Report). http://hspf.com/pdf/FinalReport218.pdf (letzter aufruf: 18.12.2011).

IUCN - The World Conservation Union and the World Bank (1997) Large Dams: Learning from the Past, Looking at the Future. Workshop Proceedings. IUCN, Gland, Switzerland and Cambridge, UK and the World Bank Group, Washington, DC. V. + 145 pp.

Jablonowski N, Mödler J, Schaeffer A, Burauel P (2008) Bioaccessibility of Environmentally Aged 14C-Atrazine Residues in an Agriculturally Used Soil and Its Particle-Size Aggregates. Environmental Science and Technology 42: 5904-5910.

Jankowski T, Strauss T, Ratte HT (2005) Trophic interactions of the freshwater jellyfish Craspedacusta sowerbii. J Plankton Res 27: 811-823.

Jopp F, Breckling B, Reuter H, DeAngelis DL (2011) Perspectives in Ecological Modelling. In: Jopp F, Reuter H,Breckling B (eds.): Modelling Complex Ecological Dynamics. Springer Berlin, Heidelberg. pp. 341-347

Kästner M, Nowak KM, Miltner A, Trapp S, Schäffer A (2014 in press) Classification and modelling of non-extractable residue (NER) formation of xenobiotics in soil - a synthesis. Critical Reviews in Environmental Science and Technology. DOI:10.1080/10643389.2013.828270

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

Keiter S, Braunbeck T, Heise S, Pudenz S, Manz W, Hollert H (2009) A fuzzy logic-classification of sediments based on data from in vitro biotests. Journal of Soils and Sediments 9: 168-179.

Kirsten H, Braunbeck T (2011) Dechorionation as a tool to improve the fish embryo toxicity test (FET) with the zebrafish (Danio rerio)."

Koethe H (2003) Existing sediment management guidelines: An overview. What will happen with the sediment/dredged material? JSS - Journal of Soils and Sediments 3: 139-143.

Kosmehl T, Krebs F, Manz W, Erdinger L, Braunbeck T, Hollert H (2004) Comparative genotoxicity testing of Rhine River sediment extracts using the comet assay with permanent fish cell lines (RTG-2 and RTL-W1) and the Ames test. Journal of Soils and Sediments 4:84-94. doi:10.1007/BF02991050

Labrada R (2003) The need for improved weed management in rice. FAO: Proceedings of the 20th Session of the International Rice Commission (Bangkok, Thailand, 23-26 July. http://www.fao.org/docrep/006/y4751e/y4751e00.htm

Lammer E, Carr GJ, Wendler K, Rawlings JM, Belanger SE, Braunbeck T. (2009) Is the fish embryo toxicity test (FET) with the zebrafish (Danio rerio) a potential alternative for the fish acute toxicity test? Comp Biochem Physiol C Toxicol Pharmacol. 2009 Mar;149(2):196-209. doi: 10.1016/j.cbpc.2008.11.006. Epub 2008 Dec 3.

Lei B, Huang S, Qiao M, Li T, Wang Z (2008) Prediction of the environmental fate and aquatic ecological impact of nitrobenzene in the Songhua River using the modi?ed AQUATOX model. Journal of Environmental Sciences 20:769-777

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), May 2006

Liang XQ, Chen YX, Nie ZY, Ye YS, Liu J, Tian GM, Wang GH, Tuong TP (2013) Mitigation of nutrient losses via surface runoff from rice cropping systems with alternate wetting and drying irrigation and site-specific nutrient management practices.. Environmental Science & Pollution Research 20: 6980-6991

Malaj E, Von der Ohe PC, Grote M, Kühne R, Mondy CP, Usseglio-Polatera P, Brack W, Schäfer RB (2014) Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. PNAS, doi: 10.1073/pnas.1321082111

McKnight US, Rasmussen JJ, Kronvang B, Bjerg PL, Binning PJ (2012) Integrated assessment of the impact of chemical stressors on surface water ecosystems. Science of the Total Environment 427-428: 319-331

Ministry of Health of Italy (2006) Propanil - Report and proposed decision of Italy made to the European Commission under 91/414/EEC. European Commission, Brussels. Volumes 1-9.

Moeckel C, Nizetto L, Di Guardo N, Steiines E, Freppaz M, Filippa G, Camporini P, Benner J, Jones KC (2008) Persistent Organic Pollutants in Boreal and Montane Soil Profiles: Distribution, Evidence of Processes and Implications for Global Cycling. Environmental Science and Technology 42: 8374-8380.

National Toxicology Program (NTP) (2009) Toxicology and Carcinogenesis Studies of 3,30,4,40-Tetrachloroazobenzene (CAS No. 14047-09-7) in Sprague Dawley rats and B6C3F1 mice (Gavage studies). Toxicity Report Series No. 558. NIH Publication No. 09-5899. U. S. Department of Health and Human Services, Public Health Service, National Institutes of Health, Research Triangle Park, NC.

Netzband A et al. (2007) Sediment management: An essential element of river basin management plans. Journal of Soils and Sediments 7: 117-132

Neumann J (1959) Maximum Depth and Average Depth of Journal of the Fisheries Research Board of Canada 16(6): 923-927

Northcott GL, Jones KC (2000) Experimental approaches and analytical techniques for determining organic compound bound residues in soil and sediment. Environmental Pollution, 108(1), 19-43.

OECD (1992) OECD Guidelines for the Testing of Chemicals. Section 2: Effects on Biotic Systems Test No. 203. Acute Toxicity for Fish. Organization for Economic Cooperation and Development, Paris, France.

OECD (2004) Guideline 202 - Daphnia sp. Acute Immobilisation Test. Adopted version of 2004

OECD (2011) Guideline 201 - Freshwater Alga and Cyanobacteria, Growth Inhibition Test Adopted version of 2011

Park RA, Clough JS (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. DRAFT October 2010

Park RA, Clough JS, Coombs Wellman M (2008) AQUATOX: Modeling environmental fate and ecological effects in aquatic ecosystems. Ecological Modeling 213:1-15

Park RA, Clough JS, Wellman MC, Donigian AS (2005) Nutrient Criteria Development with a Linked Modeling System: Calibration of AQUATOX Across a Nutrient Gradient. Pages 885-902. TMDL 2005. Water Environment Federation, Philadelphia, Penn.

Power EA, Chapman PM (1992) Assessing sediment quality. In: Burton GA (Editor), Sediment toxicity assessment. Lewis-Publishers, Boca Raton,, pp. 1-18.

Preuss TG, Hammers-Wirtz M, Hommen U, Rubach MN, Ratte HT   (2009) An individual based population model of Daphnia magna for analysis and extrapolation of population dynamics under laboratory conditions. Ecol Model 220: 310-329.

Preuss TG, Hommen U, Alix A, Ashauer R, van den Brink P, Chapman P, Ducrot V, Forbes V, Grimm V, Schäfer D, Streissl F, Thorbek P (2009) Mechanistic Effect Models for Ecological Risk Assessment of Chemicals (MEMoRisk) - A new SETAC Europe Advisory Group. Environ Sci Poll Res 16(3): 250-252.

Preuss TG, Telscher M, Ratte HT (2008) Life stage-dependent bioconcentration of a nonylphenol isomer in Daphnia magna. Environ Poll 156: 1211-1217.

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

Raimondo S, Vivian DN, Barron MG (2010) Web-based Interspecies Correlation Estimation (Web-ICE) for Acute Toxicity: User Manual. Version 3.1. EPA/600/R-10/004. Office of Research and Development, U. S. Environmental Protection Agency. Gulf Breeze, FL.

Rings U (2013) Anpassung des komplexen Ökosystemmodells AQUATOX zur Simulation von aquatischen Nahrungsnetzen am Drei-Schluchten-Stausee in China. Masterarbeit am Institut für Umweltforschung der RWTH Aachen University. pp. 106

Routledge EJ, Sumpter JP (1996) Estrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast screen. Environmental Toxicology and Chemistry (15), 241-248.

Scholz-Starke B & Ottermanns R, Rings U, Floehr T, Hollert H, Hou J, Li B, Wu LL, 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. Environmental Science & Pollution Research. 20:7009-7026. DOI 10.1007/s11356-013-1504-5.

Schultis T, Metzger JW (2004) Determination of estrogenic activity by LYES-assay (yeast estrogen screen-assay assisted by enzymatic digestion with lyticase). Chemosphere (57), 1649-1655.

Schüürmann G, Ebert RU, Nendza M, Dearden JC, Paschke A, Kuehne R (2007) Prediction of fate-related compound properties. In: van Leeuwen K, Vermeire T (eds) Risk assessment of chemicals. An introduction. Springer Science, Dordrecht, pp 375-426.

SedNet (2004) Sediment, a valuable resource that needs Europe's attention. SedNet recommendations for sediment research priorities related to the soil research clusters. http://www.sednet.org/materiale/Sediment_a_valuable_resource.pdf.

Sousa JV (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, Massachussetts. Submitted by the Propanil Task Force. EPA MRID No. 417760-01.

Strähle U, Scholz S, Geisler R, Greiner P, Hollert H, Rastegar S, Schumacher A, Selderslaghs I, Weiss C, Witters H, Braunbeck T (2012) Zebrafish embryos as an alternative to animal experiments—A commentary on the definition of the onset of protected life stages in animal welfare regulations Reproductive Toxicology 33: 128-132

Strauch K (2012) Evaluation of bioaccumulation models for different contamination scenarios in the Three Gorges Dam region in China. Diplomarbeit am Lehrstuhl für Umweltbiologie und -chemodynamik (Institut für Umweltforschung, Biologie V) der Fakultät für Mathematik, Informatik und Naturwissenschaften der Rheinisch-Westfälischen Technischen Hochschule Aachen. pp. 90.

Strauss T, Ratte HT (2002) Entwicklung eines Food-Chain-Models zur Bioakkumulation eines Pflanzenschutzmittels in terrestrischen Nahrungsketten einschließlich einer Uncertainty-Analyse Unveröffentlicher Projektbericht.

Styrishave B, Mortensen M, Krogh PH, AndersenO, Jensen J (2008) Solid-Phase Microextraction (SPME) as a Tool to Predict the Bioavailability and Toxicity of Pyrene to the Springtail, Folsomia candida, under Various Soil Conditions. Environmental Science and Technology 42: 1332-1336.

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 (2013) 20:8871-8880; DOI 10.1007/s11356-013-1859-7

Tixier C, Sancelme M, A??t-A??ssa S, Widehem P, Bonnemoy F, Cuer A, Veschambre H (2002) Biotransformation of phenylurea herbicides by a soil bacterial strain, Arthrobacter sp. N2: structure, ecotoxicity and fate of diuron metabolite with soil fungi. Chemosphere, 46(4), 519-526.

U.S. Army Corps of Engineers (2001) HEC-RAS river analysis system user's manual. US Army Corps of Engineers, Davis.

UFZ - Umweltzentrum Department of Ecological Chemistry (2012) ChemProp 5.2.8.. http://www.ufz.de/index.php?en=

US Geological Survey (USGS) (2008) The Cheney Reservoir and Watershed Study. http://ks.water.usgs.gov/studies/qw/cheney/ (last accessed 2012-10)

Weller MG, Simon E, Pfortner P, Dosch M, Niessner R (1998) Detection of bound residues by enzyme immunoassay. In: Pesticide Bound Residues in Soil (Report of a Workshop, September 3±4,1996). Ed. State Commission for the Assessment of Chemicals used in Agriculture. Report No. 2. Publ., Wiley-VCH, DFG.

Wenning R, Ingersoll C (2002) Summary of the SETAC Pellston Workshop on Use of Sediment Quality Guidelines and Related Tools for the Assessment of Contaminated Sediments;. 17-22 August 2002; Fairmont, Montana, USA. Society of Environmental Toxicology and Chemistry (SETAC). Pensacola FL, USA. online: http://www.setac.org/files/SQGSummary.pdf

White PA, Rasmussen JB, Blaise C (1998) Genotoxic substances in the St. Lawrence system II: Extracts of fish and macroinvertebrates from the St. Lawrence and Saguenay Rivers, Canada. Environmental Toxicology and Chemistry 17: 304-316.

Wu J, Huang J, Han X, Gao X, He F, Jiang M, Jiang Z, Primack RB, Shen Z (2004) The three Gorges dam: an ecological perspective. Front Ecol Environ 2(5): 241-248.

Xue XM, Xu R, Zhang BR, Li FT (2008) Current pollution status of Yangtze river and controlling measures. Int J Environ Waste Manage 2(3): 267-278.

Yang H, Battarbee RW, Tuner S, Rose N, Went RG, Wu GJ, Yang R (2010) Historical Reconstruction of Mercury Pollution Across the Tibetan Plateau Using Lake Sediments. Environ Sci Technol 42: 2918-2924.

Yang SL, Zhang J, Xu XJ (2007) Influence of the Three Gorges Dam on downstream delivery of sediment and its environmental implications, Yangtze River. Geophys Res Let 34:L10401.

VIII RESEARCH CAMPAIGNS AND EXCHANGE OF SCIENTISTS

Forschungszentrum Jülich

Günter Subklew

1 *Preliminary remarks*

Under the project entitled "Sustainable management of newly created ecosystems in China along the Yangtze River," from April 2008 to March 2012 the International Bureau of the German Federal Ministry for Education and Research promoted Chinese / German workshops in China and Germany.

2 *Year 2009: Stays of Chinese Scientists in Germany*

Both due to scheduling difficulties at the two partner networks as well as to additional events within the framework of the German-Chinese Year of Science and Education the originally planned working meetings for the year 2009 could only partially be organized in the intended way. In March 2009, during a one-week stay of seven scientists from Chongqing University in Germany, the analysis for pollutant binding to suspended solids and sediment as topic of investigation at Jülich and at Chongqing, was discussed and optimization measures were debated. From this perspective, the results obtained were discussed and further steps were fixed. For the scientists exchange it was agreed that Ms. LIANG Yan would start their work in Jülich in autumn 2009 (financed by CSC on the Chinese side) and that Dr XU Xiaoyi during the year 2010 would come for a longer research period in Germany. The stay in Jülich was complemented by a visit to the local scientific and technical equipment at the Institute of Environmental Research, as well as a visit to the Institute for Hygiene and Environmental Medicine of RWTH Aachen University and the University Hospital Aachen. The stay in Germany was finished by a presentation of the German cooperation partner "Water Technology Centre" in Karlsruhe with a detailed discussion of the mutual work issues.

3 *Year 2010: German Scientists stay in China*

In preparation of a joint Chinese / German workshop in China in spring 2011 with the aims to coordinate the cooperation and to foster practical project implementation discussions with Chinese partners were held in China from November 11 to 20, 2010.

- Standing Office of the State Council Three Gorges Project Construction Committee (TGPCC)

  At that time TGPCC was the organization, which on the Chinese side was responsible for the overall coordination of the Yangtze project. On the occasion of a presentation of the ten individual German projects funded by BMBF the currently issues arising for practical cooperation between Chinese and German partners were discussed. During that meeting the German side was informed that TGPCC had transferred the coordination of activities on the Chinese side to one of the formal science partners, but continued to be involved in all activities.

3.1 Chinese Research Academy of Environmental Sciences (CRAES)

As fulfilling in the ministerial order research; monitoring; and coordination tasks and as reporting directly to the Ministry of Environment, CRAES takes under Chinas environmental research institutions a leading role. CRAES operates a monitoring station in the Yangtze River; a vessel for sampling campaigns is available. With CRAES common sampling activities were agreed.

3.2 Chongqing University (CQU)

Investigations by CQU were carried out both on the Yangtze River itself as well as on Xiao Jiang. Behind Jialing and Wujiang that river is the third largest tributary of the Yangtze. Coming from northern direction Xiaojiang River flows downstream of Wanzhou into the Yangtze. The river Xiaojiang is about 80 km long and covers a catchment area of approximately 5,170 km^2. As its catchment area is representative of the geological conditions of large parts of the region, that river was selected for the research activities. In addition, its shores are particularly strongly affected due to the flow cross-sectional profile through the water fluctuation zone. This is the case especially for the city of Kai Xian. There some 50 % of approximately 500,000 inhabitants had to be resettled. Specifically research on the topics "water fluctuation zone (WFZ)", "wastewater treatment" (in rural areas) and sampling of water, sediment and biomass started at Wanzhou. The eutrophication problem is very evident in the Xiaojiang and was first observed on this scale in the year 2007. Also, a reinforced algal blooming can now be observed. While in former times the flow rate in the Xiaojiang was up to 3 m/s, it is now at 0.1 – 0.2 m/s. Similarly, the situation has changed at the Yangtze (reduction of flow rate from 2 - 3 m/s to 0.5 – 1.0 m/s).

In Chongqing the load of the Yangtze by arsenic of natural mineral origin was firstly pointed out. The entry is made evident by a creek. The information was later confirmed by the CAS Institute of Hydrobiology in Wuhan and by Nanjing University without providing any more detailed quantitative information.

3.3 Yangtze Water Resources Protection Institute (YWRPI)

With YWRPI the topic "Data / Data transfer" was intensively discussed, as the Chinese side deems the Three Gorges project both under political aspects and under regard of the water provision framework plan as extremely sensitive. For joint project activities corresponding agreements between the German partners and YWRPI should have been signed. Basically YWRPI was willing to do so and promised to discuss it with the superior authority. At the end these internal discussions have not led to a formalized cooperation. Also, sampling and measurement campaigns with a ship rented by YWRPI could not be realized.

3.4 CAS-Institute of Hydroecology (IHE)

The research activities of IHE focus in particular on the ecological research on the subject kairomones, fish, algae blooming, biota, etc. There is a strong link with the ecologically oriented working groups in the Yangtze project.

3.5 Tongji University Shanghai

Into the discussion at Tongji University were also involved scientists of Nanjing University and Zhejiang University (Hangzhou). The data sensitivity and the concentrations of pollutants in the Yangtze River Basin, set the main topics. The Chinese partner recommended not only to rely on the contaminants concentrations, but also to focus on processes, such as studies on degradation behavior, or sampling techniques. It was also discussed to acquire a MiniBAT (project topic KIT).

4 Year 2011

4.1 Year 2011: Workshop at Tongji University Shanghai

During the three-days-workshop “Interactions in the Water System” within the frame of the Sino-German Yangtze-Project from 27 to 29 March 2011 at Tongji University, which immediately followed the discussions of the German partners FZJ, IWW and TZW in Wuhan, Yichang, and Chongqing, the results achieved so far were reconciled with each other and at the same time the final preparations for subsequent sampling were agreed. A total of 24 scientists from all German project partners was involved in the workshop. The workshop was followed by sampling campaigns (Wushan: Rivers Daning and Yangtze; Kaixian: Rivers Xiaojiang and Puli; Chongqing: Rivers Jialing and Yangtze), headed by CRAES under participation of the German partner institutions FZJ, KIT and TZW. The results of these water-sampling have been included into the regular reports of the project partners to the BMBF.

4.2 Year 2011: Workshop in RWTH Aachen University

From 28 to 29 November 2011, Research Centre Jülich and RWTH Aachen University organized the *Sino-German Workshop: Processes in the Yangtze River system, Experiences and Perspectives* in Aachen. More than eighty participants exchanged their views on the further research results and the consequences for the future. In thirteen lectures and eleven posters with joint German and Chinese authorship the results and the progress of each project were reported. The close links between the projects and the work in the project network Yangtze GEO (Land Use Change - Soil Erosion - Mass Movements - Diffuse Matter

Inputs) was given by two lectures. In sixteen presentations and two posters the Chinese partners reported their work in the Yangtze River Basin, showing the breadth of their research. While the Germans are mainly engaged in the reservoir area and the tributaries of the Yangtze upstream of the dam, the Chinese researchers reported mostly from the lower reaches of the Yangtze. Five exhibitors from the industry took the chance to present their products portfolio.

The German side, entirely in collaboration with Chinese colleagues, focused on the themes contaminant degradation (Tiehm, TZW Karlsruhe), modeling of the lower storage area (Westrich, Stuttgart), virtual organisms as adsorbents for organic substances (Schramm, TU Munich), sorption of sediments (Klumpp, Jülich), degradation of xenobiotics (Küppers, Jülich), influences of cities (Reid, KIT), sampling with the MiniBAT, which is a towed submarine sampling device (Holbach, KIT), measurement of micropollutants in water (Wolf, IWW Mülheim / Biebesheim) behavior of model compounds in the Yangtze (Scholz-Starke, RWTH), dynamic behavior of reference compounds (Temoka, TU Munich), and modeling of contaminant transport (Wei, Stuttgart).

The Chinese side presented their research results as follows: antibiotics and resistant bacteria in the Yangtze (YIN, Tongji University), cyclic processes and warning monitors for typical pollutants in the dam (CHEN, Institute of Hydroecology, Wuhan), eutrophication and control in Taihu Lake (YANG, Nanjing University), nonylphenol removal of phenolic humus monomers (Jl, Nanjing University), bioaccumulation and biotransformation of Polybromdiphenyl-ethers in common carp (GAO, Nanjing University), methods of ecological assessment of early warning systems with Irow (WANG, CRAES Beijing), influence of transition metal ions on the formation of disinfection by-products in the chlorination of drinking water (ZHU, Tongji University), a strategic plan for water quality control of the reservoir (SU, CRAES Beijing), behavior of urban waste water in the dam area (CHENG, Tongji University) adsorption and degradation of atrazine in soil water fluctuation zone of the reservoir area-shore (MA, Tongji University), microhabitat and population structure of Leptobotia tchangi (LI, Tongji University), degradation products of organic chlorine compound in sediment and water from the Dianshan lake in the Yangtze Delta (QIU, Tongji University).

The lecture and discussion program was rounded off by technical visits to the partners RWTH Aachen University, Forschungszentrum Jülich, IWW Mülheim and TZW Karlsruhe.

5 Year 2012

In the beginning of year 2012, five scientists from Zhejiang University Hangzhou paid a visit to WTZ Karlsruhe and Forschungszentrum Jülich. This special issue of analytics and new bilateral project work was discussed.

IX BEHAVIOUR OF ORGANIC MOLECULES - Degradation of xenobiotics in water using oxidative and reductive processes

[1]Forschungszentrum Jülich GmbH & [2]Tongji University Shanghai & [3]Chongqing University & [4]Zhejiang University

[2]CHEN Lei

[3]XIANG Xin-Yi

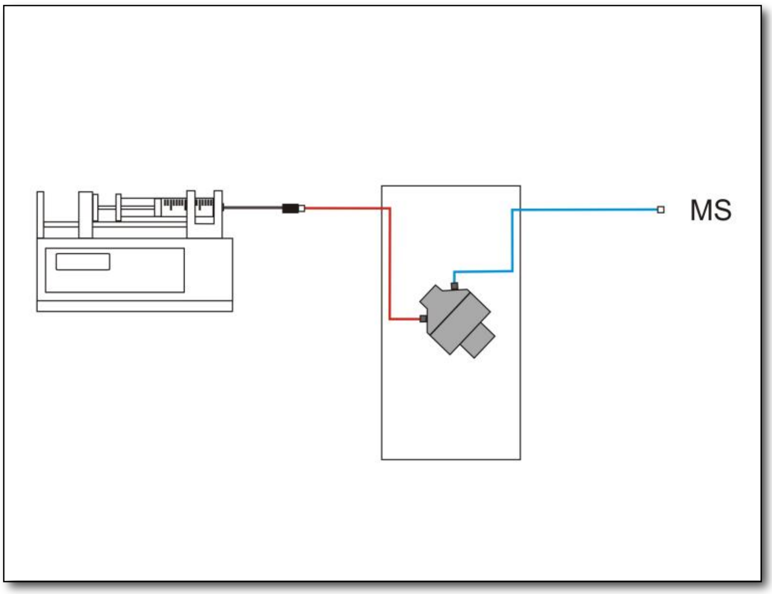
[4]ZHU Linyan

[1]Diana Hofmann

[1]Beatrix Santiago-Schübel

[1]Günter Subklew

[1]Stephan Küppers



1 Introduction

During planning of the Yangtze project network it was the idea to determine the status of the pollution of the Yangtze by heavy metals and chemicals as well as to determine the fate of the pollutants to assess the quality of the Yangtze-water. Finally the idea would have been to evaluate the changes caused by the construction of the dam. This means that besides the initially planned analysis of elements and organic contaminants contained in the river also a part of the study was the investigation of the metabolism of relevant organic contaminants.

In the original proposal of 2005 was therefore we planned to take water and sediment samples from the Yangtze to determine the quantities of pollutants or/concentrations and to determine the composition of the contaminants. Caused by changing conditions that were the change of the financing structure, which means that Jülich did not receive funding for the project contribution and due to the fact that project started in 2010, the original approach was discarded.

At the time of the project start it was already known that the large absolute amounts of water of the Yangtze lead to a significant dilution of pollutants and it has therefore to be assumed that a moderate pollution concentration analogous to rivers in Europe is found in the Yangtze River.

Since also no financial resources for the implementation of the project were available we had to skip the costly sampling and transport of samples. Instead of this together with Chinese partners funding at the Chinese Scholarship Council for exchange visits of graduate students in Jülich was successfully raised and here mechanistic studies for the degradation of pollutants were then performed with existing equipment.

Specifically, studies on degradation of chemicals under oxidative and reductive conditions were conducted with Mrs. CHEN Lei (from October 2010 to September 2011); by Ms. XIANG Xin-Yi (from July 2011 to Dec. 2011) the transfer of the degradation mechanisms was examined to photocatalytic degradation and finally Ms. ZHU Linyan (since November 2012), tries to extend the process chain to the degradation of chemicals form laboratory degradation to toxicological evaluation of the degradation products together with the group of Prof. Henner Hollert at RWTH Aachen.

Within the project a laboratory scale process has been developed which allows evaluating the fate of pollutants in the environment under oxidative or reductive conditions in significantly reduced time. It is expected to extend the process also to toxicological evaluation within the next year and it is expected that this platform than can be used for risk assessment of chemicals in the environment. The resulting knowledge platform can now be incorporated into future projects. The results are presented in scientific publications in detail (see list of publications).

2 Materials and methods

The coupling of an electrochemical cell (EC) with mass spectrometry (MS) has been known for predicting the oxidative metabolism of pharmaceutical agents in the literature. The reductive metabolism was not investigated until now. Moreover, no information on the comparability of EC-MS studies and the behavior of chemicals in the real environment was available. During this project, the well-known methodology has been applied to the prediction of metabolites of chemicals in the environment.

The basic assumption was that chemicals are metabolized in the environment in the first step, either by oxidation, by reduction or hydrolysis. With this assumption, then the oxidation and reduction as possible metabolic pathways can by evaluated by the EC-MS approach that has been successfully transferred from the research in biological systems.

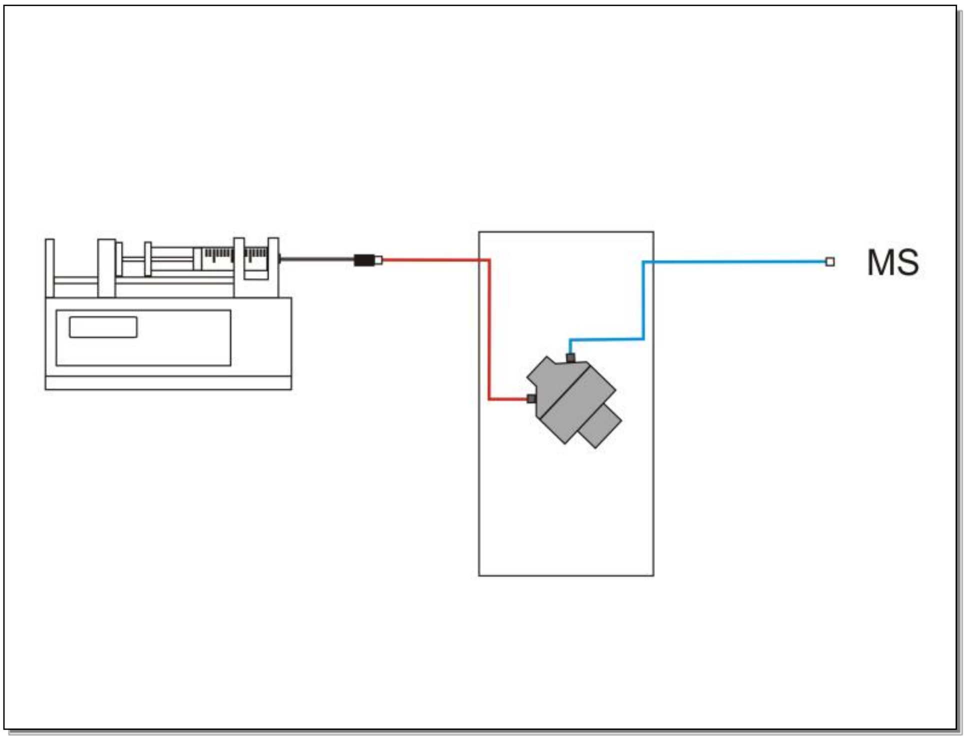


Figure IX-1 Schematic of the experimental set-up of the applied EC-MS-System.

3 Results and Discussion

It was shown that the direct coupling of electrochemistry with mass spectrometry (EC-MS) can be used to mimic the oxidative metabolism in nature [1] as already shown for biological systems before. For the first test of the approach, the oxidative degradation of Sulfadiazine, an antibiotic from livestock, has been elected and has been tested in a commercial EC-MS system as the first model substance. The reason for the choice of Sulfadiazine as a first test case was the relatively large number of metabolites that have been elucidated by extraction from environmental systems, which could be used for the "proof of concept" approach.

The coupling of the electrochemical cell to a commercial triple quadrupole mass spectrometer was carried out in complete analogy to the published work. First, a screening is carried out for oxidizability or reducibility. The screening of the decomposition of a known substance leads to additional masses that are obtained in the mass spectrum. Screening is practically performed so that a constant current rate increases (for example, 5 mV per second) in the electrochemical cell is generated, while keeping the flow through the cell constant and using the mass spectrometer to monitor all masses between 50 and 400 Dalton.

The intensities of the masses in dependence of the voltage can be used for the next step of the process. Here the voltage at which the intensity of the mass is particularly high is kept constant and the mass range of observation in the mass spectrometer is focused on the mass of interest. The structural elucidation of the newly obtained oxidative or reductive degradation products obtained was then carried out using the "highest" resolution FT-ICR mass spectrometer performing MS / MS experiments.

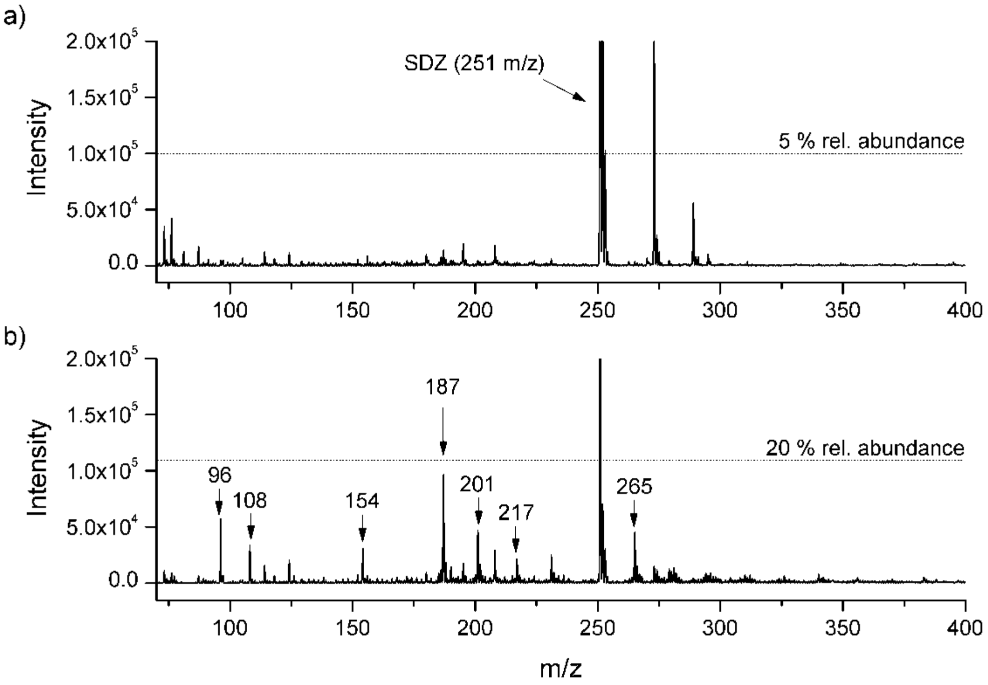


Figure IX-2 Mass Spectrum Of Sulfadiazine A) With EC-Cell Switched Off; B) With EC-Cell Switched On.

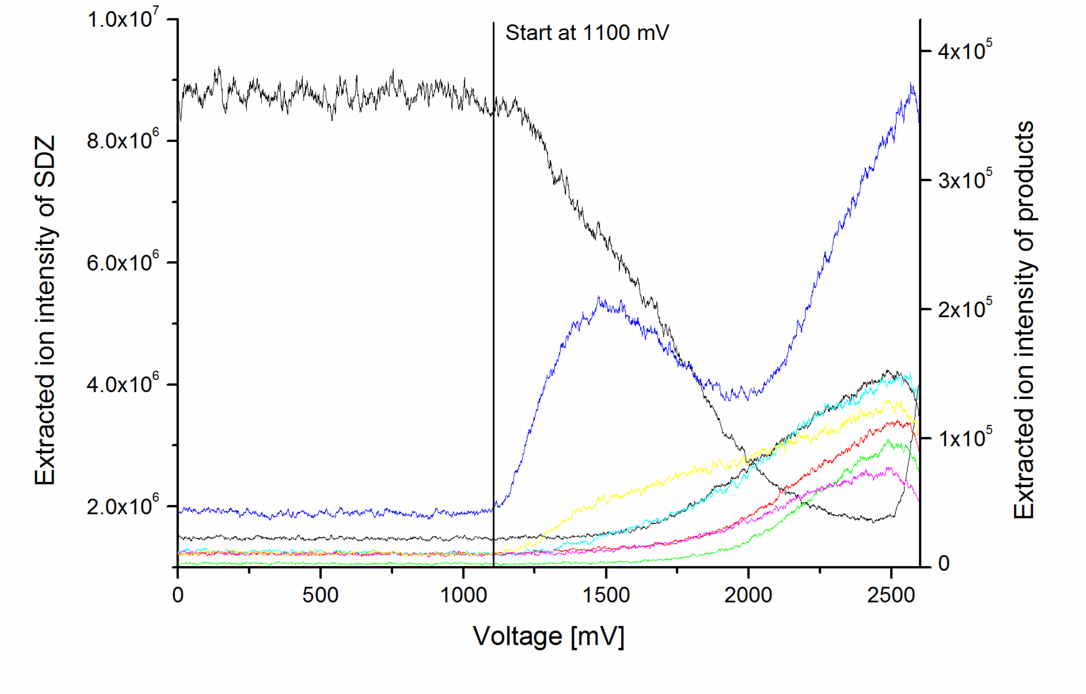


Figure IX-3: Signal intensity versus voltage for selected masses. The black curve shows the decrease of the starting material, whereas the coloured traces show the masses of the degradation products.

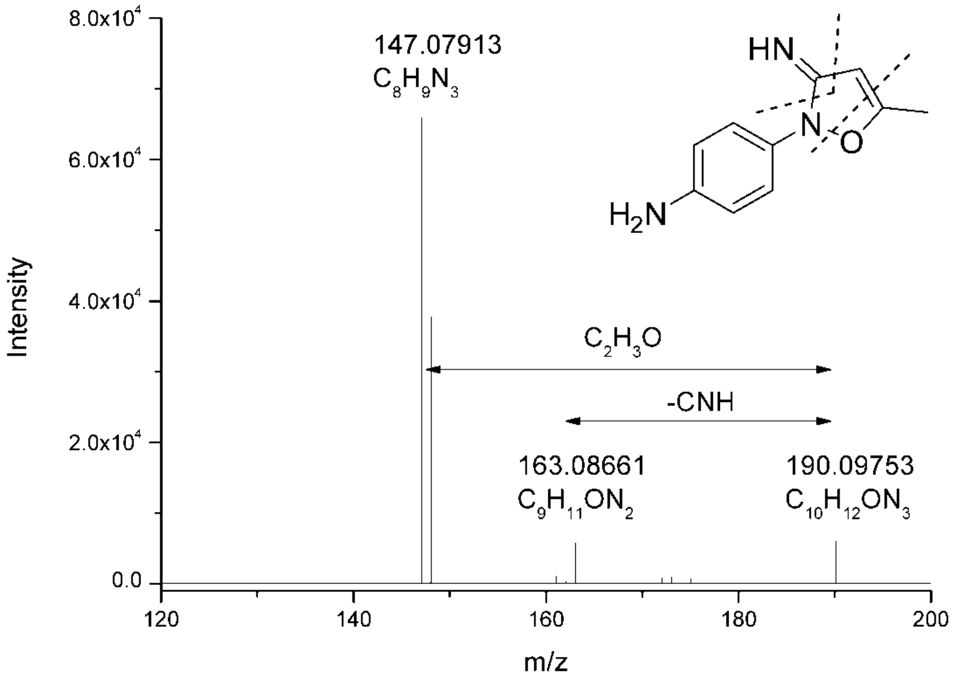
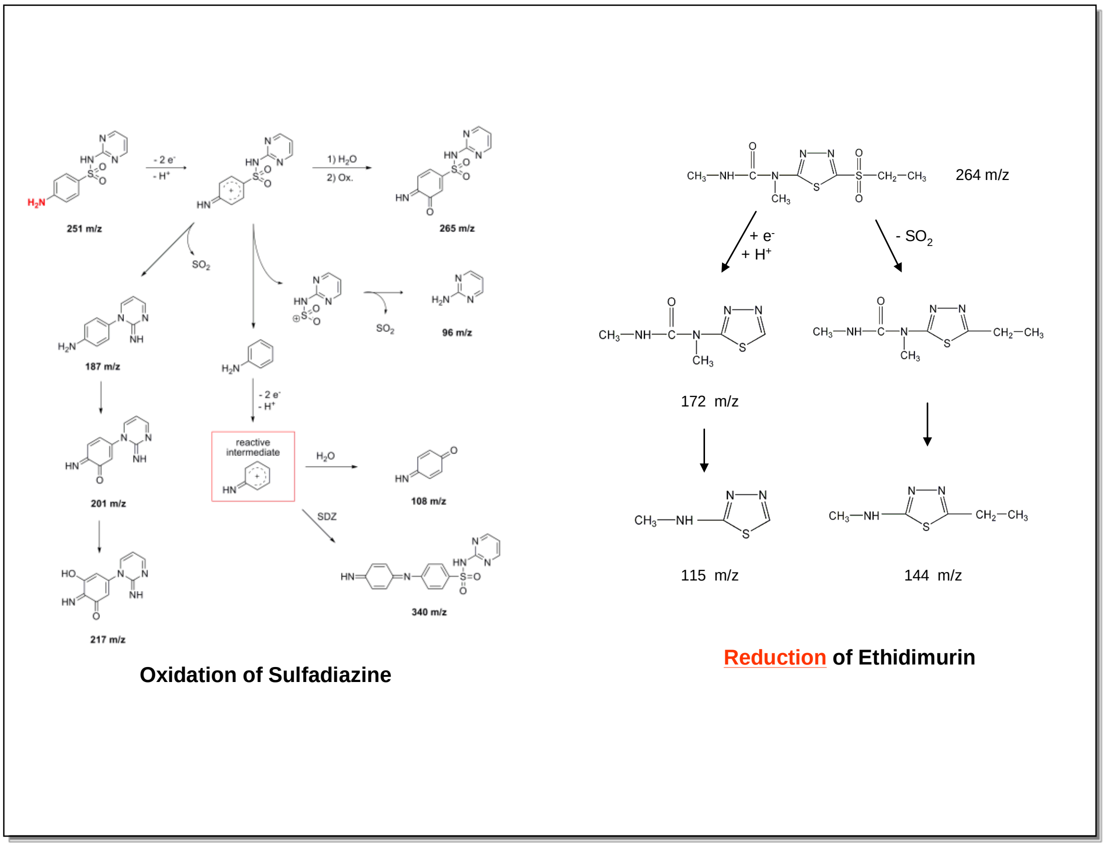


Figure IX-4: From MS/MS-Investigations at the FT-ICR-MS on one hand the molecular formula of the intermediate products is received on the other hand the mass differences can be identified by a molecular group, which allows the estimation of the structure of the degradation product as the starting materials structure is known an literature can be used to determine degradation mechanism.

In environmental systems like in dams besides the known oxidative conditions there are also reductive conditions, which might lead to reductive metabolites. The used EC-MS-system in principle can be operated in a reductive mode, but it had to be evaluated that using the reductive mode of the instrument makes sense for environmental systems. Therefore it had to be verified whether the model system is also suitable for the modelling of reductive metabolism. The reductive degradation occurs in the environment, for example, in reservoirs in deeper water layers and is therefore also relevant for the description of the changes on the Yangtze River. It could be demonstrated by way of example that the methodology can be extended to the reductive metabolism [2]. The comparison of known metabolites and the metabolites found by us shows a match of >80% in analogy to the studies of metabolites of oxidative degradation. This could be shown by the examples sulfadiazine and methabenzthiazurone under oxidative conditions and for ethidimurone under reductive conditions by comparison with literature data on these substances. In a few cases, reference substances are commercially available. In these cases, the confirmation of the degradation product may be performed by direct comparison measurement.



Oxidation of Sulfadiazine

Reduction of Ethidimurin

Figure IX-5: Example for the elucidation of the degradation mechanism of chemicals in the EC-MS system for oxidative and reductive conditions.

In some cases, the reaction mechanism of the oxidative and reductive degradation was fully understood. To study the fate of pollutants also the formation of chemical bonds with dissolved organic matter or other carbon matter in the environment has to be investigated. This is especially relevant for highly sediment-water bodies such as the Yangtze River. As the classical approaches are quite ineffective the question was, if it is possible to use the EC-MS system to establish a model system for the evaluation of possible bindings of the chemicals brought into the environment or their oxidation or reduction products. Therefore we selected model compounds and investigated the chemical reactions under oxidative or reductive conditions with this model compounds. The reaction of metabolites with model substances for organic carbon could be shown. The first interim results of this bottom-up approach, confirm findings of the typical top-down experiments in which always the extractable fraction was investigated. It was shown that relatively few reactive sites form chemical bonds, and these bonds are formed in many cases only under drastic conditions [2]. As a model substance for the organic carbon catechol, phthalic acid, reduced glutathione and histidine were chosen. The derivation of substances from a model of the organic carbon is shown in the following figure:

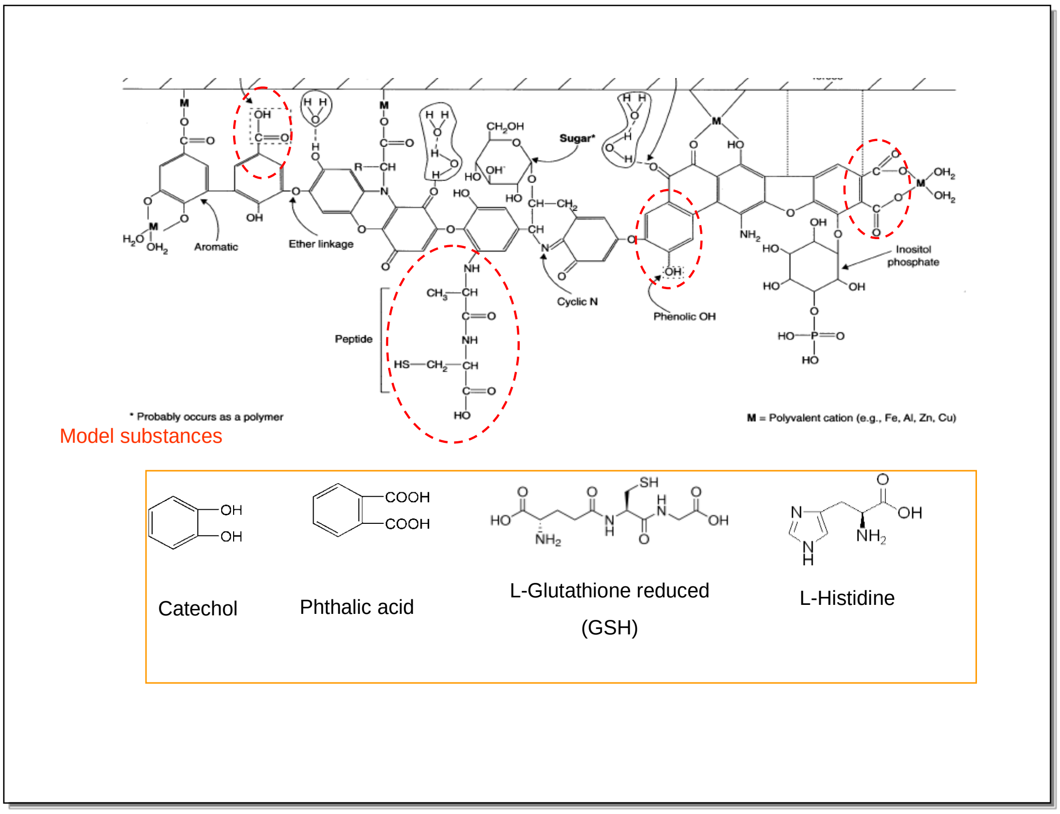


Figure IX-6: model of organic matter and the derived model substances.

The EC system itself can supply the cyclic voltammogram for the reactions. As can be clearly seen from Figure IX-7, it is therefore easily possible to determine the reaction-potential for the individual components of the oxidation of catechol and sulfadiazine and thus set the optimum voltage for the elucidation of the reaction by MS / MS.

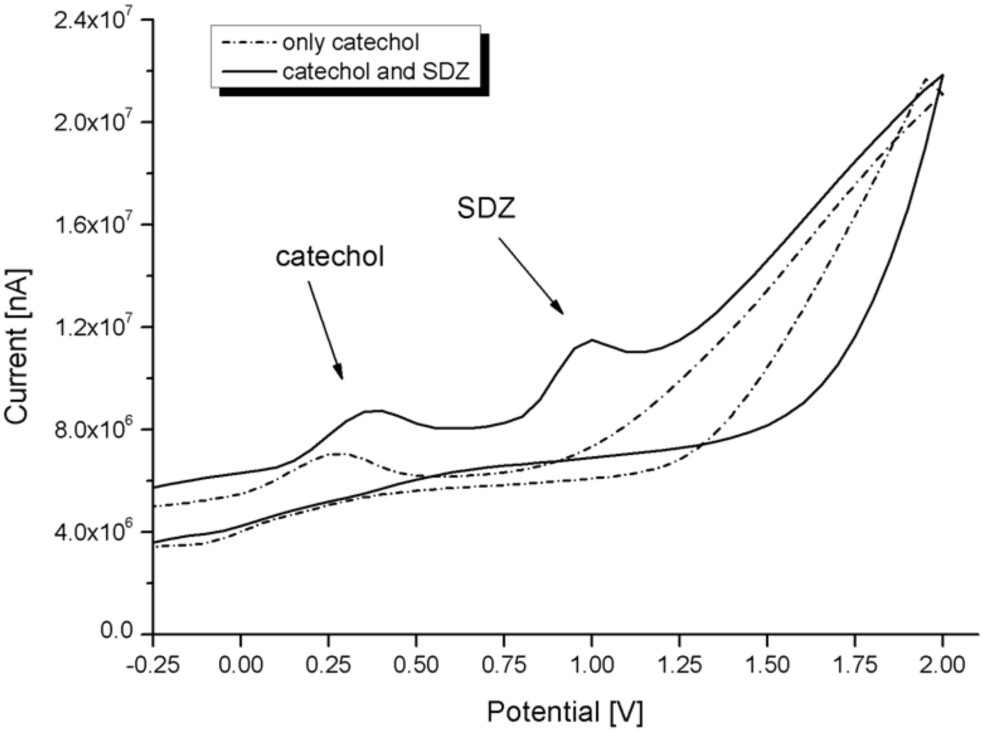


Figure IX-7: Cyclo-voltammogram of the reaction of catechol with sulfadiazine.

For the elucidation of reaction products, two different set-ups are needed. Whereas some substances under oxidative conditions lead to reactive intermediates, which can react with the relevant model substance for example for dissolved organic matter the mixture of the two compounds is directly pumped through the electrochemical cell by a syringe pump. This is, for example, been carried out with catechol and the examined xenobiotics. In some cases where it is expected that the oxidation or reduction leads to active species which react with the organic carbon as a quencher the model substance for the organic carbon is added with a second syringe pump via a T-piece behind the EC cell and then the mixture is transferred, to the MS. The results are published in detail [2].

An interesting selected result is given be the reaction of the 4-ring aromatics with catechol under oxidative conditions. From the aromatics chrysene, tetracene and benz [a] anthracene tested only the showed branched benz [a] anthracene shows sufficient reactivity under oxidative conditions. The product of the oxygen oxidation then showed a reaction with catechol as given in detail in the following figure.

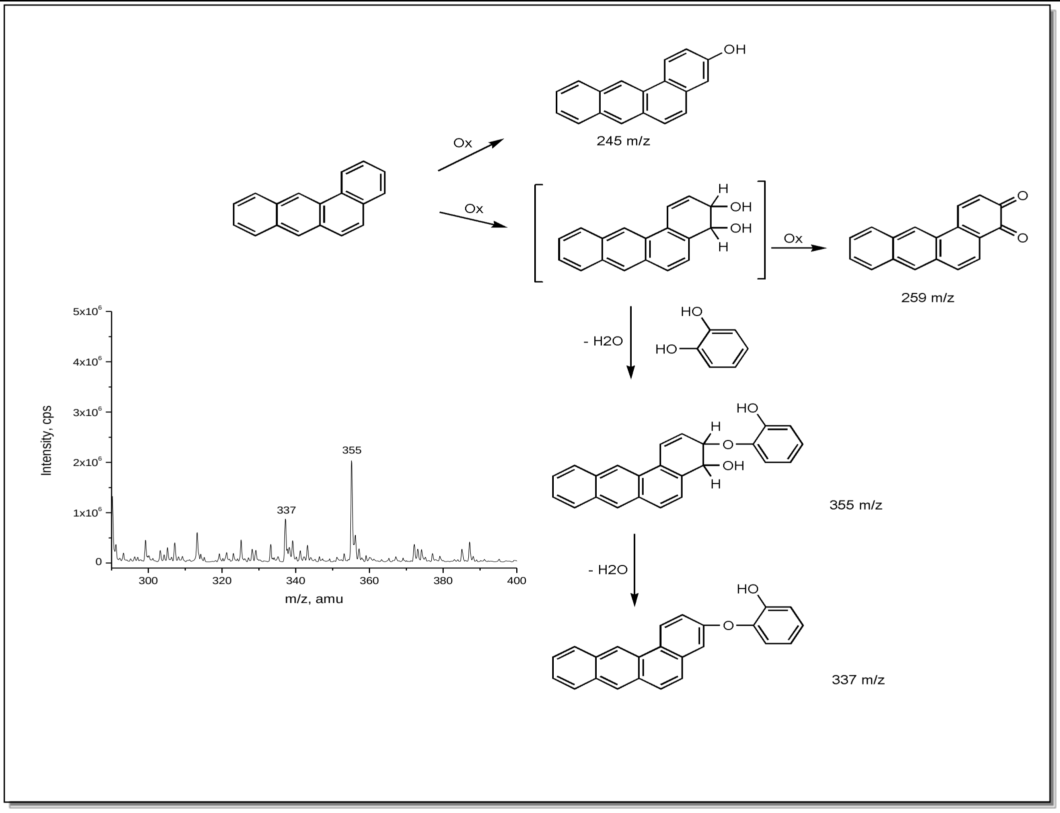


Figure IX-8: model reaction as a possible binding reaction of 4-ring-aromatics with organic matter.

This result supports the experiences that have been observed in the extraction of aromatic hydrocarbons in recent years. Here, it has been shown that a high degree that the PAH's are only adsorbed and can be extracted by suitable extraction methods also from aged samples almost completely.

The coupling of EC-MS for model compounds was then transferred to other substances. The work on the structure elucidation of model reactions for the organic carbon shows an explanation for the relative rare detection of chemical bonds of organic carbon [2]. For the process of sedimentation in the Yangtze dam this would be an indication that most of the organic pollutants can be released, especially after the mobilization of the sediment during the flushing of the dam. Measurements of samples on both sides of the dam are planned in the context of future projects, here especially the sampling of sediments and the extraction of organic pollutants could be of interest.

The collaboration with Ms. Chen has been continued during her post-doc time. One result was obtained by in depth analytics on the formation of bindings under drastic conditions [4]. A possibility of the EC-system in the existing configuration is to produce OH radicals, and therefore to perform the so-called electro-Fentons reaction, which can then be used directly coupled with mass spectrometry for the investigation of the reaction mechanisms under these drastic conditions. The electro-Fenton-process in the model system can be used to explain natural degradation processes, but can also be used in the context of optimization of processes in advanced oxidation for water or wastewater treatment. As PCB´s are an environmental problem a part of Chen Lei´s project is the examination of the degradation of PCBs 31 (2,4 ',5-trichlorobiphenyl), which she studied as a model substance for PCBs. The products of degradation of PCB 31 were able to be elucidated and bonds were found to γ-l-glutamyl-l-cysteinyl-glycine. This indicates that in oxidative cleaning of PCB containing waste water or sewage in the presence of organic carbon bonds could arise that could lead to the water that conserves structural elements of the PCBs in the dissolved carbon [4].

Furthermore also data on the predictability of the persistence of chemicals in the environment was collected. First results it do not fully explain the oxidative and reductive environmental behavior from the chemical structure. Anyway the approach seems to be promising and further work in this field should be performed in depth in other projects.

In cooperation with colleagues from Hangzhou in the context of the cooperation along the Yangtze river a publication is created with Jülich as a co-author [3]. It has been shown in the region of the inflow to the Tai Hu that the nutrient input into the lake mainly originates from diffuse sources. This prior information had been expected, however, provides a basis for further work in cooperation with Tongji University in the field of drinking water treatment from the Tai Hu.

The findings of the last phase of the project are currently stronger a preparation of other projects outside of the Yangtze dam. A continuation of the work to understand the processes in the area of the dam appears useful and necessary as soon as a funding possibility can be found.

4 Conclusions

The coupling of the electrochemical cell to mass spectrometry as a model system to understand environmental processes is now being used by many research groups. Both analytical approaches as also preparative techniques where the EC-system is used as a method for the generation of metabolites are applied. With our expertise in this field we can support mechanistic understanding in joint projects with other groups to contribute to the understanding of mechanisms in water systems and/or support optimization processes in water treatment.

5 List of Publications

Peer-Reviewed

[1] Electrochemistry-mass spectrometry for mechanistic studies and simulation of oxidation processes in the environment; Th. Hoffmann, D. Hofmann, E. Klumpp, S. Küppers, Anal. Bioanal. Chem. (2011) 399: 1859-1868

[2] Bottom up approach for the reaction of xenobiotics and their metabolites with model substances for natural organic matter by electrochemistry – mass spectrometry (EC-MS), Lei Chen, Diana Hofmann, Erwin Klumpp, Xinyi Xiang, Stephan Küppers, Yingxu Chen, Chemosphere, 89 (2012) 11, 1376 - 1383

[3] Application of (15)N- (18)O double stable isotope tracer technique in an agricultural nonpoint polluted river of the Yangtze Delta Region, X Q Liang, Z Y Nie, M M He, R Guo, C Y Zhu, Y X Chen, Küppers Stephan, ESPR 20(10), 6972 - 6979 (2013)

[4] Online electro-Fenton-mass spectrometry reveals 2,4´,5- trichlorobiphenyl oxidation products and binding to organic matter, Lei Chen, Stephan Küppers, Zheng Wang, Xinyi Xiang, Shiwei Cao, Environ Chem Lett, 12(2), 329-334 (2014)

[5] G. Subklew, J. Ulrich, L. Fürst, A. Höltkemeier: Environmental Impacts of the Yangtze Three Gorges Project: An Overview of the Chinese-German Research Cooperation. Journal of Earth Science, 2010, Volume 21, Number 6, p. 817-823; DOI: 10.1007/s12583-010-0133-x

[6] J. Zhang, J.M. Sequaris, H.D. Narres, H. Vereecken, E. Klumpp: Effect of organic carbon and mineral surface on the pyrene sorption and distribution in Yangtze River sediments. Chemosphere, 80 (2010) 11, 1321 - 1327

[7] J. Zhang, J.M. Séquaris, H.D. Narres, H. Vereecken, E. Klumpp: Pyrene and Phenanthrene Sorption to Model and Natural Geosorbents in Single- and Binary-Solute Systems. Environmental Science and Technology, 44 (2010) 21, 8102 - 8107

[8] C.M. Schreiber, B. Zeng, V.M. Temperton, U. Rascher, M. Kazda, U. Schurr A. Höltkemeier, A.J. Kuhn: Dynamics of organic acid occurrence under flooding stress in the rhizosphere of three plant species from the water fluctuation zone of the Three Gorges Reservoir, P.R. China. Plant Soil (2011) 344:111–129; DOI 10.1007/s11104-011-0732-z

[9] X. Xiang, L. Chen, S. Kueppers, M. Zhang, H. Tang, Z. Li, Y. Li: Turn Brownfield into Green Space-Eco-regeneration of Closed Land. Advanced Materials Research, 414 (2012), 63 – 67

Posters

[1] ISPAC 23, Münster: Reactions of PAC´s under oxidative and reductive conditions for the investigation of potential bound residues, L. Chen. S. Küppers, Sept. 4-8, 2011, Münster, Germany

[2] Electrochemistry-mass-spectrometry - a tool for enhanced understanding of mechanisms in environmental systems, L. Chen, X. Xiang, S. Küppers, D. Hofmann, S. Küppers, 1st ELCHEM^{2}S, Münster, 2011

[3] Investigation of environmental transformation and potential bond residues of PACs by Electrochemical Simulation, L. Chen, X. Xiang, S. Küppers, 1st ELCHEM^{2}S, Münster, 2011

[4] Analytical Tools in the evaluation of oxidative processes in the production of drinking water, S. Küppers, Workshop on Processes in the Yangtze River System, 22.Sept. 2012, Shanghai, China.

[5] Investigation of environmental transformation and potential bond residues of PACs by Electrochemical Simulation Lei CHEN, XinYi XIANG, Diana HOFMANN, Stephan KÜPPERS and
Photo-degradation of Chlortetracycline under Different Conditions and the Proposed Pathway XinYi XIANG, Lei CHEN, Diana HOFMANN, Stephan KÜPPERS in:
Processes in the Yangtze River System – Experiences and Perspectives - S. Küppers, G. Subklew, R.-D. Wilken (Eds.), Schriftenreihe des Forschungszentrums, Energie und Umwelt – Band 123, 2011, 84 S, ISBN 978-3-89336-744-3

[6] Linyan Zhu; Beatrix Santiago-Schuebel; Agnieszka Kraj; Zhiliang Zhu; Yanling Qiu; Björn Thiele, Stephan Kueppers; Degradation processes of environmentally relevant pharmaceuticals; 2013, June 9-13; Minneapolis, Minnesota; 61st Conference on Mass Spectrometry and Allied Topics

[7] Linyan Zhu; Beatrix Santiago-Schuebel; Agnieszka Kraj; Zhiliang Zhu; Yanling Qiu; Björn Thiele; Stephan Kueppers; Fate of Environmentally Relevant Pharmaceuticals; 28.02.2013 - 24.05.2013; Münster, Germany; ElCheMS 2: 2nd International Workshop on Electrochemistry/Mass Spectrometry

Non peer-reviewed

[1] Ökologische Auswirkungen des Drei-Schluchten-Damms; R.-D. Wilken, G. Subklew, S. Küppers, GIT Labor-Fachzeitschrift, 55 (6), 2011, 388-391.

[2] Die elektrochemische Zelle – Prozessverständnis für den Abbau von Chemikalien in der Umwelt; L. Chen, S. Küppers, GIT Labor-Fachzeitschrift, 55 (8), 2011, 543-544.

[3] The Yangtze-HYDRO Project: a Chinese–German environmental program; A. Bergmann, Y. Bi, L. Chen, T. Floehr, B. Henkelmann, A. Holbach, H. Hollert, W. Hu, I. Kranzioch, E. Klumpp, S. Küppers, S. Norra, R. Ottermanns, G. Pfister, M. Roß-Nickoll, A. Schäffer, N. Schleicher, B. Schmidt, B. Scholz-Starke, K.-W. Schramm, G. Subklew, A. Tiehm, C. Temoka, J. Wang, B. Westrich, R.-D. Wilken, A. Wolf, X. Xiang, Y. Yuan, Environ Sci Pollut Res DOI 10.1007/s11356-011-0645-7

[4] Processes in the Yangtze River System – Experiences and Perspectives - S. Küppers, G. Subklew, R.-D. Wilken (Eds.), Schriftenreihe des Forschungszentrums, Energie und Umwelt – Band 123, 2011, 84 S, ISBN 978-3-89336-744-3

[5] Processe im Yangtze River System – Bericht zu einem Workshop von chinesischen und deutschen Wissenschaftspartnern, R.-D. Wilken, G. Subklew, S. Küppers, GIT Labor-Fachzeitschrift, 56 (1), 2012, 8-9.

[6] W. Kempkens, G. Subklew: Radarfalle für Erdrutsche.. intern – Magazin für Mitarbeiterinnen und Mitarbeiter des Forschungszentrums Jülich, Januar 2012, S. 12

[7] W. Kempkens, G.Subklew: Radar Detection for Landslides - Ten years of research on the Three Gorges Dam. intern – In-House Magazine of Forschungszentrum Jülich, January 2012, p. 12

X General conclusion and outlook

This Yangtze-HYDRO project is now finished. The results are summerized in this report. Generally, the common topic ‘interactions between toxicants, water and sediment’ of the five sub- and two special-projects within the joint Yangtze-HYDRO project offered a variety of opportunities to joint research, to data and knowledge exchange. In this chapter, we sketch briefly our cooperative activities with our German and Chinese partners from science, government and industry.

- **Publications, Scientific Qualification**

More than 60 publications are specified in this report, which were compiled in the context of the project. In addition also about 30 scientific qualification works such as masters, diploma and PhD theses were performed and came to an end.

Joint workshops in Germany and China, as well as frequent project meetings (from the level of project managers to processor level) served the intense exchange of experiences in a challenging scientific environment.

- **‚Yangtze Scientists‘ PhD Meetings, Yangtze - HYDRO – YANGTZE- GEO**

– Interconnection within Yangtze Hydro & Geo Network between PhD candidates

2012 January 26-27	- TZW Karlsruhe	(Hydro)
2012 September 5-6	- IWW Biebesheim	(Hydro)
2013 June 13-14	- University Kiel	(Hydro & Geo)
2013 October 21-22	- RWTH Aachen	(Hydro & Geo)

The cooperation with Chinese Scientists in this project can be shown not only in joint publications, but also in the three workshops in China and Germany during the project.

- **Sino-German Workshops**

– Interconnection between German and Chinese scientific institutions

1.) 2011 March 27 – April 2 – Tongji University, Shanghai, China ‘Workshop on Interactions in the Water System – in the Frame of the Sino German Yangtze Project’

2.) 2011 November 28-29 – RWTH Aachen University, Aachen, Germany ‘Processes in the Yangtze River System-Experiences and Perspectives’

3.) 2012 September 21-23 – Tongji University, Shanghai, China ‘Processes in the Yangtze River System - 10th Anniversary of Sino-German Cooperation’

The scientific connections to China are established. Invitations are going in the meantime bidirectional. German water and environmental science are well established and became a model for Chinese scientific education.

1 Support of MOST, BMBF, Projektträger Karlsruhe

(PTKA-WTE)

We have to thank our supporters, especially MOST and the cooperating universities in China mentioned in this report, the BMBF-staff in Germany, especially PTKA-WTE team in Karlsruhe, namely Dr. Rüdiger Furrer, and all organizations working with us. We hope to stay also in further co-operation with our Chinese partners to continue research.

2 A Glance into the Future

How will the cooperation with China and the internal cooperation continue?

The co-operation with the Chinese scientific groups of researchers has been very well developed. The exchange of knowledge In the meantime is well established; invitations from China reach us, in order to use our common expert's assessment. The Chinese environment and water problems seem the same as we had in Europe in the middle of last century; these problems are on the way to be solved as it did Europe.

Further projects in the water and ecology sector are in preparation, whereby the BMBF in Germany and the appropriate organizations in China hopfully continue to co-operate.

One example is the Taihu Lake, which is up to now both used as water discharge body and drinking water reservoir. That must be changed to reach a good drinking water quality and supply in the area.

The available report shows however that co-operation between the two different cultures was successful and has a future.