



## **Project Report**

# **Application of the Geography-Referenced Environmental Assessment Tool for European Rivers (GREAT-ER) in the Catchment of the River MAIN (Germany)**

Dr. Jörg Klasmeier

Prof. Dr. Michael Matthies



Institut für  
Umweltsystemforschung  
Universität Osnabrück



# **Application of the Geography-Referenced Environmental Assessment Tool for European Rivers (GREAT-ER) in the Catchment of the River MAIN (Germany)**

Dr. Jörg Klasmeier

Prof. Dr. Michael Matthies

*and co-workers:*

Sören Haubrock

Annette Kantrowitz

Christiane Zarfl

Dominik Reusser

Institute of Environmental Systems Research

University of Osnabrück

49069 Osnabrück

*sponsored by*

Clariant GmbH, 65840 Sulzbach

IKW Industrieverband Körperpflege und Waschmittel e.V.

**December 2001**

The Clariant GmbH is conceded the right to use the software 'GREAT-ER Main' developed throughout this project for their own purposes. Additionally, it is agreed that 'GREAT-ER Main' can be used and further developed free of charge by other interested parties after completion. The Institute for Environmental Systems Research reserves the right to charge third parties for the cost of data carrier and handling. Clariant GmbH will also get further developments of 'GREAT-ER Main' for their own use free of charge.

# TABLE OF CONTENTS

<b>SUMMARY .....</b>	<b>.....</b>
<b>1 INTRODUCTION .....</b>	<b>1</b>
<b>2 SCOPE OF THE PROJECT .....</b>	<b>1</b>
<b>3 GENERAL INFORMATION AND PREREQUISITES .....</b>	<b>2</b>
3.1 Area of investigation .....	2
3.2 Monitoring data .....	3
3.3 Selected model compounds .....	4
3.4 Data requirements .....	4
<b>4 DATA ACQUISITION AND DATA PROCESSING .....</b>	<b>5</b>
4.1 River network data .....	5
4.2 Topological structure and segmentation.....	5
4.3 Hydrological data.....	6
4.4 Discharge site data .....	7
4.5 Substance-specific information .....	7
<b>5 RESULTS AND DISCUSSION .....</b>	<b>9</b>
5.1 Test phase – Exclusive simulation of the ‘Bavarian Main’ river stretches .....	9
5.2 Calibration - Simulation of the Bavarian Main and major tributaries.....	9
5.3 Application - Simulation results for the whole catchment .....	12
5.4 Discussion.....	16
<b>6 CONCLUSIONS AND OUTLOOK.....</b>	<b>16</b>
<b>7 LITERATURE .....</b>	<b>17</b>



## SUMMARY

The Geography-referenced Regional Exposure Assessment Tool for European Rivers (GREAT-ER) has been applied to three typical household chemicals in the mid-sized catchment of the *Main*. Input data are geo-referenced information about river topology, flow data from gauging stations and specific discharge site data provided by the Bavarian Water Management Agency (LfW) and the Hessian State Office for Environment and Geology (HLUG). Simulated concentrations have been compared with monitoring data measured by the LfW in the *Bavarian Main* during a monitoring campaign in May, 1998. In a two-stage process, it has been shown that a simplistic approach of modeling solely the main river stretches does not lead to satisfying results. However, a more detailed treatment with the major tributaries included result in the conclusion that GREAT-ER is successfully applicable in mid-sized river catchments like the *Main*.

The Bavarian part of the *Main* was taken for calibration using LAS and HHCB as model compounds. The results were in good agreement with available monitoring data showing the general applicability. It has also been demonstrated that the calibrated model can be extended to the Hessian part of the *Main* catchment and to other 'down-the-drain' chemicals such as the pharmaceutical Diclofenac. The project was the first step in the direction of establishing such a large catchment for routine use with GREAT-ER. Further investigations will include simulations with a wider variety of compounds, completion of input data sets (especially possible industrial emitters), refinement of the hydrology and more detailed sensitivity analyses.



## 1 Introduction

The Geography-referenced Regional Exposure Assessment Tool for European Rivers (GREAT-ER) has been developed as a prediction tool for spatial aquatic exposure assessment of typical 'down-the-drain' chemicals (Feijtel et al., 1997; Boeije et al., 1997; Matthies et al., 2001). The methodology has so far been successfully applied to various small catchments in different European countries (e.g. Schulze et al., 1999; 2001). Recently, first investigations of the application of GREAT-ER in larger catchments have been started in two German river basins, the *Rhine* and the *Elbe* sponsored by the Federal Environmental Agency (UBA).

In order to receive a preferably complete picture of the aquatic exposure it is desirable to explicitly incorporate the major tributaries of the investigated rivers. One of the major tributaries of the *Rhine* is the river *Main* flowing from its two sources in the northeastern part of Bavaria to the mouth at Wiesbaden/Mainz. Especially in the densely populated and high industrialized area around Frankfurt, significant emissions of organic chemicals via household wastewater or direct industrial emissions can be expected. The implementation of the *Main* catchment into GREAT-ER could add to closing one of the gaps in the German *Rhine* river basin. Thus, the project 'GREAT-ER Main' was initiated in cooperation with the Bavarian Water Management Agency (LfW).

## 2 Scope of the project

'GREAT-ER Main' was intended to enable the geo-referenced simulation of selected typical household chemicals in the river *Main*. The project consists of two phases: The first phase deals with the Bavarian part of the *Main* and a subsequent calibration step. In the second phase, the river network is enlarged by the Hessian part of the catchment. On the basis of existing information about the topology, the hydrological flow regime and discharge site data in the catchment, selected parts of the river net are implemented into GREAT-ER software and model runs for selected chemicals are to be performed. In the very first step the preparation of the river net is restricted to the river stretches of the *Main* itself. Simulated concentrations should then be compared with monitoring data measured by the Bavarian Water Management Agency (LfW) during a monitoring campaign in May, 1998. During the calibration step it shall be investigated whether this focus on the main river stretches without explicitly modeling the tributaries allows a reliable exposure assessment for a mid-sized catchment like the *Main*.

The provision of necessary geo-referenced data is the main contribution of the LfW within this project. Besides the monitoring data this encompasses the river topology, discharge site data and the hydrological flow regime in the catchment calculated with the ATV water quality

model (Christoffels, 2001). In this respect, it is planned to seek for possibilities for a useful data exchange or coupling between GREAT-ER and the ATV model to facilitate future work. Substance data have to be collected by the Institute of Environmental Systems Research. These are the physico-chemical properties, elimination efficiencies and degradation rates as well as consumption quantities.

### 3 General Information and Prerequisites

#### 3.1 Area of investigation

The catchment of river *Main* covers a total area of about 27,700 km<sup>2</sup> with its main part located in Northern Bavaria. The *Main* has a total length of about 524 km and is roughly divided into three major parts, namely the *upper Main*, the (*middle*) *Main* and the *lower Main*. The *upper Main* comes into being at the confluence of *Weisser Main* and *Roter Main* near Kulmbach having a mean volumetric water flow (MNQ) of about 40 m<sup>3</sup>/s. After the confluence with the *Regnitz* near Bamberg (km 380) it is called (*middle*) *Main* with mean flow values of 90 - 120 m<sup>3</sup>/s. The last part called the *lower Main* starts near Aschaffenburg and is located mostly in the state of Hessen with mean flow values of 120 - 200 m<sup>3</sup>/s. A small part of the whole *Main* catchment, namely the tributary *Tauber* is located in the state of Baden-Wuerttemberg. Figure 1 shows the whole catchment area of the *Main* with the highlighted subcatchments of the *Regnitz* (green) and the *upper Main* (yellow).

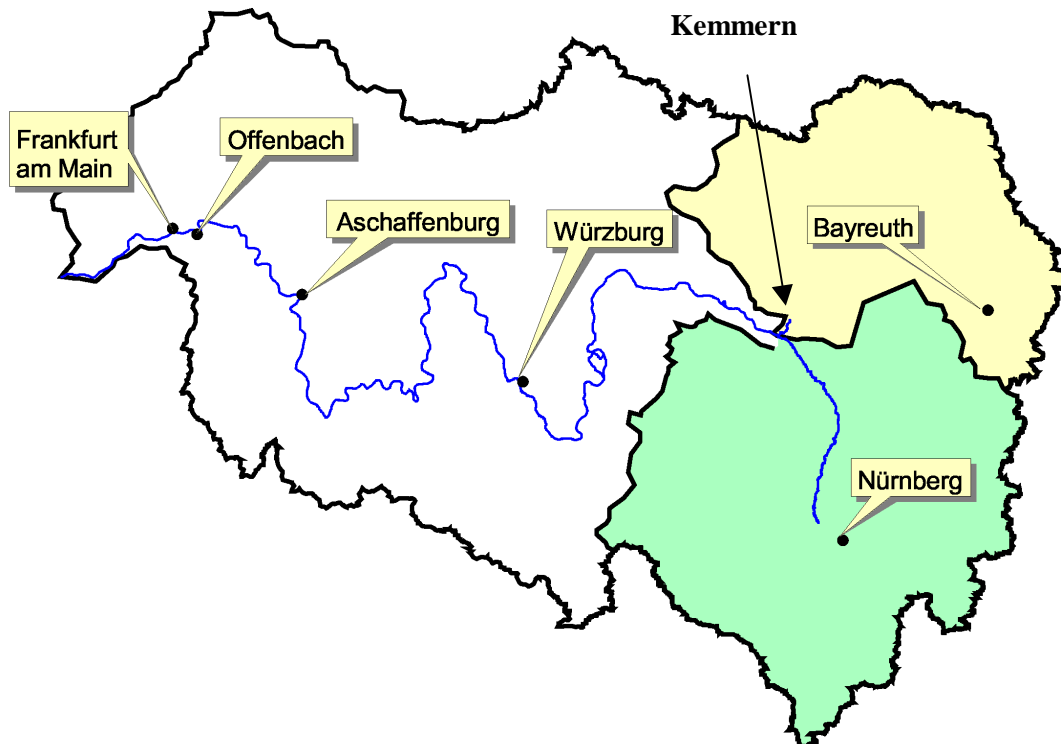
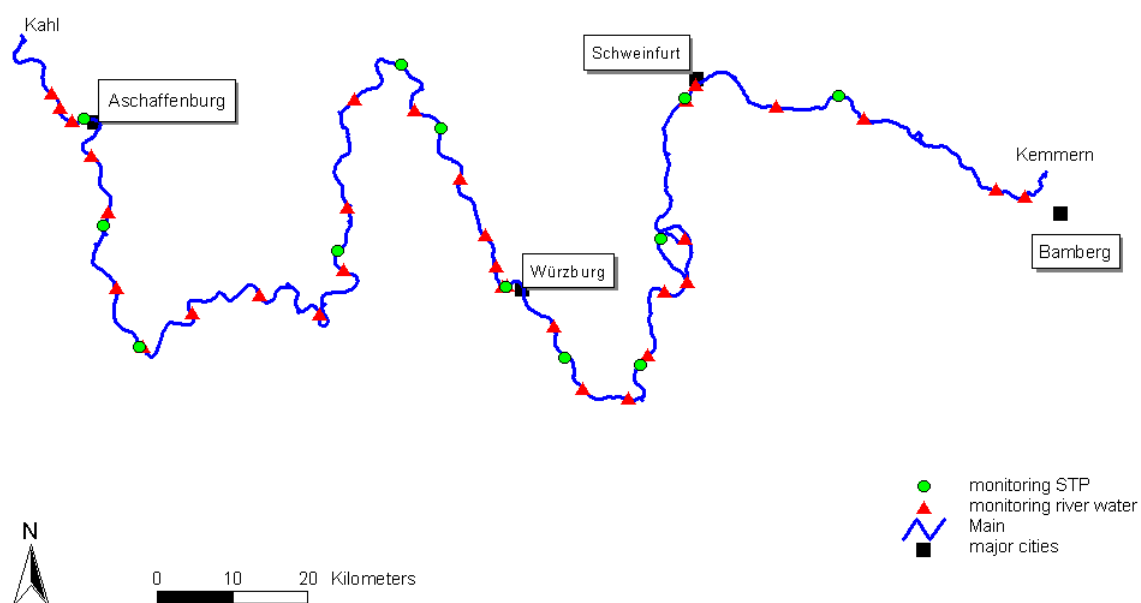


Figure 1: Survey of the investigated part of the *Main* catchment

The investigations within this project, however, focus on the *Main* itself from the gauging station at Kemmern (km 391) to the mouth into the river Rhine at Wiesbaden/Mainz. The *upper Main* upstream of Kemmern was not part of the project. Due to missing data in the first phase of the project the investigations were restricted to the *middle Main* and a small part of the *lower Main* ending at the Hessian border.

### 3.2 Monitoring data

In order to test the reliability of model results obtained by GREAT-ER simulations, they are compared with monitoring data. In a calibration step, reasons for identified differences are sought and the respective information and data are compiled in order to enhance the performance of the model. The monitoring data for this project have been measured during a water quality survey of the rivers *Main* and *Donau* aboard the MS Burgund from May 10-18, 1998. Besides chemical and biological standard analyses, water and sediment samples as well as influent and effluent samples of municipal sewage treatment plants (STP) were analyzed for a couple of organic micropollutants. In the river basin of the *Main* a total of 35 water samples were analyzed. Water samples of the *Main* were taken at regular intervals from the gauging station at Kemmern (km 391) to the Hessian border (km 68). Only one sample each was taken from the tributaries *Tauber* and *Fränkische Saale* just before they meet the *Main*. There were no measurements for the other tributaries and the Hessian part of the *Main*. The distribution of the sampling locations in the *Main* is shown in Figure 2.



**Figure 2: Sampling locations of monitoring campaign (May 1998)**

### 3.3 Selected model compounds

The compounds were chosen from the list of substances analyzed during the above-mentioned monitoring campaign. According to the design of the GREAT-ER software typical household chemicals were regarded as first priority compounds. Other criteria for the selection were actual relevance in terms of production volumes and emission rates, comparability with already conducted studies in other catchments, and availability of substance parameters. For the first tier the following substances were selected as model compounds:

- the anionic surfactant *linear alkylbenzene sulfonate* (LAS)
- the polycyclic musk fragrance *1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylclopenta- $\gamma$ -2-benzopyrane* (HHCB)
- the pharmaceutical *2-[(2,6-Dichlorophenyl)-amino]-benzeneacetic acid* (Diclofenac)

### 3.4 Data requirements

In order to run the GREAT-ER software several data sets for the investigated catchment are required. These comprise

1. geography-referenced river network data
  - digital river network information
  - hydrological data (volume flow, flow velocity)
2. discharge site information
  - location of discharge sites (wastewater treatment plants, direct industrial discharges)
  - size of municipal sewage treatment plants (actual population connected)
  - type of municipal sewage treatment plants (trickling filter or activated sludge)
  - emission data for direct discharge sites
3. substance-specific information
  - physico-chemical data of the substances
  - elimination efficiency of treatment plants for the substance
  - production or consumption data (on a per-capita basis)
4. monitoring data
  - sampling location
  - type of sample (grab, composite)
  - frequency of measurements (single data points or mean values)
  - analytical errors and detection limits

The compilation of reliable data sets is the most time-consuming steps. Originally, with the exception of the substance-specific property information all data were meant to be compiled and made available to us in a suitable data format by the Bavarian Water Management Agency (LfW) or the industrial contractor, respectively.

## **4 Data acquisition and data processing**

### **4.1 River network data**

At the start of the project, geo-referenced data sets for the Bavarian part of the river basin were delivered from the LfW as shapefiles based on ATKIS data (1:25,000). The major rivers were included in a polygon shapefile additionally giving the width of the respective river stretches. For use with GREAT-ER, however, these data had to be transformed into line objects by a time-consuming step of manual re-digitalization.

Due to internal communication problems the data set for the Hessian part of the *Main* was not available until the second phase of the project. The geo-referenced river net data were then delivered in the form of a line object shapefile ready for use. As a basis for the small part in Baden-Wuerttemberg, a line object shapefile based on lower resolved data (1:200,000) delivered by the Federal Environmental Agency (UBA) was used.

### **4.2 Topological structure and segmentation**

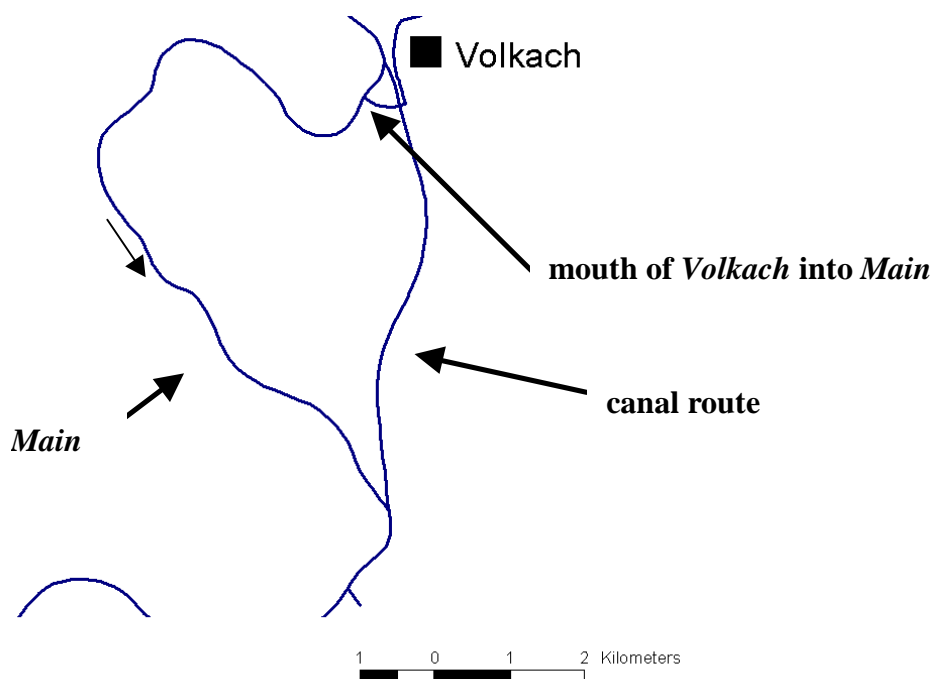
The geo-referenced river net data from the different sources were put together to build up the topology of the selected parts of the river basin to be investigated. In the first phase only the stretches of the Bavarian part of the *Main* were included. During the project it proved to be necessary to also include the major tributaries which led to a stepwise enlargement of the implemented river network. The Hessian part of the river basin including the missing river stretches of the *Main* and the major tributaries in Hessen was added in the second phase of the project as soon as the data were available.

In order to run the model the river topology has to be divided into segments which carry the respective attribute data important for the model. The segmentation is given by the following preconditions:

- Input from discharge sites (WWTP or direct industrial emissions) always takes place at the beginning of a new segment.
- Tributaries always meet the superior river at the beginning of a new segment.
- Weirs influencing the hydrological regime enforce a new segment.

- Segment lengths should not exceed 2000 m.
- Location of gauging stations or monitoring sites should - if possible - be at the start of a new segment.

Special attention has to be paid to so-called bifurcations, where the river splits up into two new stretches, which combine again after a certain flow distance. This is the case at the *Volkacher Mainschleife* (km 298). Here, on a length of about 13 km the natural river course is passed by a canal route for the shipping traffic (see Figure 3). Nevertheless most of the water is flowing along the natural course, as the canal is artificially held at a volume flow of 5 m<sup>3</sup>/s most of the time.



**Figure 3: Canal by-pass of the *Main* near Volkach**

Another critical issue is the course of the tributary *Volkach*, which crosses under the canal before it flows into the *Main*. The final segmentation at this point was cautionary double-checked after data processing.

### 4.3 Hydrological data

The river segments carry the attribute data necessary for the model simulations. For the hydrological flow regime knowledge of the water flow ( $Q$ ) and the flow velocity ( $v$ ) for each river segment is necessary. These data are available for the gauging stations in the river basin and have to be interpolated for the other segments. At the beginning of the project the Bavarian Water Management Agency (LfW) agreed on calculating the missing flow and

velocity data by using the ATV model. However, these data were not delivered in time so that the hydrology had to be additionally worked out. The necessary water flow data (long-term mean values) for the Bavarian gauging stations were provided by the LfW, whereas for Hessen and Baden-Wuerttemberg they had to be taken from the hydrological yearbook (DGJ, 1992). For the interpolation between the gauging stations a sophisticated hydrological model was considered not necessary due to the fact that only selected parts of the whole river network were incorporated into 'GREAT-ER Main' and the main focus of the project was on the river stretches of the *Main* itself. Moreover, the *Main* is a regulated navigable waterway which means that its water level and hence the flow is kept constant. For the same reason the approach of a nonlinear regression with the accumulated river lengths (Schulze & Matthies, 2001) is not useful. Instead, a simple linear interpolation with the segment lengths was used to compile the values between the gauging stations. For the stretches of the *Main* and the major tributaries the error introduced by this procedure can be regarded as acceptable small. Special attention was paid on the plausibility of the calculated values in the whole river system.

The respective flow velocities were calculated with the internal routine (empirical regression relationship) of the GREAT-ER software, which also has a restricted applicability for non-UK catchments.

#### **4.4 Discharge site data**

Discharge site information for Bavaria were delivered as EXCEL sheets by the LfW at the start of the project. This included an almost complete data set of the municipal sewage treatment plants (STP) as well as information about direct industrial emitters. The latter, however, were incomplete with respect to actual emission data of the investigated compounds. Data sets for the STPs in Baden-Wuerttemberg and Hessen were delivered in the second phase of the project, but there are still no data of the industrial emitters available. All data were double-checked for plausibility and then converted into the GREAT-ER format.

#### **4.5 Substance-specific information**

Physico-chemical properties of the compounds of interest as well as the elimination efficiencies of the treatment plants were compiled from the scientific literature. In-stream removal of Diclofenac is dominated by photodegradation and minimum and maximum degradation rates for surface water were estimated using literature data from lake Greifensee in Switzerland (Poiger et al., 2001). For the in-stream removal of HHCB it was concluded

from the literature that degradation processes do not play an important role and the removal from river waters is almost exclusively due to volatilization. Thus, minimum and maximum volatilization rates for HHCb in the *Main* were estimated by the formula of Southworth (1979).

Emission rates were estimated as per-capita consumption from available information about production volumes and use patterns or taken from the literature. For Diclofenac the mean annual daily doses prescribed (Schwabe & Pfaffroth, 1998) were multiplied by the mean dose of active ingredient (Diclofenac) per prescription to calculate this value. Table 1 summarizes the important substance properties of the three compounds used in the first tier.

**Table 1: Important substance properties of model compounds**

	LAS <sup>1</sup>	HHCb <sup>2</sup>	Diclofenac <sup>3</sup>
CAS number	68411-30-3	1222-05-5	15307-86-5
Molar mass	338.2 g/mol	258.4 g/mol	296.2 g/mol
log K <sub>OW</sub>	1.75	5.9	4.5
Water solubility	1100 mg/L	1.75 mg/L	2.37 mg/L
Vapor pressure	unknown	0.073 Pa	8.2E-6 Pa
K <sub>AW</sub> (dim.less)	not relevant	0.0044	1.9E-10
in-stream removal rate (h <sup>-1</sup> )	0.01 - 0.69 h <sup>-1</sup>	0.005-0.03	0.008-0.06
Estimated per-capita consumption	1095 g/a	4.015 g/a	0.594 g/a
<u>STP elimination efficiencies</u>			
Activated sludge	98.0 - 99.6 % <sup>4</sup>	92 % <sup>5</sup>	69 ± 4 % <sup>6</sup>
Trickling filter	80 - 87 %	83 % <sup>5</sup>	69 ± 4 % <sup>6</sup>

<sup>1</sup> data from Rippen (1999), Schulze et al. (1999)

<sup>2</sup> data from van de Plassche & Balk (1997), Schwartz et al. (2000)

<sup>3</sup> data from PHYSPROP database (<http://esc.syrres.com/interkow/>)

<sup>4</sup> data from Matthijs et al. (1999)

<sup>5</sup> data from Simonich et al. (2000)

<sup>6</sup> data from Ternes (1998)

## 5 Results and Discussion

### 5.1 Test phase – Exclusive simulation of the ‘Bavarian Main’ river stretches

For the aquatic exposure assessment of chemicals a preferably complete coverage of the important emission sites is necessary. Typical household chemicals are to a great extent emitted with household wastewater and enter the river system after passage of sewage treatment plants. In the Bavarian part of the *Main* catchment the population is concentrated more or less along the main river. Thus, in the first phase only the river stretches of the *Main* itself from the gauging station at Kemmern (km 391) to the Hessian border (km 68) were implemented into GREAT-ER. The input from the *upper Main* (upstream of Kemmern) was estimated via the monitoring data just before the confluence with the *Regnitz*. Here, the values for the selected model compounds were comparably low so that the uncertainty caused by this procedure is considered to be sufficiently small.

For the major tributaries of the *Bavarian Main*, the input estimation was planned to be conducted in the same way. However, the monitoring data set of the LfW was not sufficient to reliably estimate the input of the model compounds into the *Main* via these tributaries. This is especially true for the sub-catchment of the *Regnitz* including the densely populated area Nürnberg / Fürth / Erlangen with its approximately 1 million inhabitants. The major input of the target compounds into the *Main* headwater is suspected to happen in this region. For this reason, a stepwise enlargement of the river network was started. The emission strength in each sub-catchment of the tributaries was estimated considering the actual population connected to sewage treatment plants. Then, the tributaries which proved to carry possibly relevant loads of the compounds of interest were additionally added to GREAT-ER Main. This also encompassed the *Tauber*, which is mainly located in Baden-Wuerttemberg. Figure 4 gives a complete picture of the digitized river system finally used for the GREAT-ER simulations in the calibration phase. In this state about 78% of the population in the Bavarian part of the *Main* catchment (excluding the *upper Main* area) were connected to the 'GREAT-ER Main' river system via the respective sewage treatment plants.

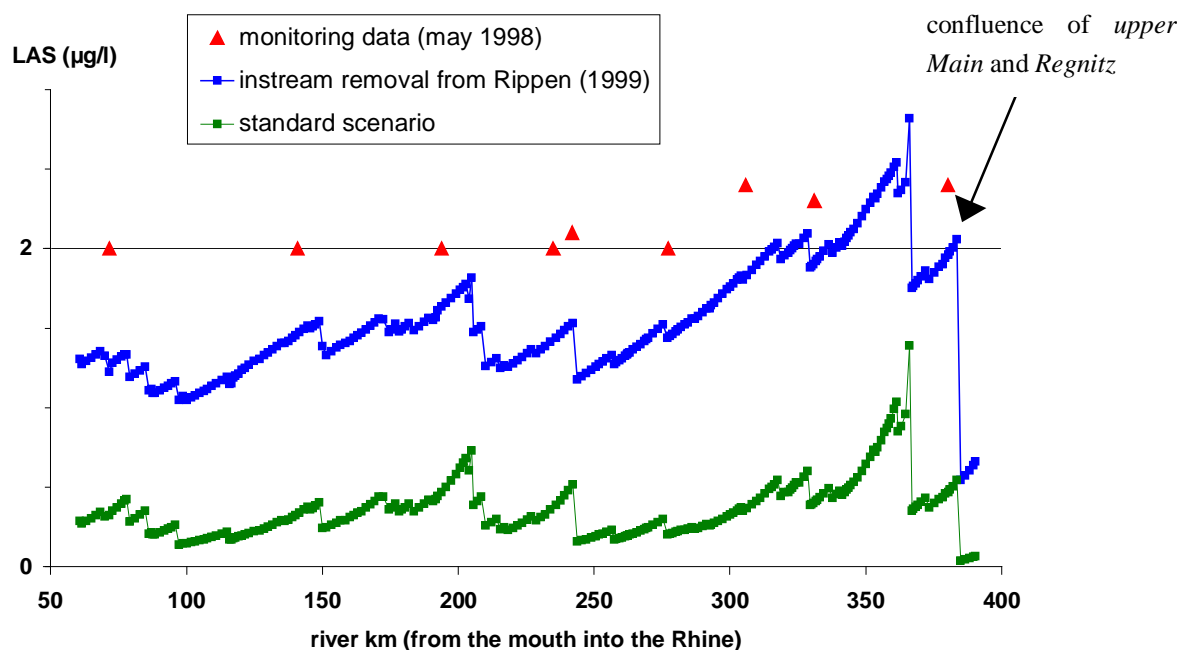
### 5.2 Calibration - Simulation of the Bavarian Main and major tributaries

For the calibration of 'GREAT-ER Main' different scenarios for two of the selected model compounds (LAS and HHCB) were run using the Bavarian river network shown in Figure 4. The third compound Diclofenac was not used for calibration purposes, as the monitoring data were below the detection limit of 10 ng/L at almost all sites. Although the problems with

rough input estimations at the mouth of the tributaries were known, this had still to be done for *Gersprenz* and *Mümling* due to a lack of data.

The results of the simulations were then compared with the monitoring data in the *Main*. The measured concentration profile along the *Main* was satisfactory represented by the GREAT-ER simulations. However, significant underestimations of the actual HHCB concentrations occurred at all sites. This could be ascribed to a mismatch between the long-term averaged flow rates used for the GREAT-ER simulations and the actual water flow during the monitoring campaign in May, 1998. At this time, an unusual low water flow had been regarded for the *Main* due to a prolonged period of relative dryness. This special situation could not be represented by the long-term mean values used for the GREAT-ER calculations. To enable a realistic comparison with the monitoring data, the attribute file for the river stretches was changed and the actual flow rates measured during the monitoring campaign were used for the following calculations.

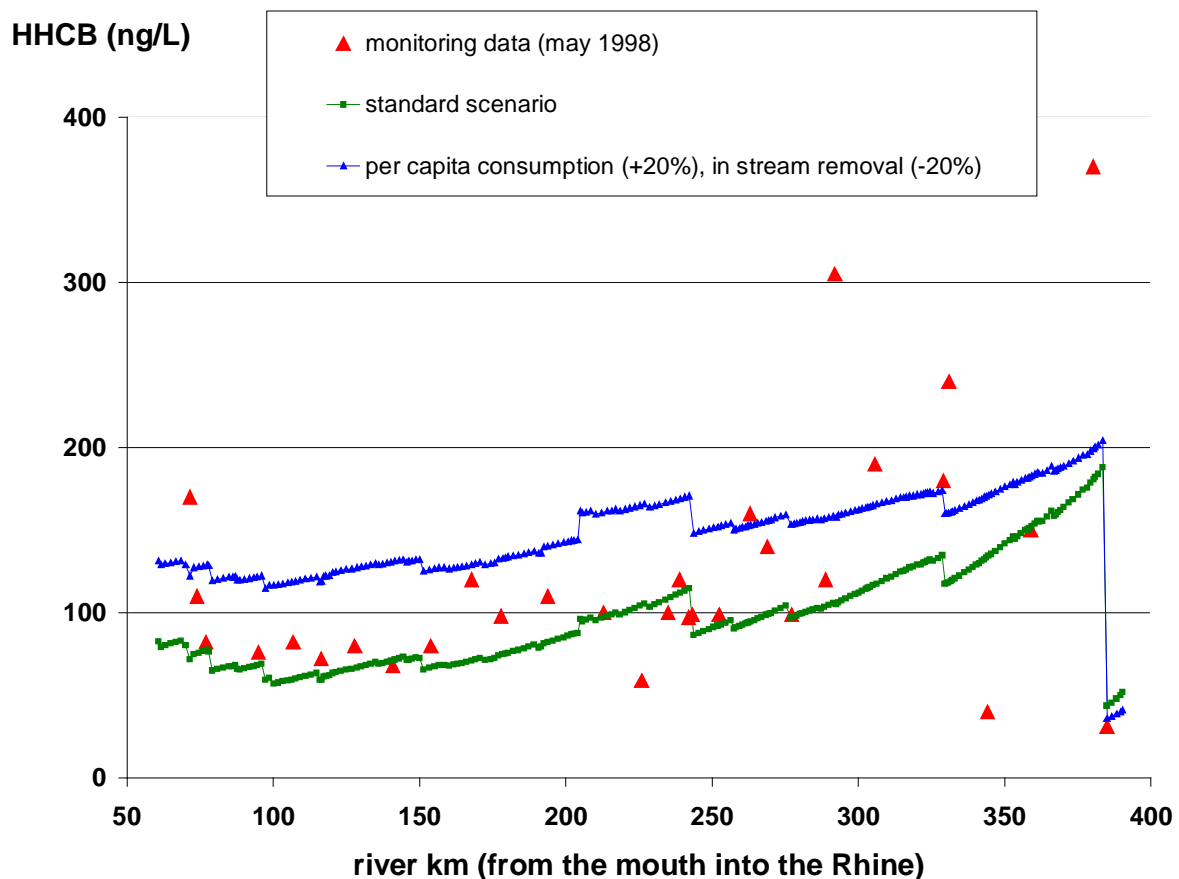
**LAS:** Model scenarios were run for LAS with the adapted hydrology and the results compared to monitoring data. For the first scenario referred to as standard scenario, a uniformly distributed in-stream removal rate of  $0.01 - 0.69 \text{ h}^{-1}$  was used (Schulze et al., 1999). In an alternative scenario a smaller range from  $0.021 - 0.046 \text{ h}^{-1}$  was assumed (minimum / maximum values from Rippen, 1999). Figure 5 shows the results of these two model scenarios for LAS.



**Figure 5: Mean simulated LAS concentrations in the *Main* (May, 1998)**

The detection limit of LAS was  $2\mu\text{g/L}$ . Data points marked on the horizontal line in Figure 5 actually had proved to be below this detection limit. Although this is unsatisfactory it can be seen that the results of both scenarios are not contradictory to the data and the alternative scenario better represents the concentrations after the confluence of *upper Main* and *Regnitz*. According to the high load of the *Regnitz* the LAS concentration increases after the confluence just above the detection limit and decreases again along the course of the river.

**HHCB:** For HHCB a standard scenario with data from Table 1 was performed and compared to an alternative one with an arbitrarily increased per-capita-consumption (+ 20%) and a higher in-stream removal rate (by a factor of two). Figure 6 shows the results of the two scenarios in comparison with the monitoring data.



**Figure 6: Mean simulated HHCB concentrations in the *Main* (May, 1998)**

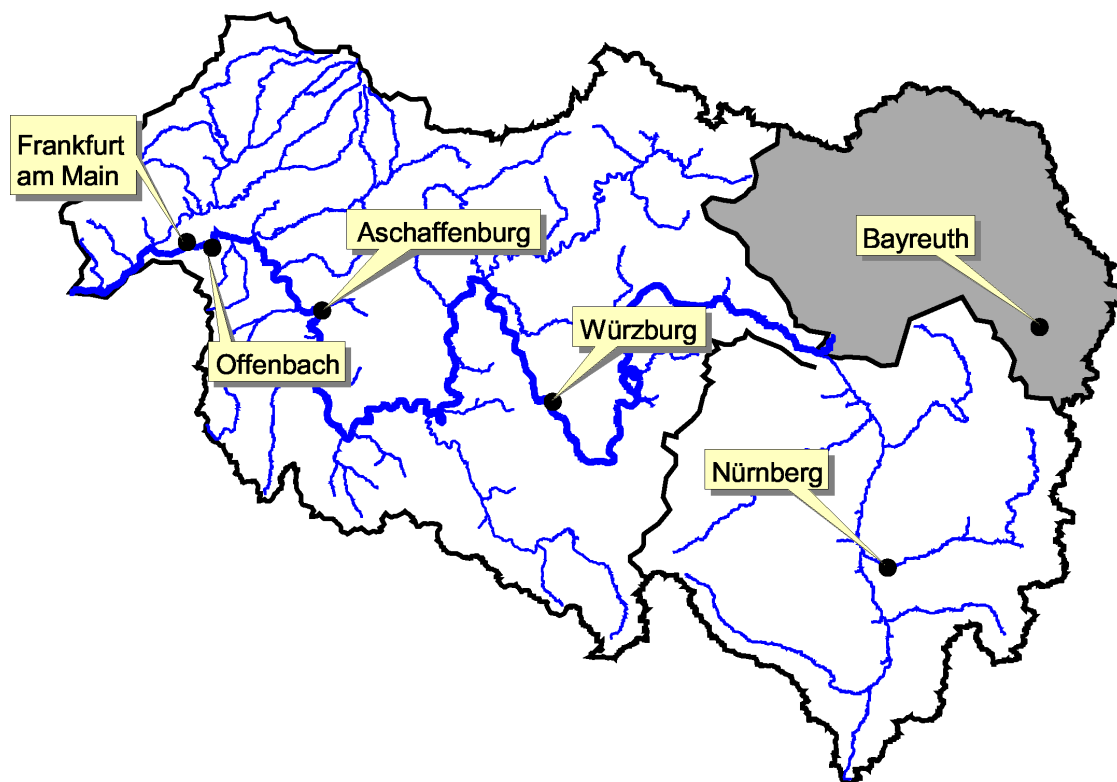
It can be seen that the standard scenario results in a good agreement with most of the monitoring data points. The accuracy of the predictions are well within a factor of three,

which has earlier been defined as a target value for GREAT-ER performance (Matthies et al., 2001). Nevertheless, there are some obvious deviations in the region after the confluence of *upper Main* and *Regnitz*. In this respect, it has to be kept in mind that the monitoring data are not representing the mean temporal and spatial concentration as they are unique values in space and time. To clarify the situation on the first 50 km after the confluence more data points would have been necessary.

Plausibility analyses running different scenarios, however, showed that the monitoring data set seems to be inconsistent. The huge increase of the concentration given by the first data point after the confluence can be hardly explained by the load of the *Regnitz*. The result of a scenario with arbitrarily changed values for the per-capita consumption (+ 20%) and the in-stream removal rate (- 20%) support this conclusion. Even with a significant parameter change the concentration at this point is still underestimated. On the other hand, we can see no explanation for the strong concentration drop and re-rise in between a distance of about 40 km indicated by the following data points. As a consequence of the change in input parameters, however, almost all other values are more or less overestimated by the test scenario. Thus, it can be concluded that the standard scenario best represents the HHCB concentrations in the *Main*.

### **5.3 Application - Simulation results for the whole catchment**

During the second phase of the project the database was continuously expanded. Especially the data regarding the Hessian part of the *Main* catchment were then delivered from the Hessian State Office for Environment and Geology (HLUG). Finally, this part of the catchment could also be implemented into 'GREATER Main'. In this version more than 90% of the total population in the *Main* catchment (excluding the *upper Main* area) is connected to 'GREAT-ER Main'. Given the good agreement of simulated LAS and HHCB concentrations with most of the monitoring data, the calibration of 'GREAT-ER Main' can be regarded as successful. Therefore, it seems to be valid to extrapolate 'GREAT-ER Main' calculations to the Hessian region not used for calibration and also to other 'down-the-drain' chemicals. Figure 7 shows the final version of the 'GREATER Main' project including the major tributaries of the *Main* in Bavaria, Baden-Württemberg and Hessen.



**Figure 7: Final version of 'GREATER Main' river network**

It can be seen that the main tributaries as well as some of the smaller ones are now connected to the *Main*. This enables more detailed statements about the exposure situation in the catchment. In order to give an almost complete picture of the aquatic exposure of HHCB and Diclofenac in the *Main* catchment, model simulations with these compounds using the standard scenario parameters (see section 5.2) were performed with the final version of 'GREAT-ER Main'. For these simulations the long-term mean values and 5-percentiles were used to represent the hydrological flow regime.

Monitoring data for the selected compounds in the Hessian part of the *Main* were not available so that an advanced calibration step in this part of the catchment was not possible. Figures 8 and 9 on the following pages show the results of the simulations for HHCB and Diclofenac in form of color-coded maps of the whole catchment.

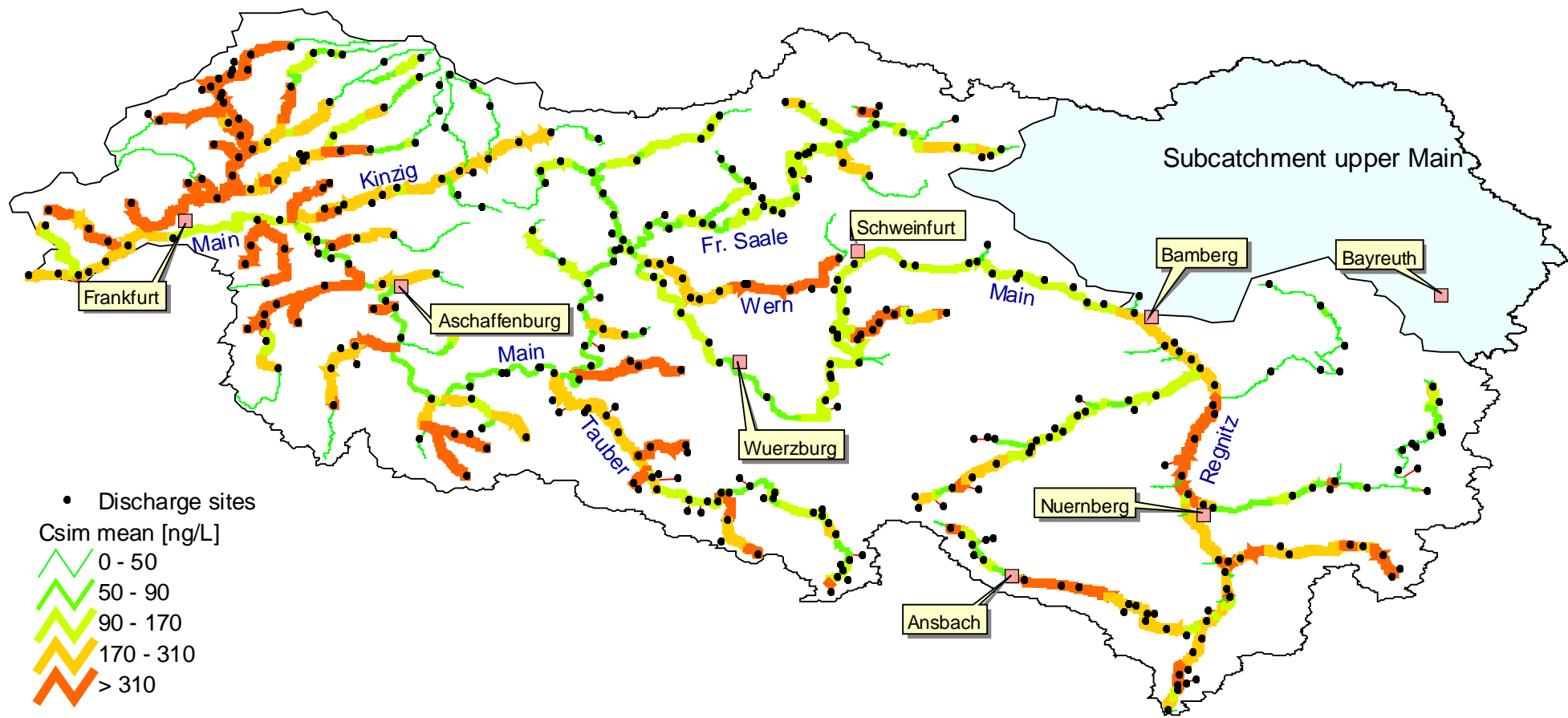


Figure 8: Simulated mean HHCb-concentrations in the MAIN catchment

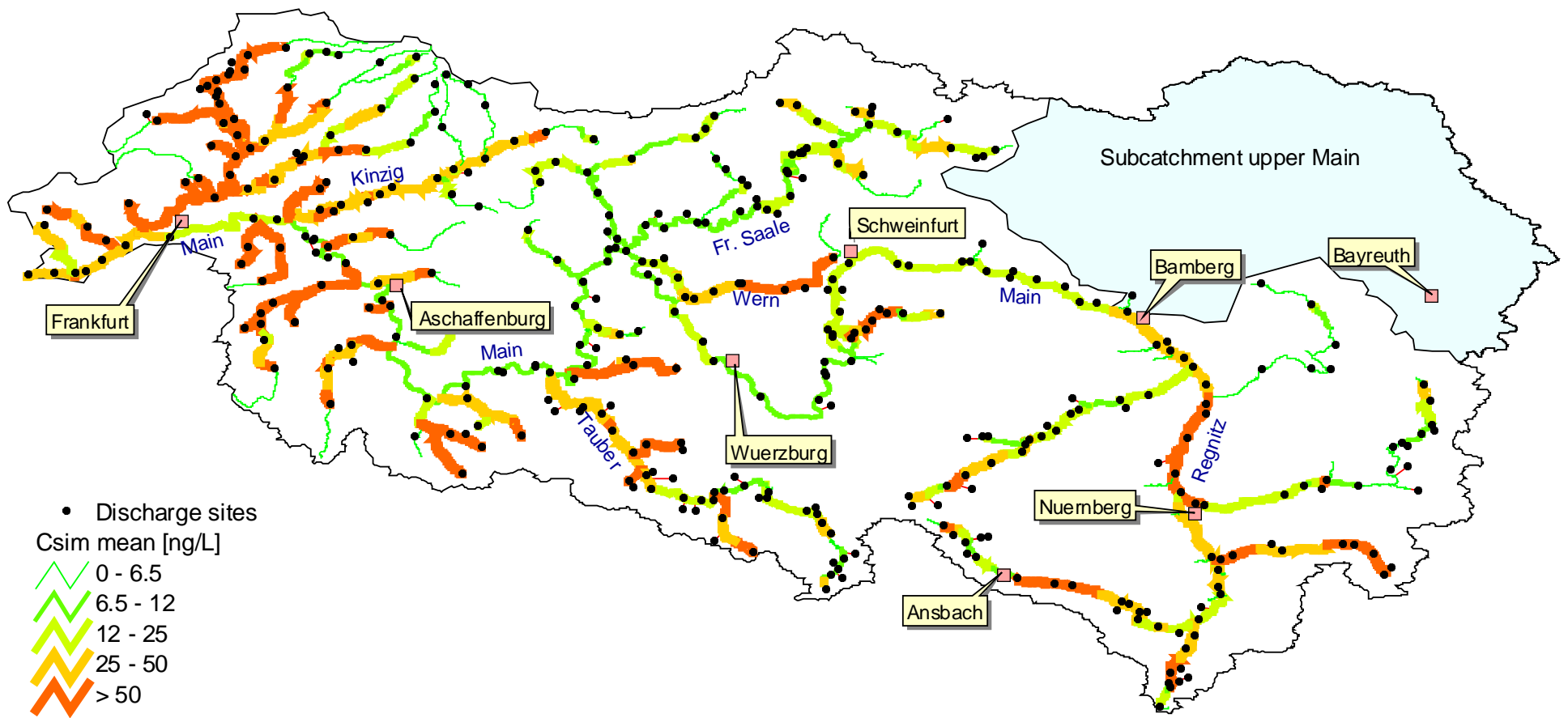


Figure 9: Simulated mean Diclofenac concentrations in the MAIN catchment

## 5.4 Discussion

From Figure 8 it can be extracted that the relative HHCB concentration profile along the *Bavarian Main* is more or less consistent with the previous simulations. However, the absolute concentrations have changed due to the different input data for the flow rates. Mean simulated concentrations in the *Bavarian Main* are all below 170 ng/L with a tendency to higher values in the region after the confluence of *upper Main* and *Regnitz*. The considerable load from the densely populated area Nürnberg / Fürth does lead to elevated concentrations in the *Regnitz*, which are reduced relatively fast along the course of the river by dilution and degradation. Concentrations in the *Hessian Main*, however, are somewhat higher especially beyond the mouth of the *Nidda* which brings a considerable HHCB load. Nevertheless, the simulated concentrations in the *Main* itself do not exceed 310 ng/L in any stretch. This seems reasonable compared to measured values in the river *Rhine* ranging from 10 ng/L – 220 ng/L (van de Plassche & Balk, 1997).

The situation for Diclofenac (Figure 9) is very similar with most of the stretches being below 25 ng/L and an increase of up to 50 ng/L after the mouth of the *Nidda*. The Figures also clearly show that stretches with high concentrations can above all be found in tributaries with low water flows and a comparably high substance load. This holds for example for the *Wern* and the *Tauber*. However, it has to be kept in mind that in the small rivers the calculation of the water flow with the simple approach described earlier possibly results in higher uncertainties than for the main river stretches. Before a detailed evaluation of these small river stretches can be done, this part has to be improved.

## 6 Conclusions and outlook

It has been shown that GREAT-ER is applicable in mid-sized river catchments like the *Main*. However, it is necessary to at least include the major tributaries instead of modeling solely the main river stretches. In the Bavarian part of the *Main* calibration of 'GREAT-ER Main' was successful with LAS and HHCB showing the general applicability. It has also been demonstrated that the calibrated model can be extended to the Hessian part of the *Main* catchment and to other 'down-the-drain' chemicals such as the pharmaceutical Diclofenac. The project was the first step in the direction of establishing such a large catchment for routine use with GREAT-ER. Further investigations will include simulations with a wider variety of compounds, completion of input data sets (especially possible industrial emitters), refinement of the hydrology and more detailed sensitivity analyses.

## Acknowledgement

We gratefully acknowledge the cooperation with the Bavarian Water Management Agency (LfW), especially the lots of data provided. We are also thankful to the Hessian State Office for Environment and Geology (HLUG) for providing us with the river network shapefile and the STP data. Special thanks to Roland Schröder (Henkel KGaA) for all his support of the project.

This project was financially supported by Clariant GmbH (Sulzbach/Taunus) and IKW Industrieverband Körperpflege und Waschmittel (Frankfurt/Main).

## 7 Literature

1. Boeije G., Vanrolleghem P., Matthies M.: A georeferenced aquatic exposure prediction methodology for 'down-the-drain' chemicals, *Water Sci. Tech.* **36(5)**, 251-58, 1997.
2. Christoffels E.: Ein Instrument zur Unterstützung wasserwirtschaftlicher Planungsaufgaben am Beispiel der Erft - ATV Gewässergütemodell, *Korrespondenz Abwasser* **48(7)**, 968-72, 2001.
3. Deutsches gewässerkundliches Jahrbuch (DGJ), Rheingebiet, Abschnitt Main, 1992.
4. Feijtel T., Boeije G., Matthies M., Koch V., Schröder R. et al.: Development of geography-referenced regional exposure assessment tool for European rivers - GREAT-ER, *Chemosphere* **34(11)**, 2351-73, 1997.
5. Matthies M., Berlekamp J., Koormann F., Wagner J-O.: Georeferenced regional simulation and aquatic exposure assessment, *Water Sci. Tech.* **43(7)**, 231-38, 2001.
6. Mattheijs E., Holt M. S., Kiewiet A., Rijs G. B. J.: Environmental monitoring for linear alkylbenzene sulfonate alcohol ethoxylate, alcohol ethoxy sulfate, alcohol sulfate, and soap, *Environ. Tox. Chem.* **18 (11)**, 2634-44, 1999.
7. Poiger T., Buser H-R., Müller M.D.: Photodegradation of the pharmaceutical drug diclofenac in a lake: Pathway, field measurements, and mathematical modeling, *Environ. Tox. Chem.* **20 (2)**, 256-63, 2001.
8. Rippen G.: Handbuch Umweltchemikalien, Ecomed-Verlag, Landsberg/Lech, 1999.
9. Schulze C., Matthies M.: Georeferenced aquatic fate simulation of cleaning agent and detergent ingredients in the river Rur catchment (Germany), *The Science of the Total Environment* **280 (1-3)**, 55-77, 2001.
10. Schulze C.; Matthies M., Trapp S., Schröder R.: Georeferenced fate modelling of LAS in the Itter stream, *Chemosphere* **39 (11)**, 1833-1853, 1999.

11. Schwabe U., Pfaffroth D. (eds.): Arzneiverordnungs-Report 1998, Springer Verlag, Berlin, 1999.
12. Schwartz S., Berding V., Matthies M.: Aquatic fate assessment of the polycyclic musk fragrance HHCB, *Chemosphere* **41**, 671-79, 2000.
13. Simonich S. L., Begley W. M., Debaere G., Eckhoff, S. M.: Trace Analysis of Fragrance Materials in Wastewater and Treated Wastewater, *Environ. Sci. Technol.* **34** (6), 959-65, 2000.
14. Southworth G.R.: The role of volatilization in removing PAHs from aquatic environments, *Bull. Environ. Contam. Toxicol.* **21**, 507-14, 1979.
15. Ternes T.A.: Occurrence of drugs in German sewage treatment plants and rivers, *Water Research* **32**, 3245-60, 1998.
16. van de Plassche E.J., Balk F.: Environmental risk assessment of the polycyclic musks AHTN and HHCB according to the EU-TGD, RIVM report no. 601503008, National Institute of Public Health and the Environment, Bilthoven, The Netherlands, 1997.