A Hydrological Framework for Geo-referenced Steady-state Exposure Assessment in Surface Water on the Catchment Scale

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Abstract

The major benefit of geo-referenced exposure modelling tools is the provision of spatially distributed information on expected environmental concentrations. This allows for identifying local and regional concentration differences in the environment which facilitates the development of efficient mitigation strategies. Predicted substance concentrations in the environment are governed by emission rates and representation of the substances' transport and transformation processes on the one hand and by the description of the spatial environmental heterogeneity and temporal variability on the other hand.

The shape of river basins and streamflow variability within them is a product of physiographic and climatic factors like e. g. topography, land use, precipitation, or evapotranspiration. These factors are very variable in space and time. This heterogeneity in river basins may have an impact on surface water concentrations of various substances.

In this work a hydrological framework for geo-referenced exposure assessment in river networks has been developed which predominantly addresses spatial heterogeneity of river basins. The theoretical background for parameterising a river network for the application of GREAT-ER (Geo-referenced Regional Exposure Assessment Tool for European Rivers) is elaborated and implemented. Quantity of discharge, flow velocity of river water and depth of river bed have to be determined at any location in a river network for the representation of substance dilution, transport and degradation. Temporal variability is handled by a probabilistic approach which demands choice and parameterisation of probability distribution functions to describe the river network characteristics.

It is substantiated that discharge and its variation can be described by a log-normal probability distribution. This distribution can be parameterised by spatially distributed information on effective precipitation and specific low flow discharge from the German Hydrological Atlas. Geoprocessing methods are applied to couple information from these maps and the river network. Evaluation of discharge probability distributions by means of gauging data demonstrates good agreement.

River depth and flow velocity are estimated on the basis of spatially distributed river structure data and therefore account for actual river morphology more than former approaches do. A comparison with hitherto used flow velocity and depth estimation shows significant differences which trigger perceivable differences in surface water concentration estimates.

Identification of the sensitivity of hydrological parameters in terms of chemical fate estimation attaches importance to spatial explicit consideration of river networks. The main benefit of the presented methods is comprehensive incorporation

of geo-referenced river basin characteristics into the data basis for the GREAT-ER model because this provides the basis for successful prediction of surface water concentrations by GREAT-ER.

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Glossary

Term	Definition[1]	German translation
Baseflow	The part of discharge that enters rivers during prolonged dry weather periods, base flow is mainly fed by groundwater	Basisabfluss
Discharge[2]	Volume of water that flows through a river cross section per unit of time	Abfluss/Durchfluss
FDC	Flow duration curve	Abflussdauerlinie
Groundwater flow	The part of runoff that enters groundwater	Grundwasserabfluss
Interflow	The part of runoff that infiltrates into the ground but flows to channels above the groundwater table	Zwischenabfluss
MAM(10)	Mean annual minimum flow on 10 consecutive days	MN10Q
MQ	Mean discharge (of a long-term period)	Mittlerer Abfluss
Q_{95}	Discharge that is exceeded 95 % of time	Q_{95}
Specific discharge	Discharge per unit area	Abflussspende
Streamflow	Water flowing through a river channel	Abfluss
Subsurface runoff	Part of runoff that infiltrates into the ground, sum of interflow and groundwater runoff	Unterirdischer Abfluss
Surface runoff	The part of runoff that flows overland into river channels	Oberirdischer Abfluss

[1] according to German IHP/HWRP National Committee (1998)

[2] The term "discharge" is also used in the context of sewage disposal. The context makes plain which meaning is meant.

Chapter 1

Introduction

1.1 Scope of the Problem

Quality of riverine ecosystems is determined by the biological community, by chemical and hydromorphological surface water status (Nixon *et al.*, 2003). Especially the chemical surface water status is impaired by elevated pollutant concentrations which affect aquatic ecosystems adversy and threatens human health (Nixon *et al.*, 2003). Elevated pollutant emissions are frequently observed in many European rivers (van Dijk *et al.*, 1994; LAWA, 1997; Nixon *et al.*, 2003; BMU, 2005b; European Environment Agency, 2007; German Federal Environment Agency, 2007).

European legislation like the European Water Framework Directive WFD (Commission of European Communities, 2000) or the Integrated Pollution Prevention and Control Directive IPPC (Commission of European Communities, 2008) aim at improving the ecological status of aquatic ecosystems by inter alia reducing chemical emissions to aquatic ecosystems.

Another European legislation which recently came into force is the Regulation concerning the Registration, Evaluation, Authorisation, and Restriction of Chemicals REACh (Commission of European Communities, 2006). This regulation aims at reducing risk of human health and the environment from chemical exposure. Manufacturers and importers are obligated to identify and to manage risks which emanate from exposure to their products. Exposure assessment is hence stipulated by REACh for substances with production volume of more than 10 t/a or which are persistent, bioaccumulative and toxic (PBT properties). It has to include the development of exposure scenarios and exposure estimation for these scenarios.

Management of riverine ecosystems has to consider chemical exposure assessment in the aquatic environment and in a second step, development of mitigation strategies against river water pollution. For both purposes understanding of emission, transport and fate of substances is essential, as it enables source apportionment and identification of relevant emission pathways (Bogestrand *et al.*, 2005). Such an understanding can be supported by chemical exposure modelling (Trapp & Matthies, 1998; van Leeuwen & Vermeire, 2007).

1.2 Chemical Exposure Modelling

Typical exposure models are based on partitioning of substances between environmental compartments (Trapp & Matthies, 1998). Lumped models which simulate chemical fate in a generic world are frequently used. The assumption of homogeneous environmental compartments is characteristic of these models (Mackay *et al.*, 1992). The European Union System for the Evaluation of Substances EUSES is an example applied for risk assessment in the European Union (Commission of European Communities, 2003). At a screening level such generic models produce valuable insights into environmental fate, but they do not account for spatial variability in the environment. Spatially varying distribution of emission sources and pathways as well as locally different characteristics of receiving environmental compartments lead to local and regional differences in environmental concentrations (Boeije *et al.*, 1997; Wind, 2004; Suzuki *et al.*, 2004). In-depth analysis of emission patterns, chemical transport and immission concentrations in a real world thus requires incorporation of a spatially explicit description of the environment. To cope with such requirements geo-referenced exposure assessment approaches have been developed. Also legislation demands spatially distributed approaches. REACh for instance envisages consideration of spatio-temporal variability of exposition patterns (Commission of European Communities, 2006). The Water Framework Directive stipulates provision for differences in different ecoregions (Commission of European Communities, 2000).

1.2.1 Geo-Referenced Exposure Modelling in Surface Water

Various geo-referenced simulation tools for modelling chemical fate or nutrient concentrations in rivers and lakes with regard to spatial variability have been developed (Feijtel *et al.*, 1997; Barra *et al.*, 2000; Christoffels, 2001; Matthies *et al.*, 2001; United States Environmental Protection Agency, 2001; Behrendt *et al.*, 2002; Reuter *et al.*, 2003; Röpke *et al.*, 2004; Toose *et al.*, 2004; German Federal Environment Agency, 2004). Their application requires plausible emission assumptions on the one hand and adequate representation of dilution, transport, and loss processes by the model on the other hand. As these processes are controlled by spatio-temporal varying hydrological and hydromorphological characteristics, an appropriate description of these conditions is important to obtain reliable estimates of surface water concentrations. Both spatial and temporal variability is pronounced in natural hydrological systems (Chow, 1964; Blöschl & Sivapalan, 1995; Poff *et al.*, 1997). The main driving forces for variability of hydrological conditions are hydrological regime and separation of runoff into a surface and a sub-surface component (Haberlandt *et al.*, 2001; Poff *et al.*, 1997).

1.2.2 GREAT-ER

A prominent example of a geo-referenced exposure assessment tool is GREAT-ER (Geography-referenced Regional Exposure Assessment Tool for European Rivers). GREAT-ER is a steady-state model which has been successfully applied to predict fate of household chemicals, pharmaceuticals and heavy-metals in several river basins (Matthies *et al.*, 2001; Schulze & Matthies, 2001; Wind *et al.*, 2004; Robinson *et al.*, 2007; Johnson *et al.*, 2007a; Johnson *et al.*, 2007b; Hüffmeyer *et al.*, 2009). Processes represented in GREAT-ER are emission of substances, transport in sewer systems, removal in waste water treatment plants, discharge into rivers, dilution and transport in river networks, degradation, and loss via volatilization and sedimentation. All processes are specified geo-referencedly. Therefore, the model is combined with a geographic information system (Boeije & Koormann, 2003; Wagner & Koormann, 2005).

In GREAT-ER both point and non-point emissions can be handled (Hüffmeyer *et al.*, 2009). The first applies for instance to household chemicals or pharmaceuticals, which are emitted into rivers via waste water treatment plants, or industrially used substances, that are either emitted directly into surface water or indirectly via sewage treatment plants. Substances entering water bodies diffusively are typically transported by either surface runoff (e. g. wash off of fertilizer from agricultural area) or by base flow (e. g. washed-out metals from bedrock or soil matrix).

Emission loads are estimated by certain reference parameters like per-capita consumption or wash-off rate per square meter (Hüffmeyer *et al.*, 2009). While waste water from sewage treatment plants and natural background emissions from groundwater are emitted roughly continuously, other emissions are often event-driven. For instance, substances transported with surface runoff only enter surface waters when surface runoff occurs and enters water bodies. In order to deal with these non-continous phenomena, emissions via runoff pathways are correlated to elevated streamflow quantities in the GREAT-ER model (Hüffmeyer, 2010).

Emitted substance loads constitute only one aspect which determines surface water concentrations. A crucial factor is dilution of this load once it reaches surface water. Dilution is controlled by the amount of water at each point within the river network.

In GREAT-ER, substance transport within a river network is simulated using a river network topology (Wagner & Koormann, 2005). The river network consists of short river segments. For each of these river segments mean flow velocity has to be specified. Together with the segment's length a mean residence time can be determined which is an important parameter to model substance loss by degradation. It is possible to calculate substance loss at different levels of detail from aggregated loss rate over a division between degradation, sedimentation and volatilisation processes and finally to a split up of degradation into different types, viz. biodegradation, photolysis and protolysis. The relevance for each of these loss processes depends on physico-chemical properties of a substance, but also on river depth which influences photolysis, sedimentation and volatilisation (Boeije & Koormann, 2003).

GREAT-ER models these processes for different substances with respect to spatial variability in the river basin. Variables which mainly influence concentration estimation are thus discharge, river depth and flow velocity. Lakes within a river network are a special case. They are handled as homogeneously mixed water bodies for which water volume, residence time and depth have to be specified.

Up to now, quantification of spatially distributed discharge is based either on an empirical approach which interpolates between observed streamflow data from gauging stations or on a relation between discharge and accumulated river length (Rodriguez-Iturbe & Rinaldo, 1997; Schulze, 2001). It does not take into account catchment heterogeneity like spatial variation in drainage area extent, topography, land use, precipitation or river structure. Temporal streamflow variability is addressed by a probabilistic approach and is thus represented time-independently.

Flow velocity and river depth have up to now been estimated in relation to discharge. By means of regression analysis relations between these parameters have been derived for natural, small and medium river channels in the UK (Round & Young, 1997; Round *et al.*, 1998). It is transferred to river networks of larger sizes or with remarkable artificial influences. Local river structure is not considered.

In summary, weaknesses of the GREAT-ER model reside in the absence of a consistent hydrological framework which makes allowance for local and regional catchment characteristics. Especially geo-referenced information on streamflow and its variability is missing in the ungauged parts of the rivers basins. Parameterisation of river depth and flow velocity does not take into account actual river structure although they are significantly affected by it.

1.3 Objectives

The overall objective of this study is to provide a hydrological framework for realistic concentration estimation with GREAT-ER and to overcome present weaknesses in the data preprocessing methodologies for the incorporation of new river basins in the GREAT-ER model suite.

An appropriate (in terms of spatial resolution and process detail) spatially distributed representation of river network variability is essential for estimating real-world substance concentrations in surface water and takes centre stage in this work. Necessary parameters to sufficiently describe river morphology and flow regime for the processes considered in the GREAT-ER model have to be identified. To derive values for these parameters, a methodology is developed which makes allowance for the steady-state assumption and for the spatial resolution of GREAT-ER. The special case of lakes is not covered in this study.

In detail it copes with the following tasks:

- Discharge has to be described for ungauged river sites. By means of long-term gauging data general assumptions concerning river flow variability are evaluated. The derivation of flow duration curves enables a link between discharge and exceedance duration.

- To separate runoff into a subsurface and a surface part is beneficial for estimating emissions that are transported by these runoff components, respectively.

- Alternative river depth estimation approaches are analysed to evaluate if hitherto derived river depth is appropriate or if a more sophisticated depth estimation procedure is required.

- It is essential to investigate the influence of flow velocity on concentration predictions to identify those combinations of substance type and flow velocity which react sensitively. An alternative approach for flow velocity estimation is presented which accounts for local river structure.

- By means of GREAT-ER simulations, the influence of hydro(morpho)logical river network parameterisation is illustrated. Sensitivity of hydromorphological parameters is assessed.

Additionally to a sound theoretical background, both basin-wide data availability and automatised data processing is important. Parameterisation of the river network is a balancing act between management of sparse data availability and incorporation of local and regional river network characteristics. In order to guarantee a simple parameterisation of new river basins transferability of the approach has to be ensured.

Chapter 2

Data and Methods

2.1 Study Area

A hydrological description of four different German river basins is compiled to assess surface water concentrations of different substances by means of GREAT-ER simulations. All basins include both densely and sparsely populated, natural and anthropogenically modified, low mountainous and flat regions. They are situated in the west, the east and the south of Germany and are representative for a large part of German river basins. Figure 2.1 illustrates their spatial expansion. Table 2.1 summarises the main basin characteristics.

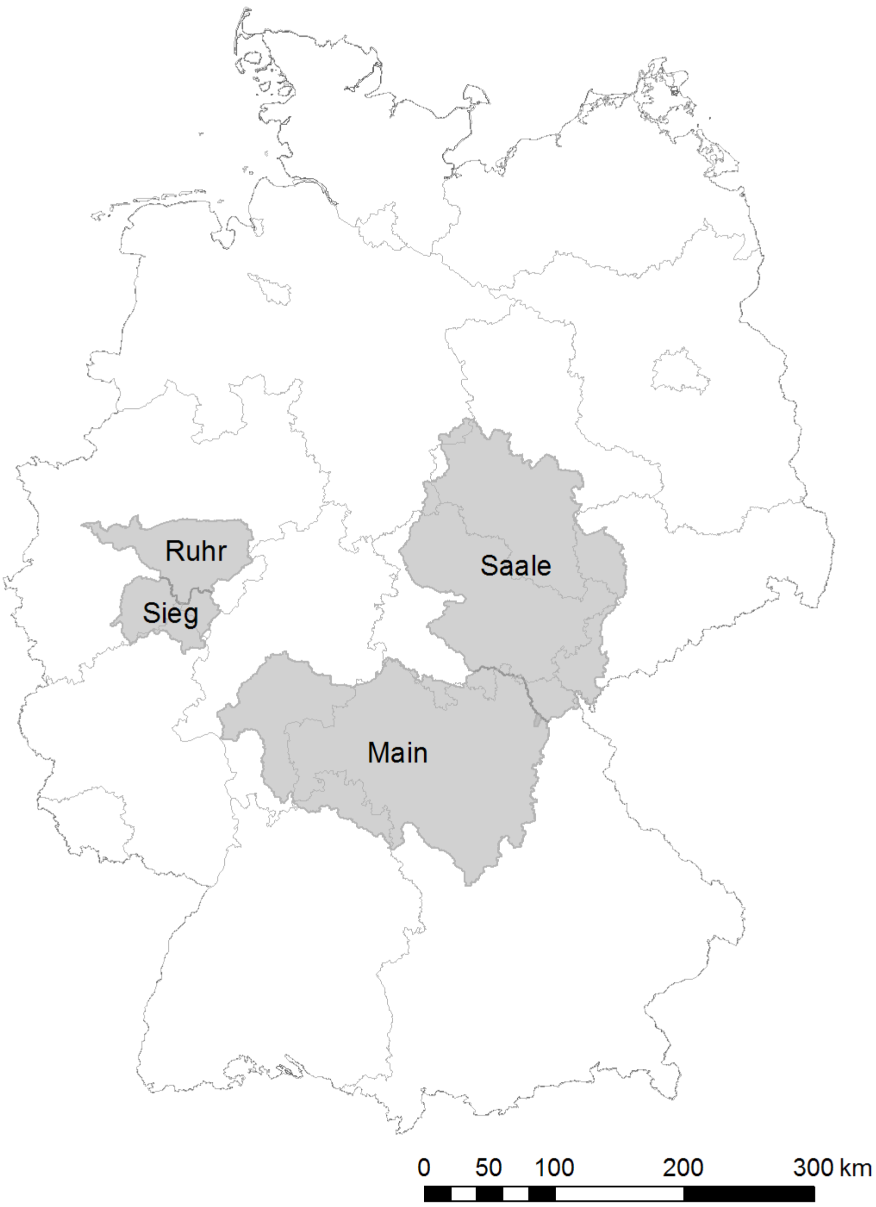

Figure 2.1: Location of the selected river basins Main, Ruhr, Saale, and Sieg

Table 2.1: Summary of river basin characteristics for Main, Ruhr, Saale, and Sieg

River Basin	**Main**	**Ruhr**	**Saale**	**Sieg**
River Basin District	Rhine	Rhine	Elbe	Rhine
Drainage Area Size	27840 km^2	4485 km^2	27167 km^2	2832 km^2
Length of main river	527 km	219 km	427 km	155 km
Total flow length considered	9900 km	1912 km	9188 km	1182 km
Main tributaries	Franconian Saale Regnitz	Möhne Lenne Volme	Unstrut Weiße Elster Bode	Agger Nister
Hydrogeology	fractured aquifers karstic aquifers	fractured aquifers porous aquifers in river valleys	fractured aquifers porous aquifers regional occurrence of karstic aquifers	fractured aquifers porous aquifers in river valleys
Precipitation	550 mm/a - 1400 mm/a 800 mm/a on average	640 mm/a - 1390 mm/a 1057 mm/a on average	450 mm/a (Unstrut, Bode) - 1600 mm/a (Harz, Brocken)	900 mm/a - 1200 mm/a 1070 on average
Land use	$\sim$ 6 % settlement area $\sim$ 55 % agricultural area $\sim$ 39 % forest and semi-natural area	$\sim$ 15 % urban area $\sim$ 13 % agricultural area $\sim$ 18 % grassland $\sim$ 52 % forest	$\sim$ 5 % settlement area $\sim$ 61 % agricultural area $\sim$ 20 % forest and semi-natural area	$\sim$ 10 % settlement area $\sim$ 6.5 % agricultural area $\sim$ 31 % grassland $\sim$ 46 % forest
Inhabitants	6610183	2128000	4201653	970000

2.1.1 Main

The Main is the third-largest tributary of the river Rhine with a mean discharge of 225 m^3/s at its mouth. It is 527 km long and has two source rivers: the Red and the White Main starting in the Fichtelgebirge and confluencing near Kulmbach. The complete river network with rivers whose drainage area size is larger than 10 km^2 comprises approximately 9900 km (STMUGV et al., 2005).

The basin size is 27840 km^2 and spans over the federal states of Bavaria, Hesse, Baden-Württemberg, and Thuringia. The landscape is characterised by low mountain ranges, and the dominating aquifers are karstic or fractured (STMUGV et al., 2005).

Most parts of the basin are rural areas, except for the urban agglomeration Rhine-Main around Frankfurt and the Nürnberg/Fürth region (STMUGV et al., 2005). 6.6 million inhabitants live in the river basin. The Main itself as well as parts of one of its major tributaries Regnitz are part of the waterway between Danube and Rhine. It has therefore been made navigable entailing numerous watergates and artificial flow regime.

Among the four river basins this one is substitutional for a basin with rather low precipitation. Regarding the settlement structure the major part of the catchment can be described as rural, whereas single regions (Frankfurt, Nürnberg/Fürth) are shaped by a strong anthropogenic influence.

In this study the Main river basin is mainly used to analyse the impact of flow velocity on substance degradation. For this purpose data on flow velocity from the ATV model is used for some river sections in the Main river basin.

2.1.2 Ruhr

The Ruhr is a river in North Rhine-Westphalia and a tributary of the Rhine with a length of 219 km. Its basin extends over an area of approximately 4485 km^2. The population density of 474 inhabitants per km^2 is primarily determined by the urban Ruhr area, the largest urban agglomeration in Germany, in the lower reaches (MUNLV NRW, 2005a). The high population density and the high degree of industrialisation are responsible for the chemical burden of the streams in the Ruhr catchment. The Ruhr secures drinking water supply for the 2.1 million inhabitants of the basin as well as for inhabitants of neighbouring basins. For this purpose numerous reservoirs and embankments exert a severe influence on the hydrological regime of the stream. Owing to its use as drinking water the quality of the Ruhr water is of special interest. Besides, protection of the riverine ecosystem is as well important against the background of its recreational function.

The Ruhr river basin is an example of a densely populated basin. High specific discharge in the headwaters is balanced by intensive river regulation.

2.1.3 Saale

The Saale river is the second-longest tributary of the Elbe river with a length of 427 km. The complete considered river network comprises almost 9200 km. With 115 m^3/s average discharge at the mouth the Saale also is one of the largest Elbe tributaries with respect to flow rate. Its drainage area comprises 24167 km^2 and is located in the federal states of Thuringia, Saxony-Anhalt and Saxony. Small parts in the north and the south, respectively, are in Lower-Saxony and Bavaria (MLU SA, 2005). The Saale originates in the Fichtelgebirge at 778 m above sea level. It flows into the Elbe at Calbe (50 m above sea level). The landscape encompasses mountainous regions like the Harz or the Franconian Forest, and also very fertile plains like the Magdeburger Börde or the Leipziger Bucht. Its location in the rain shadow east of the Harz is one of the reasons for the relatively low annual precipitation between 450 and 500 mm/a, whereas in the mountainous areas precipitation reaches up to 1300 to 1600 mm/a (MLU SA, 2005).

Northern and eastern parts of the basin are characterised by many artificial river alterations. The largest cities are Leipzig, Halle and Erfurt with approximately 950000 inhabitants. Altogether 4.2 million people live in the basin (MLU SA, 2005).

The Saale river basin is substitutional for large river basins with spatially very variable precipitation patterns. Its artificially modified river network especially in the flatter parts of the basin are characteristic of many lowland rivers.

2.1.4 Sieg

The Sieg is a smaller tributary of the Rhine river with a drainage area of 2832 km^2 and a length of 152 km. It is situated in North Rhine-Westphalia and Rhineland-Palatinate between Bergisches Land, Westerwald and Rothaargebirge. From its source in Netphen the Sieg overcomes an elevation difference of approximately 550 m before it discharges into the Rhine near the city of Bonn (MUNLV NRW, 2005b). As the Sieg basin is part of the Rhenish Slate Mountains its geology mainly consists of consolidated rock which is not hydrogeologically productive due to its impermeability (MUNLV NRW, 2005b).

In the Sieg river basin population density is 347 inhabitants per km^2 and significantly lower than in the Ruhr area. Precipitation is rather high in the basin with an average annual precipitation of 1070 mm/a. In spite of this high precipitation there are artificial reservoirs in order to secure drinking water supply for almost 1 million people. Otherwise the steep topography would cause a high fraction of fast runoff (MUNLV NRW, 2005b). Runoff in the Sieg river basin thus mirrors hydrological conditions in flashy river basins.

2.2 Data

For all four considered river basins geo-referenced data on river networks and drainage areas is required. In principle, this data origins from different sources. Some information is based on remote sensing data whereas other data has been cartographed. Depending on whom collects data it might be available only for single river basins but not on a national or even European scale. To enable for comparisons between the river basins, uniform data sources are prefereable. If that is not possible data should at least include the same or comparable information, and its spatial resolution should be in the same order of magnitude.

2.2.1 Hydrological Data

The basis for GREAT-ER simulations consists of the river network. Its parameterisation is based on point measurements of different parameters, which are presented in the following section.

2.2.1.1 River network topology

For the GREAT-ER model a digital river network is used which is based on the Digital Landscape Model 1:250000 (BKG, 2007). This model is built up from several sources (analogue and digital maps scaled from 1: 250.000 to 1:25.000) (BKG, 2007). In spite of heterogeneous sources it delivers a uniform and topologically consistent representation of the network of all rivers with a drainage area of at least 10 km^2 or special oro-hydrographic relevance which are the selection criteria for the Water Framework Directive (Commission of European Communities, 2000). The WFD reporting in Germany is based on the more generalised DLM 1000 (LAWA, 2003). Therefore, river networks derived from the DLM 250 cover all rivers whose status has to be reported within the scope of the WFD.

2.2.1.2 Gauging data

Gauging data is mainly taken from German Hydrological Yearbooks (DGJ) which are available for basically all river basin districts in Germany. They list daily discharge values for gauging stations as well as characteristic hydrological values for the period of record and the flow duration curves for the complete period of record. Altogether circa 560 gauging stations are listed in all German hydrological yearbooks. For the Saale river basin 30 year time series (1976 - 2005) of daily discharge records for 15 gauging stations are taken from DGJ. For the Main river basin, gauging data from DGJ is only available for a period-of-record of 11 years (1989 - 1999).

Besides, for the North Rhine Westphalian basins Ruhr and Sieg data is provided by the State Ministry of the Environment and Conservation, Agriculture and Consumer Protection (MUNLV NRW, 2009). The MUNLV NRW provides georeferenced river-related data on-line. 30-year discharge time series for 14 gauging stations in the Sieg river basin and 15 gauging stations in the Ruhr river basin are taken from these. The Ruhr River Association, which is responsible for managing water quantity and quality in the Ruhr river basin, also provides both daily discharge and stage values on-line (Ruhr River Association, 2009), partly for gauging stations which are listed in DGJ, partly for smaller gauging stations which are operated by the Ruhr River Association. Here, data from 2008 only is used to investigate relations between stage and discharge.

2.2.1.3 River structure

A river structure survey has been carried out in North Rhine-Westphalia by environmental authorities (LUA, 1998). River structure characteristics are systematically collected on a very fine spatial resolution in order to assess habitat quality and to initiate measures to renaturalise rivers whose structure is degraded by human alterations. The survey is based on an objective assessment of single parameters (e. g.

profile type, bed material, riparian vegetation, etc.) which is then successively aggregated to functional entities and main parameters developing of the water course, longitudinal profile, river bed structure, cross section, riparian structure and river periphery. These are grouped into the domains bed, bank and land as can be seen in table 2.2 (LUA, 2005). River section length for the survey is 100 m in normal cases. Single parameters are geared to defined criteria (e. g. classes of width, choice between parameter values).

The assessment of river structure quality is based on the survey, but additionally makes allowance to landscape-specific conditions. Spatially based type-specific reference conditions are developed to take the current potential natural status as benchmark (LUA, 2005).

2.2.2 Catchment Data

Rivers and lakes are strongly connected to their surrounding environment in terms of runoff concentration (Horton, 1933), water quality (Schwoerbel & Brendelberger, 2005) and river bed formation (Leopold & Maddock, 1953). Therefore, data related to a river's drainage area are required for a description of a river network and its hydrological conditions. Necessary data comprises information on topography, land use, effective precipitation and specific low flow discharge.

2.2.2.1 Topography

A digital elevation model based on elevation data from the Shuttle Radar Topology Mission (Farr *et al.*, 2007) is used to automatically derive surface drainage area polygons, which is performed by hydrological analysis tools from ArcGIS (Maidment, 2002). Cell sizes vary depending on latitude, and is approximately 90 m x 90 m.

2.2.2.2 Land use

CORINE Land Cover data provide information on land use (Haines-Young *et al.*, 2006). 44 different land use classes are identified from digital satellite images for Europe. These land use classes are grouped into artificial areas, agricultural areas, forest and semi-natural areas, and wetlands. Geometric precision of CORINE Land Cover data is reported to be better than 100 m, while thematic accuracy exceeds 85 % (Büttner & Maucha, 2006).

2.2.2.3 Effective precipitation

A 1 km x 1 km grid with values for effective precipitation is provided by the Hydrological Atlas of Germany HAD (BMU, 2005a). Values are based on corrected precipitation grids and estimated actual evaporation. Actual evaporation, which is difficult to measure, has been derived by the BAGLUVA approach (Glugla *et al.*, 2003). It is a modification of the Bagrov method for arid and humid regions and takes inter alia into account soil water storage capacity, land cover and summer precipitation heights. The underlying theory assumes that precipitation which is not evaporated or transpirated sooner or later accumulates in rivers and streams.

Table 2.2: River structure parameters according to LUA (2005)

Area	**Main parameter**	**single parameters**	
		small to medium size rivers	**medium size to big rivers**
bed	channel development	loops loop erosion longitudianl banks special channel structures weirs tubbing casing	shape loop erosion - special channel structures weirs tubbing casing
	longitudinal profile	back water lateral banks flow diversity depth variance -	back water lateral banks flow diversity - outlet
bank	bed structure	bed substrate bed sheeting substrate diversity special bed structures special burden macrophytes	bed substrate bed sheeting substrate diversity special bed structures special burden -
	cross section profile	profile type profile depth latitudinal erosion latitudinal variance culvert -	profile type recess latitudinal erosion latitudinal variance culvert/bridge narrowing/expansion
	riparian zone	riparian vegetation bank fixation special riparian structures special burden	riparian vegetation bank fixation special riparian structures special burden
land	river environment	land use riverside special surrounding structures harmful surrounding structures - -	land use riverside special surrounding structures harmful surrounding structures overflowing frequency flood plain

Therefore, for data verification a comparison with observed gauging data has been carried out. It revealed that mean deviations are lower than 5 %. Higher deviations are ascribed to anthropogenic influences on flow regime (BMU, 2005a).

2.2.2.4 Specific low flow discharge

The Hydrological Atlas of Germany additionally provides data on specific low flow discharge. This is based on the lowest arithmetic mean discharge on 10 consecutive days (BMU, 2005a) and denoted MAM(10). A specific low flow discharge value for every raster cell is derived from gauging stations and their drainage area by a multiple regression approach. MAM(10) is a function of summer precipitation height, lithology, land use and stream density (BMU, 2005a). For 330 small basins (between 22 km^2 and 675 km^2) a comparison between observed MAM(10)-values (based on gauging measurements) and spatially interpolated MAM(10)-values (based on the map) has been carried out to evaluate the regression approach used for the construction of the map. The comparison shows no systematic deviations. However, it was found that in most cases the measured values of MAM(10) are over- or underestimated by approximately 1.1 $l/(s \cdot km^2)$. The standard deviation of the residuals is 1.83 $l/(s \cdot km^2)$ at average. A river basin related analysis of the residuals shows a slightly larger deviation for the Rhine than for the Elbe (BMU, 2005a). The values are only available in an aggregated manner because they are classified with an interval of 1 $m^3/(s \cdot km^2)$.

2.3 Representation of Hydrological Regime and River Characteristics

River networks take centre stage in the hydrological cycle (Thompson, 1999), as they interact with atmospheric water, with surface water, soil water and with groundwater (figure 2.2). Only a marginal fraction of the earth's freshwater is stored in rivers (0.62 %), but its low residence time of approximately 16 hours (Baumgartner & Reichelt, 1975) indicates its importance for transport of water and exchange between freshwater storages. When freshwater does not occur as surface water like for instance in river networks, water is stored as vapour in the atmosphere (0.04 %), as soil water and groundwater in the pedosphere (22 %).

Rivers are fed by precipitation which reaches the channel via different pathways, viz. surface runoff, sub-surface runoff and groundwater runoff (Horton, 1933; Chow, 1964). The contribution of each of these runoff components and finally of streamflow is regionally and temporally different as it depends on both climatic factors (precipitation, evapotranspiration) and physiographic factors (catchment and channel characteristics) (Chow, 1964). Models of river systems have to represent this variability with respect to space and time.

Models of hydrological systems can in principle be of different types. Depending on whether randomness, spatial variation or temporal variation is considered simplified relationships between system elements are assumed (Chow *et al.*, 1988). Hydrological phenomena are partly deterministic and partly random (Chow *et al.*,

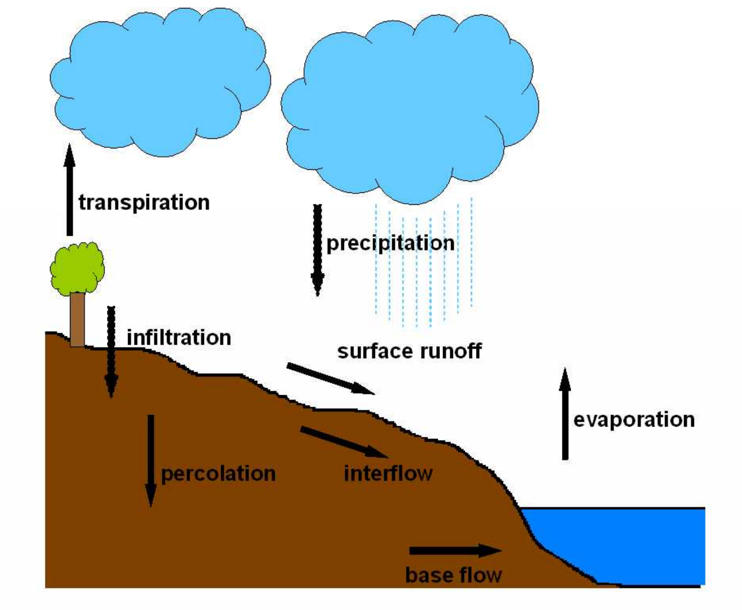

Figure 2.2: A simplified water cycle

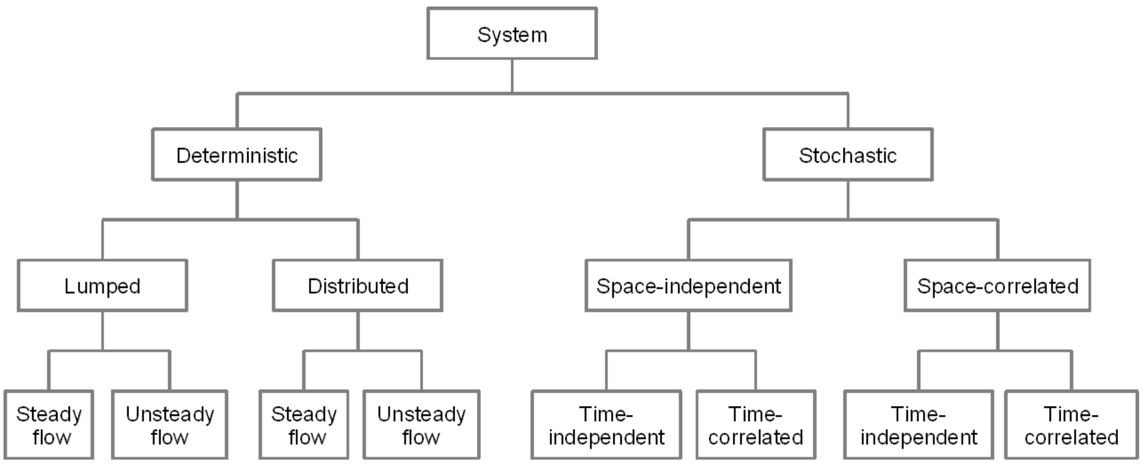

Figure 2.3: Model classification scheme according to Chow et al. (1988)

1988; Borgman *et al.*, 1970). Whether a deterministic or a stochastic model is more appropriate depends on whether the deterministic or the random part of the model elements dominates. When choosing between lumped and distributed, or in case of stochastic models, space-independent and space-correlated models one has to make allowance for the influence of spatial variation on the model result. The third decision a modeller has to take is if temporal variability is regarded or disregarded in a model. All three decisions are merely yes-no questions. In a second step modellers have to decide how to implement their choices, i. e. elaborating deterministic relations, identifying dominant processes, finding suitable probabilistic descriptions, choosing an adequate spatial and temporal scale of a model, etc. (cf. (Blöschl & Sivapalan, 1995; Sivakumar, 2008)).

The driving force for the choice of a certain model type and finally the formulation of a model description is the intended purpose of the model application. For instance, in a model aiming at operationally forcasting flood events (e. g. NASIM-HWV (Hydrotec, 2009)) temporal development of the hydrograph should be one of the central aspects, whereas for a model with the intention of helping to understand long-term water availability within a catchment (e. g. WaterGAP (Alcamo *et al.*, 2003)) the actual chronology of high or low flow periods is of minor interest. Determining an appropriate spatial choice requires allowance for the model's goal, too. A model representing water fluxes in a larger basin (e. g. SWAT, TOPMODEL, HBV, etc.) needs a different spatial resolution than a model which addresses river hydraulics and sediment transport (e. g. HEC-models) (Santhi *et al.*, 2001; Beven *et al.*, 1995; Bergström, 1995; Feldmann, 1981).

GREAT-ER's intention is to spatially explicit model fate of continuously discharged substances in rivers. Temporal variability of hydrological conditions is considered, i. e. it is accounted for occurrence of low flow and high flow periods. However, sequence of hydrological events is neglected. Therefore, the variability of hydrological variables is represented by a probabilistic approach which assigns occurrence probabilities to hydrological events instead of considering them explicitly. The considered river networks are analysed on catchment scale with a spatial resolution of 2 km river segments. All chosen rivers are of second order and thus their drainage area sizes are relatively large, i. e. macroscale approaches which have to be space-correlated have to be used to represent chemical fate in these river basins. As GREAT-ER is a steady-state model stationary surface water concentrations are computed. Continuous substance emissions and long-term average hydrological conditions are assumed.

Thus, for a description of the hydrological regime and of channel characteristics, models incorporated in GREAT-ER have to be stochastic, space-correlated and time-independent (according to (Chow *et al.*, 1988)).

Information on discharge quantity, river morphology and flow velocity has to be provided in order to hydrologically parameterise GREAT-ER and to model substance concentrations. In the following the theoretical background of the approaches used in this study for a characterisation of hydrological regime and river characteristics as well as the methodology in deriving the required parameters is presented.

2.3.1 Streamflow Variability

The hydrological cycle is represented in a simplified way. The water balance relates precipitation, evapotranspiration and runoff to the amount of water stored as ground water. A mathematical formulation of the water balance is

$$\Delta S = P - R - E \tag{2.1}$$

with ΔS denoting change in groundwater storage, P precipitation, R runoff and E evapotranspiration.

To reduce complexity steady-state is assumed which implies that the system is treated as time-invariant. With this assumption and when the principle of conservation holds (Hornberger *et al.*, 1998), change in storage is zero. The water balance equation then reduces to

$$R = P - E \tag{2.2}$$

Under the assumed conditions effective precipitation thus equals runoff.

The steady-state assumption reflects long-term behaviour and neglects short-term changes. When analysing runoff from a more detailed point of view with respect to temporal changes, it is noticeable that groundwater runoff contributes to a varying degree to streamflow maintenance. Runoff occurs after storm events and is partitioned into overland flow, interflow and base flow and each of these processes proceeds in a different time frame (Blöschl & Sivapalan, 1995).

The high temporal variability of natural river flow is crucial for maintaining the integrity of riverine, riparian and floodplain ecosystems (Poff *et al.*, 1997; Richter *et al.*, 1998; Clausen & Biggs, 2000; Stewardson & Gippel, 2003; Pyrce, 2004; Tharme, 2003). Five components form the natural flow regime: magnitude, frequency, duration, timing and rate of change (Poff *et al.*, 1997). Former investigations of the influence of flow regime on river ecosystems have concentrated on discharge only. Compared to this simple approach which aimed at securing a defined minimum discharge to maintain the ecological functions this sophisticated view on flow regime is advocated by Poff et al. (1997) for detailed assessment of the impact of flow regime alterations.

In terms of river pollution by chemicals, however, the emission dilution capacity is important. For this purpose magnitude of streamflow is the most important component.

Amount of discharge also indirectly influences other parameters like flow velocity or river bed depth (Round & Young, 1997). For simplicity reasons the other flow regime components are neglected, although they might influence chemical water quality even though to little extent. Apart from dilution capacity, streamflow quantity is also related to substance emission via runoff and therefore interesting in terms of chemical concentrations in surface waters (Haberlandt *et al.*, 2001).

2.3.1.1 Theoretical Streamflow Distribution

Timing of discharge is less important than duration because of the steady-state assumption and the probabilistic approach. A link between discharge quantity and exceedance durations is established by flow duration curves. Their approach is thus suitable, and their utilisation is encouraged.

Flow duration curves (FDC) are simple, probabilistic tools for analysis of discharge data. They are widely applied in hydrological science, e. g. for irrigation, water supply and wastewater allocation planning (Chow, 1964; Vogel & Fennessey, 1994). A FDC relates discharge values and their exceedance times. To construct such a curve discharge values at a given time interval (e. g. annual, monthly, daily, etc.) are arranged in order of their magnitude. This magnitude is plotted against the percentage of time a given magnitude is exceeded.

A FDC does not consider sequence of discharge values and hence does not contain any information about length of the interval below a threshold discharge value. In spite of this limitation FDCs are informative with respect to river flow respond of a catchment. The shape of a curve provides information about groundwater contribution (Smakthin, 2001). A flat curve hints at a continuous groundwater contribution while a steep curve indicates a variable base flow contribution.

Conventionally, FDCs are calculated for a given period-of-record and thus depend on this period. (Vogel & Fennessey, 1994) showed that such FDCs are especially sensitive to extreme flow values. To avoid an inadequate influence of extreme events they introduced an approach that is based on annual percentiles. For each percentile and for every year statistics can be calculated. A annual mean FDC represents the exceedance times of a typical, but hypothetical year and is less sensitive to extreme flow events (Vogel & Fennessey, 1994). In the following these types of flow duration curves are denoted conventional FDC and annual mean FDC.

On the one hand the German hydrological yearbooks provide annual FDC of the current year and information about the complete period-of-record on the other hand. The latter includes upper and lower boundary curves which are constructed from minimum and maximum values of annual FDCs and a conventional FDC.

Mathematically spoken a FDC is a cumulative distribution function. If the curve is derived from large data amounts, it approximates a limiting distribution function (Chow, 1964). To link theoretical probability distributions with streamflow distribution, frequency analysis of daily mean flow values can support the choice of certain distribution types. In general a frequency analysis demonstrates that discharge distributions show positive skewness (Chow, 1964; Smakthin, 2001). Figure 2.4 exemplarily shows the frequency distribution of discharge values at a gauging station in one of the study catchments where positive skewness is observed, too.

Among commonly applied skewed distribution functions in hydrological science which describe magnitude of streamflow, lognormal and Gamma distributions prevail (Chow, 1964; Chow *et al.*, 1988; Thompson, 1999; Smakthin, 2001; McMahon *et al.*, 2007).

Lognormal distribution. A random variable X follows a lognormal distribution if its logarithm is normally distributed (Sachs & Hedderich, 2006). This assymetrical probability distribution is applied if a random variable results from a product of different influencing factors in contrast to distributions resulting from added effects like normal distribution (Limpert *et al.*, 2001). The density function

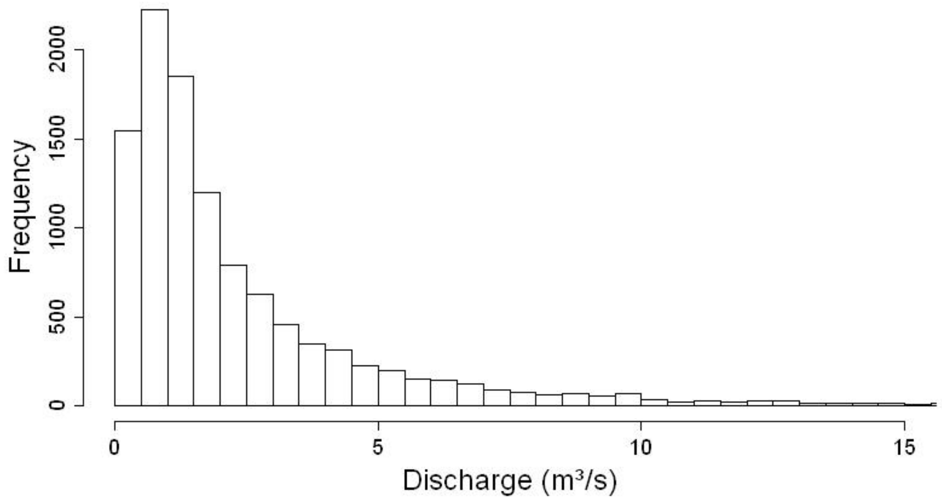

Figure 2.4: Frequency distribution of daily mean discharge values at a gauging station

is

$$f(x) = \begin{cases} \frac{1}{\sqrt{2\pi}\sigma x} exp(-\frac{(lnx-\mu)^2}{2\sigma^2}) & x \geq 0 \\ 0 & x \leq 0 \end{cases} \tag{2.3}$$

The probability distribution is thus determined by the two parameters mean value μ and standard deviation σ of $ln(X)$. Figure 2.5 illustrates the influence of different parameter values.

Gamma distribution The Gamma distribution is also a skewed distribution function. It is a generalisation of the exponential distribution and describes the time in which a given number β of events following a poisson process occur (Chow *et al.*, 1988). (Chow *et al.*, 1988) specify the distribution function as

$$f(x) = \frac{\lambda^\beta x^{\beta-1} e^{-\lambda x}}{\Gamma(\beta)} \tag{2.4}$$

with shape parameter β and scale $1/\lambda$. λ is often called rate parameter. $\Gamma(\beta)$ denotes the gamma function. In comparison to lognormal distribution probability density parameterised by different values is displayed in figure 2.6.

2.3.1.2 Parameterisation of Streamflow Distribution

Parameterisation of streamflow distributions has to be based on a link between observed streamflow characteristics and spatially distributed catchment characteristics. As a first step, most appropriate probability distribution functions for describing streamflow variability at the considered gauging stations are parameterised. In a second step, results from these analyses are used for describing streamflow at any arbitrary point of the river network.

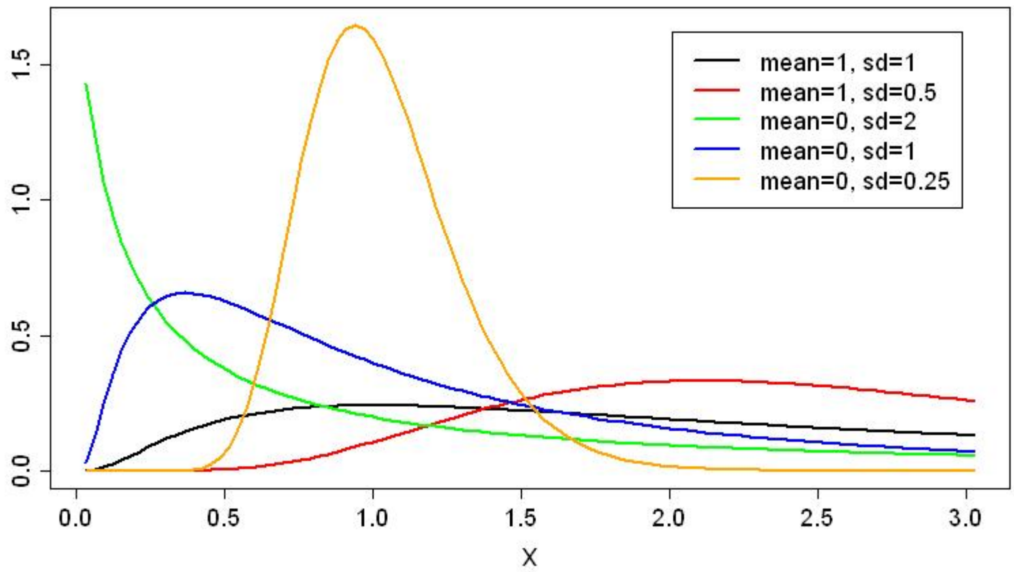

Figure 2.5: Lognormal distribution density functions with different parameters

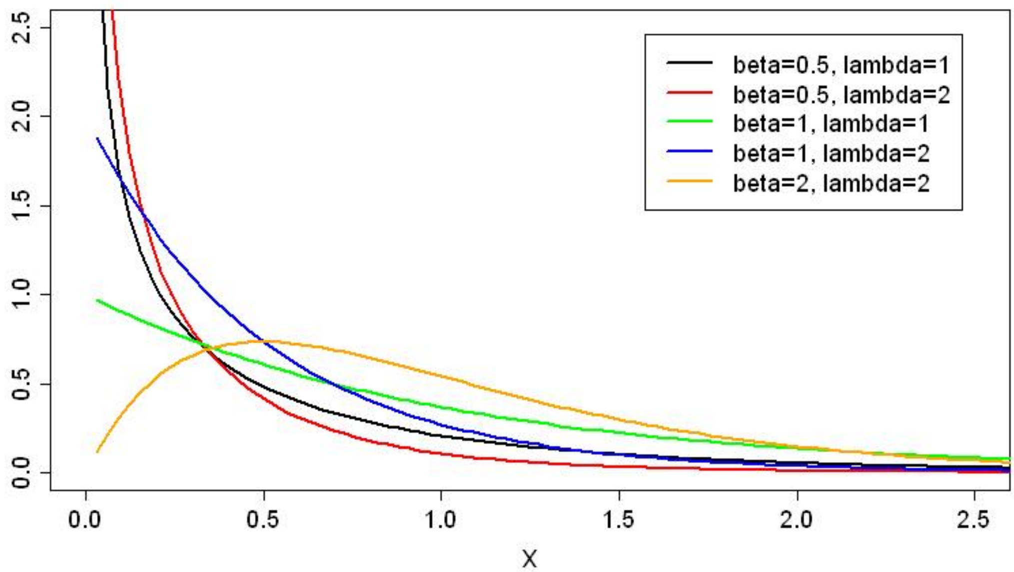

Figure 2.6: Gamma distribution density function with different parameters

River networks in the study catchments consist of many river segments which have to be characterised individually with respect to their hydrological characteristics by probability distributions. On the one hand, the data basis for this parameterisation consists of gauging stations with 30 years of streamflow records. On the other hand, catchment characteristics such as thematic maps of runoff and specific discharge as well as topographical information are available for the drainage areas.

It might be too simple a concept to draw upon observed streamflow only and to linearly interpolate between gauging stations in order to quantify streamflow for every river segment as the amount of streamflow does not only depend on upstream streamflow, but is related to drainage area characteristics in a complex way and is thus spatially variable.

Parameter estimation. The easiest method for parameter estimation is the method of moments (MoM) (Chow, 1964; Sachs & Hedderich, 2006). Moments are calculated from the sample data set and are used as moment estimators for the population. The largest advantage of MoM estimators is their simplicity. They can normally be directly calculated from any sample data set. Disadvantages of MoM-estimators are that they are not always sufficient and efficient (Sachs & Hedderich, 2006).

A more sophisticated method is the maximum likelihood estimation (MLE), which estimates the most probable parameters on basis of the given sample. Its characteristics are consistency, asymptotic unbiasedness, asymptotic efficiency and sufficiency (Sachs & Hedderich, 2006). Because of these characteristics maximum likelihood estimators are used below. MLE estimators for the lognormal distribution are

$$\mu = \frac{\sum_{i=1}^{n} lnx_i}{n} \tag{2.5}$$

and

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (lnx_i - \mu)^2}{n}} \tag{2.6}$$

(NIST/SEMATECH, 2009). For the Gamma distribution MLE estimators have to be calculated numerically (Choi & Wette, 1969). The statistical software R provides the MASS library and within it the function fitdistr() to derive MLE estimators (Venables & Ripley, 2002).

For every gauging station with available daily discharge values parameters for the three distribution functions are computed automatically by R.

In order to obtain more samples and finally more representative estimators for describing probability distributions of streamflow the resampling method bootstrapping is applied (Efron & Tibshirani, 1993; Good, 2006). Bootstrapping is based on sampling with replacement. Each sample has to be of the same length. (Sachs & Hedderich, 2006) recommends to draw at least 500 sub-samples of the original sample. Streamflow time series might be influenced by outliers resulting from extreme events. By drawing smaller sub-samples bootstrapping might help to diminish the influence of outliers.

Goodness-of-fit tests. Correspondence of the resulting probability distribution functions with observed data is checked by means of goodness of fit tests. A first impression of compliance of sample data with a theoretical probability distribution is given by QQ-Plots that plot sample percentiles against percentiles which are based on a theoretical distribution function.

Commonly applied approaches to compare data samples with probability distributions are the non-parametric Pearson's Chi-square test and the Kolmogorov-Smirnov test. Pearson's chi-square test is applicable for all distributions for which a cumulative distribution function can be derived. The test is based on a classification of data, and one of its disadvantages is the dependency on the chosen classification (Sachs & Hedderich, 2006; Duller, 2008). The test statistic is

$$X^2 = \sum_{i=1}^{n} \frac{(O_i - E_i)^2}{E_i} \tag{2.7}$$

with k classes. O_i is the observed frequency of class i, while E_i corresponds to the expected theoretical frequency (Sachs & Hedderich, 2006). The number of classes might be chosen according to (Moore, 1986) as

$$k = 2n^{2/5} \tag{2.8}$$

for n observations. The null hypothesis that sample data follow a given distribution is rejected if X^2 is greater than the corresponding value delivered by the Chi-square distribution for significance α and $k-3$ degrees of freedom (for two estimated parameters).

Kolmogorov-Smirnov's test can only be applied to continuously distributioned random variables. Theoretical probability distributions that are compared to sample data by this test have to be fully specified. Otherwise, the test is more imprecise in boundary area than in the distribution's middle (Sachs & Hedderich, 2006; Duller, 2008). The test statistic is

$$D = \underset{1 \leq i \leq n}{max} (F(Y_i) - \frac{i-1}{i}; \frac{i}{n} - F(Y_i)) \tag{2.9}$$

The null hypothesis is rejected if D is greater than a critical value which depends on the distribution to be tested and on the significance level. To overcome the problem that the test is conservative if distribution functions are not fully specified, (Lilliefors, 1967) suggested a modification for the choice of critical values. Tables of these values can theoretically be computed for every probability distribution (d'Agostino & Stephens, 1986). As these values have only been found for a normality test and not for tests of lognormal and gamma-distributed values, p-values are used for the decision to accept or reject the null-hypothesis. P-values denote the probability of obtaining a sample that is at least as extreme as the observed sample given the true null hypothesis. Therefore, the lower the p-value, the more likely the null hypothesis can be rejected. p-values do not measure the probability that the null hypothesis is true, but rather state that it cannot be rejected at the given significance level. Deciding upon them is thus a weaker technique than using critical values from the tests.

The two goodness-of-fit tests are performed for bootstrapped sub-samples of the time series at each gauging station. Additonally normality tests are used to test for a lognormal probability distribution. As by definition a random variable X is lognormally distributed if its logarithm is normally distributed, $log(X)$ can be tested against the null hypothesis that $log(X)$ follows a normal distribution. Here, critical values are known for the Kolmogorov-Smirnov test.

Geo-referenced water balance model. To address ungauged parts of the catchments, parameterisation of probability distributions cannot be based on observed streamflow data, but has to rely on understanding of runoff-generating processes and deriving characteristic numbers for runoff quantification. The approach in this study is based on the simple water balance (equation 2.1). Assuming steady-state conditions, differences in the time scales within which runoff proceeds are neglected. Mean flow has to be derived whose generation is not purely event-driven. Therefore, a rather continuous runoff generation is assumed. Sooner or later overland flow, interflow and base flow reach the channel network.

If precipitation, evapotranspiration and drainage area are known for a given location runoff generated at this location can easily be calculated. A raster dataset representing effective precipitation (P - E) is used to evaluate the water balance in a geo-referenced way (BMU, 2005a). Effective precipitation multiplied by drainage area yields specific discharge. A map for specific low flow discharge supplements discharge information for low flow situations (BMU, 2001). The displayed specific discharge corresponds to the lowest arithmetic mean of streamflow on 10 consecutive days (MAM(10)).

To model spatially explicit stream flow or runoff accumulation in streams the river basin's topography has to be considered. A digital elevation model is used to derive water divides between rivers and to derive sub-catchments for each river segment. The runoff that is generated within such a sub-catchment is assumed to reach the corresponding river segment. The discharge from upstream segments has to be added to the runoff from the sub-catchment entering each segment. A routing routine is used to accumulate mean and low flow discharge. At gauging stations derived mean streamflow values are compared to observed mean values (see figure 2.7).

It is analysed by means of measured streamflow data if there is a systematic coherence between MAM(10) and exceedance percentiles. These percentiles can then be used to parameterise the probability distribution parameters (see figure 2.8).

2.3.1.3 Runoff Pathways

When considering fate of substances that enter surface water via different runoff pathways, composition of runoff is essential (Poff *et al.*, 1997; Haberlandt *et al.*, 2001). Runoff pathways can be classified into surface runoff, interflow, and groundwater runoff. Surface runoff occurs directly during or shortly after precipitation events. Interflow is composed of water that infiltrates into soil and flows through ephemeral zones of saturation into river channels, whereas groundwater runoff con-

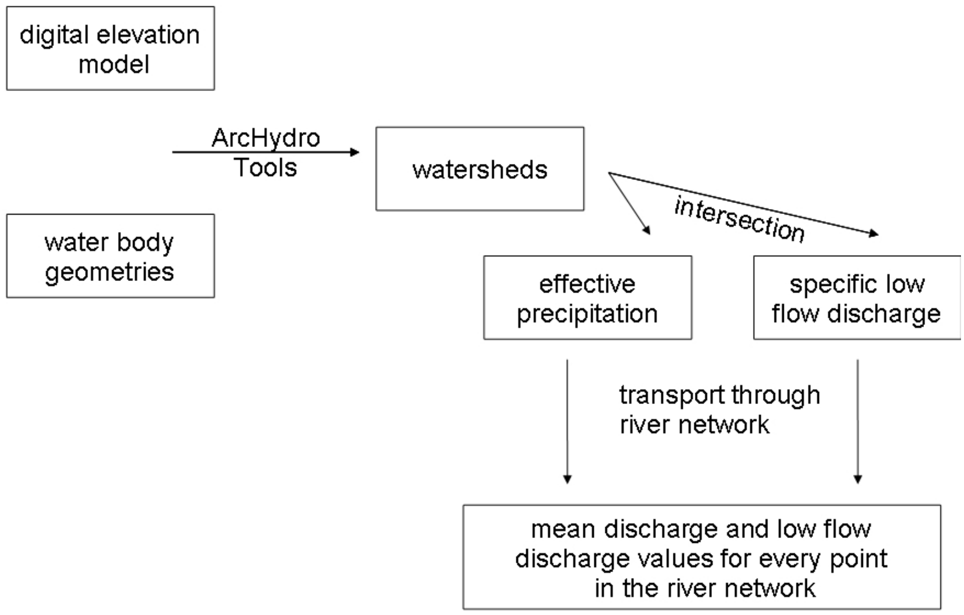

Figure 2.7: Delineation of mean and low flow discharge

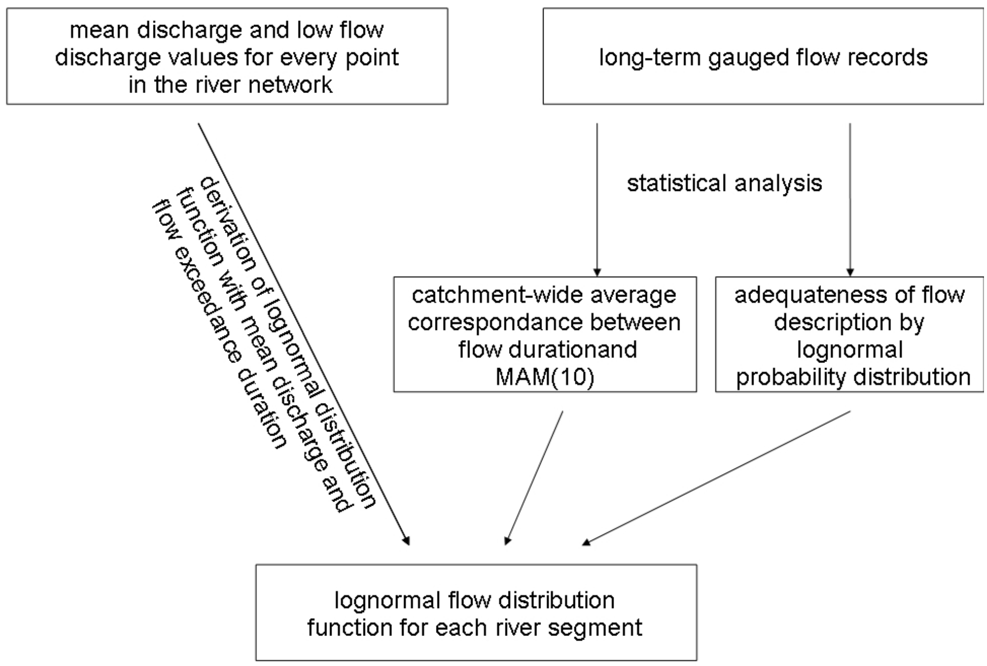

Figure 2.8: Determination of probability distribution parameter

sists of precipitation water which percolates to deeper layers below the groundwater table. One part of interflow enters the channel directly and fast, while the other part is delayed. In case of delayed interflow and groundwater runoff, soil and aquifers serve as a buffer. In this way fast, direct runoff component and delayed base runoff can be differentiated (Chow, 1964). Base flow provides a continuous input to rivers and streams (Wundt, 1958) and is thus important for perennial water flow especially during prolonged dry weather periods.

Low flow hydrology. Low flow hydrology is an issue recently more intensively investigated due to increased anthropogenic uses of water resources and their ecological and economical implications (Smakthin, 2001). Human water demands for drinking water supply, irrigation or coolant competes with ecological water demands for maintaining functions in aquatic ecosystems (Tharme, 2003). Especially in low flow situations dilution capacity with respect to substance emission has to be considered carefully. In order to prevent concentrations that might induce adverse ecotoxicological effects waste water allocation especially has to consider the occurrence of low flow periods (Vogel & Kroll, 1992).

Low flow periods are caused by a variety of circumstances which are induced by natural and anthropogenic factors. As low flow naturally forms a part of the hydrograph, it is subject to the factors also determining the hydrological regime. These are both climatic and physiographic ones. Low flow commonly occurs during periods with deficient precipitation (Chow, 1964). Groundwater inflow is the main contributing water source during these periods. Groundwater yield is determined by the characteristics of the aquifer, or more general, of the hydrogeology of the catchment. Other water storages supplying rivers with water during dry periods might be lakes, glaciers or channel banks (Smakthin, 2001). The existence and location of storages is individual for each catchment.

Gains are accompanied by natural losses due to evapotranspiration, groundwater recharge or storage as snow. The role of evaporation strongly depends on climate, soil moisture and plant cover of the riparian zone and shading of the river (Smakthin, 2001). Anthropogenic impact on low flows occurs both directly via e. g. river abstractions, irrigation return flows or effluent emission and indirectly. Any intervention in the groundwater processes such as groundwater abstractions or artificial drainage affects the sub-surface runoff components. In addition, also evapotranspiration is influenced by vegetation regime changes, land use patterns or urbanisation (Smakthin, 2001).

Against the background of the high spatial variability of catchment characteristics and the interrelations of natural processes and anthropogenic modifications it is difficult to draw a general conclusion of low flow generation. Uniform relations between low flow and catchment characterisics can therefore hardly be found. Instead, catchment specific information like e. g. specific low flow discharge or observed streamflow data, has to be used.

According to both variety of low flow situations and of application fields for low flow analysis, many different approaches and methods exist. According to Gustard et al. (1992), different definitions of low flow events and of expressing frequency as well as considering different durations lead to a broad diversity of low flow analysis approaches. Among commonly used low flow analysis methods many are based on probability analysis, too. The variety of low flow measures and indices also mirrors the variety of applications where low flow analysis is applied.

$\boldsymbol{Q_{95}}$. For low flow analysis the discharge that is exceeded 95 percent of the time prevails. It is named differently in different studies. In Switzerland it is denoted Q_{347} referring to 347 days per year with higher discharge (Aschwanden & Kan, 1999). By definition the Swiss Q_{347} is a parameter that only should be used for sites where flow is not significantly artificially influenced by e. g. river regulation or abstraction. In the UK low flow studies by Young *et al.* (2000a; 2000b) it is denoted as Q_{95}, often standardised by mean flow to secure comparability between catchments of different size. Schulze & Matthies (2001) call this index Q_5 referring to the percentage of time the discharge falls below this threshold value.

MAM(10). Another kind of low flow indices incorporate duration of low streamflows. Among these are e. g. the mean annual x day minima. The mean annual 10-day minimum denotes the lowest arithmetic mean of daily discharge values on 10 consecutive days (BMU, 2005a). According to the Hydrological Atlas of Germany the MAM(10) is mainly fed by groundwater contribution (BMU, 2005a). It is independent from any - often arbitrarily chosen - threshold value.

Gustard & Gross (1989) found out that variability of low flow regime characterised by MAM(10) is related to magnitude of low flow and that MAM(10) is similar for hydrometric similar regions.

Schreiber & Demuth(1997) used this index to characterise yearly variation of low flow. Besides, long-term flow behaviour is analysed based on average MAM(10) of at least a 10-year record period. As in their study values of MAM(10) do not vary significantly over years, they concluded that MAM(10) is a stable low flow index. Coefficients of variation range from 28 % to 69 %.

In both studies relations between MAM(10) and catchment characteristics are established by regression analysis. In the study of Gustard & Gross (1989) the independent variables are soil, drainage area size and annual average rainfall in the study of Gustard & Gross (1989), whereas according to Schreiber & Demuth (1997) they are geology, hydrogeology, petrography and land use, respectively. The latter study further states that geology is the dominating parameter for estimation of the quantity of MAM(10), whereas hydrogeology and land use determine the variance of MAM(10). The strong dependency on geology leads to the fact that MAM(10) is rather homogeneous within catchments with similar geological characteristics.

Composition of runoff. Low flow situations are strongly interrelated with the delayed sub-surface runoff component. Composition of runoff is spatially distributed as it depends on spatially distributed catchment characteristics such as climate, land use, topography, hydrogeology, or soil type (e. g. (Chow, 1964; Kunkel & Wendland, 2002). The buffer function of both unsaturated zone and groundwater aquifers remarkably influences flashiness of river flow regime (Smakthin, 2001). Chemical composition of sub-surface runoff differs in comparison with surface runoff as infiltration through soil layers leads to sorption and desorption of substances that are found in either surface water or soil matrix (Haberlandt *et al.*, 2001). Therefore, a quantification of delayed sub-surface flow is essential to estimate both river regime

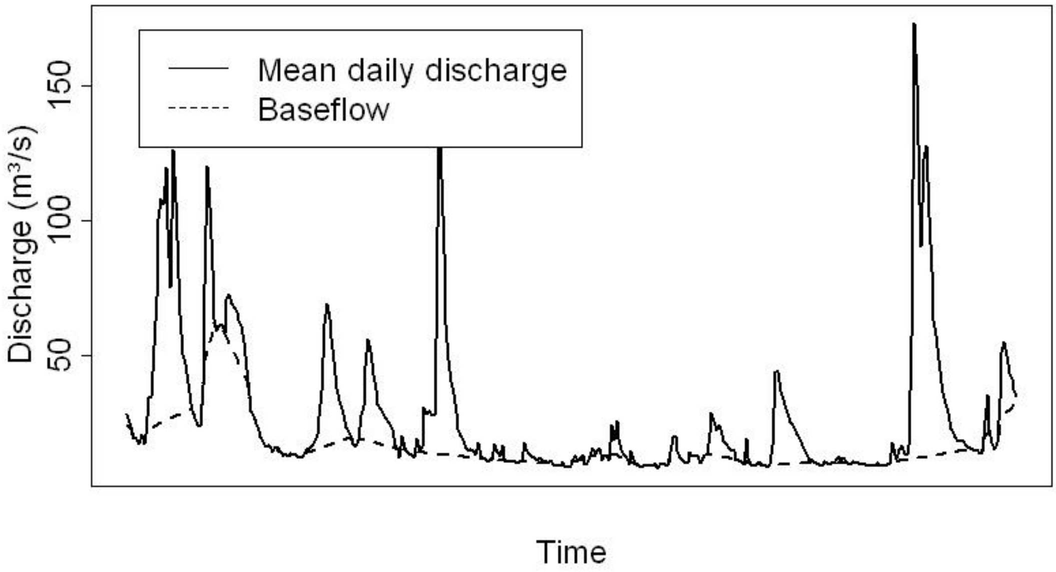

Figure 2.9: Baseflow separation according to Gustard *et al.* (1992)

and substance loads realistically.

2.3.1.4 Quantification of baseflow contribution

For baseflow separation from hydrographs various approaches have been developed (Tallaksen, 1995). A commonly used index to quantify baseflow contribution to total runoff is the base flow index BFI. It is independent of catchment size or total runoff amount. The baseflow index denotes the long-term ratio of baseflow runoff volume and total runoff volume. To derive this ratio baseflow fractions have to be separated from runoff volumes. Direct measurements of groundwater recharge are difficult and only possible at small spatial scale (Demuth, 1993). Therefore, methods to estimate groundwater recharge from hydrograph analysis have been developed (e. g. (Chapman, 1999; Wundt, 1958; Demuth, 1993; Gustard *et al.*, 1992)). While some of these runoff-separation methods focus on analysis of runoff recession after a single rain event (Chapman, 1999), others concentrate on long-term groundwater contribution to streamflow (Wundt, 1958; Gustard *et al.*, 1992; Demuth, 1993).

Gustard's method is based on the calculation of MAM(5) values for non-overlapping 5-day periods. Between turning points in this sequence of minima a linear interpolation is carried out whereupon actual streamflow is an upper boundary for base flow. Underneath the resulting base flow hydrograph base flow volume can be computed and compared to total runoff volume. Figure 2.9 exemplarily illustrates the baseflow part of a hydrograph according to the separation method by Gustard *et al.* (1992).

In contrast the approach firstly applied by Wundt (1958)and later improved and objectified by Demuth (1993) assumes monthly minimum values to indicate base flow amount. These minima are ranked according to their magnitude and plotted against

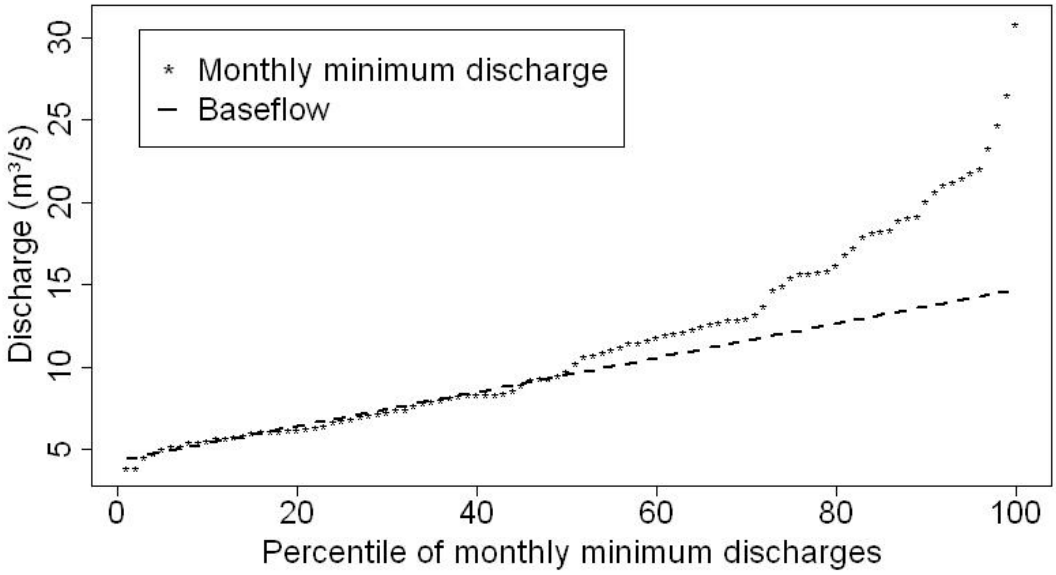

Figure 2.10: Baseflow separation according to Demuth (1993)

their rank. The lower part of the graph resembles a linear line (see figure 2.10). At some critical point slope increases, which is interpreted as additional contribution to baseflow by interflow or surface runoff. The linear part of the minima curve is estimated stepwisely by linear regression to points between the 5-percentile and the critical point. By optimizing the correlation between the linear regression equation and monthly minimum discharges the critical point is found (Demuth, 1993). The mean value of baseflow can then be utilised to derive baseflow volume and finally base flow index.

Statistical analyses of daily discharge time series are performed to determine streamflow percentiles (e. g. Q_{95} and MAM(10)) directly from observed streamflow. Two periods-of-record are compared: 1976 - 1989 and 1976 - 2005. The first serves as reference period for the construction of the specific low flow discharge map in the hydrological atlas of Germany (BMU, 2005a). The latter is additionally analysed in order to investigate if low flow indices depend on the period-of-record or on its length.

Annual MAM(10)-values are used to compute average values for the two periods. They are analysed with respect to their inter-annual variability. The intervals in which values of Q_{95} and MAM(10) range leave a mark of the variability. The variation coefficient provides information about the variability which is independent of the magnitude of low flow. A comparison of average values and variation coefficients from the 14-year period (1976 - 1989) and the complete 30-year period shows if the considered indices are rather stable or if they perceivably depend on the length of the period-of-record.

For every examined gauging station low flow discharge is additionally derived by means of the specific low flow discharge map from the hydrological atlas of Germany (BMU, 2005a), and they are compared to observed MAM(10)-values. For the evaluation of the map such a comparison has already been carried out for small basins. Here, a comparison is additionally drawn for larger basins. In this manner it can be ascertained or disproved whether low flow discharge can reliably be estimated from a specific low flow discharge map also for larger catchments and it can be found out if the usage of data only from the reference period provides sufficient results or if longer time series better fit the information from the map. If there is good agreement between the values of MAM(10) at gauging stations, which are equally distributed throughout the basin, it can be assumed that the procedure is also suitable for any other point in the river basin.

2.3.2 River Morphology

River or fluvial morphology deals with formation of river beds and flood plains by water flow (German IHP/HWRP National Committee, 1998). Dominant processes in shaping land-forms within a watershed are erosion and sedimentation (Leopold *et al.*, 1964). Within the channel system a maximum equilibrium is aspired between channel form and transported water and sediment (Leopold & Maddock, 1953). River morphology involves a broad diversity of aspects.

Compilation of a comprehensive data basis on morphological river structure is recommended because of its importance for the ecological status of riverine ecosystems (Logan & Furse, 2002).

The federal German Working Group on Water Issues (LAWA) defined standards for river structure surveys in Germany in 2000 (LAWA, 2000). River structure is defined as

> "spatial and physical differentiations of the river bed and its environment as far as they are hydraulically, river morphologically and hydrobiologically active"

(LUA, 2005). It is one measure of ecological quality. Surveyed parameters are listed in chapter 2.2.1.3. Data from the river structure survey is a valuable pool for hydromorphological characterisation of a river segment.

For the application of the GRAT-ER model only single aspects of river structure are considered. River bed depth has to be specified directly. This parameter influences sedimentation, photolysis and volatilisation of substances in the model. River structure data can also be used to derive flow velocity estimates. As the relation between river structure and flow velocity is rather complex, the issue of flow velocity estimation is addressed in more detail in chapter 2.3.3.

2.3.2.1 Estimation of River Structure Variables

For the area of North-Rhine Westphalia data on river structure is available. By means of GIS-tools results from river structure field mapping is assigned to GREAT-ER river segments in the Ruhr river basin. For each river segment, which might be up to 2 km long, multiple river structure survey points are available because they are normally chosen with a distance of 100 m. This means that recorded depth values have to be aggregated in space to assign one value per segment. To check whether the assumption of one morphological parameter per segment is appropriate, variability of depth is exemplarily analysed. For small and medium rivers depth is classified into 6 classes ($< 0.1\ m$, $0.1\ m$ - $0.3\ m$, $0.3\ m$ - $0.5\ m$, $0.5\ m$ - $1\ m$, $1\ m$ - $2\ m$, and $> 2\ m$) in the river structure survey. For the analysis each of these classes is represented by an average value.

Variability of river structure survey depth values within one river segment is visualised by mapping variation coefficients for each segment. As pointed out in chapter 1.2.2, hitherto, parameterisation of river networks for GREAT-ER with respect to depth and flow velocity has been considered so far as solely dependent on discharge (Round & Young, 1997; Round *et al.*, 1998). Power relations elaborated by Leopold & Maddock (1953) form the basis for the applied approach.

Leopold & Maddock (1953) introduced a concept of linking hydraulic variables such as channel width, channel depth and velocity to discharge as power functions. The basic equations for width, depth and velocity are, respectively,

$$w = a \cdot Q^b \tag{2.10}$$

$$d = c \cdot Q^f \tag{2.11}$$

$$v = k \cdot Q^m \tag{2.12}$$

The exponents have to be derived empirically. Their concrete figures thereby depend on the representativeness of the dataset which is used for regression analysis.

By means of regression analysis with data from small and medium river stretches in the UK, the relation for estimating river bed depth has been derived (Round *et al.*, 1998).

$$d = \begin{cases} 0.61 + 0.93 \cdot r & r > 2.13 \\ 1.21 \cdot r & r \leq 2.13 \end{cases} \tag{2.13}$$

Morphology of river beds is thus not considered for river parameterisation directly, but only through the given regression analysis.

The largest advantage of this approach is that information on discharge for every river segment suffices and no further data is required. However, it is not obvious if transferring regression analysis results from UK rivers yields realistic results in German rivers that might have very different physiographic and climatic catchment characteristics. A comparison between depth values from the power relation and from river structure survey is drawn. Such a comparison, however, is limited to small and medium rivers because for larger rivers the survey does not contain information on water depth (LUA, 1998; LUA, 2001).

To derive depth from other data than river structure data, a method based on stage-discharge relations is elaborated and tested as additional possibility. Dependency between discharge and river depth or in fact stage is used. These relationships are available at gauging stations. Stage usually depends on gauge datum; i. e. stage is not the same as river depth, but usually is higher (German IHP/HWRP National

Committee, 1998). If it is possible to determine a so-called "zero-flow stage", river depth can be derived as difference between stage and zero-flow stage.

An approach developed by Gawne & Simonovic (1994) is applied to derive stage-discharge relationships by means of a transformed linear regression analysis with data from gauging stations. The variability of resulting rating curves within a river basin is analysed in order to find out if similar sub-basins have similar stage-discharge relationships. Gawne & Simonovic (1994) assume that in spite of the concave form of a stage-discharge relationship, a linear regression approach can be applied with a power transformation for stage. Transformed stage can then be described as

$$S_t = S^{TE} \tag{2.14}$$

with the transformation exponent TE. The linear regression model thus is

$$D_m = b_0 + b_1 S_t \tag{2.15}$$

with coefficients b_0 and b_1 to be estimated by regression analysis. The transformation exponent ranges from 1.5 to 3.5 (Gawne & Simonovic, 1994). Regression analyses are carried out with varying TE values (from 1.5 to 3.5 in 0.05 steps). The most suitable model with respect to coefficient of determination and SEE statistic is finally chosen. SEE is given by (Gawne & Simonovic, 1994) as

$$SEE = \left(\frac{\sum_{i=1}^{n} (D_i - D_{mi})^{1/2}}{n-2} \right)^{1/2} \tag{2.16}$$

For each pair of variates the Euclidean distance to the best theoretical point (maximum r^2 and minimum SEE) is calculated. The transformation exponent corresponding to the optimum pair of variates is used to determine the zero-flow stage which equals the intercept b_0. By inverting the regression relation stage can be described as function of discharge.

$$S = \left(\frac{D_m - b_0}{b_1} \right)^{1/TE} \tag{2.17}$$

Setting discharge to zero yields zero-flow stage which has to be subtracted from stage value to obtain depth. Depth values derived in this way are compared to data from the river structure survey in the analysed sub-basins.

2.3.3 Flow Velocity

The decline of the surface water concentration within a river segment depends on the water's residence time within the segment because it determines the time available for degradation processes. This residence time can be computed by means of flow velocity and length of the segment. The substance load at the end of a river segment is calculated from load at the start and loss processes within the segment during the residence time (Boeije & Koormann, 2003). An average flow velocity is transformed into the water's residence time by the following formula

$$HRT = \frac{L}{v \cdot 3600} \tag{2.18}$$

with $L(m)$ denoting length of a segment and $v(m/s)$ mean flow velocity. With this residence time first-order degradation is calculated. However, as flow velocity in a river bed is very variable, determination of an average flow velocity is difficult, and even with the simplified assumption of one average flow velocity value the parameterisation of each river segment with such a value remains difficult due to limited data availability on river basin scale, as furthermore, velocity measurements are rare. Therefore, a model to predict flow velocity is valuable in the context of GREAT-ER.

2.3.3.1 Flow Velocity Models

By the continuity equation of steady flow the following relation is given:

$$Q = v \cdot A \tag{2.19}$$

with Q denoting discharge, v average velocity and A the cross section area of the channel (Chow, 1964). It implies that with rising discharge velocity or cross section area increase, too. However, these values depend on various factors which are strongly related to river morphology (Leopold & Maddock, 1953) and which are thus very variable in space.

A value for average flow velocity is actually only an aggregated instrument to describe flow dynamics in a natural channel which neglects the 3-dimensionality of open channel flow.

Fluid dynamics approaches are therefore frequently used to describe open channel flow on a high spatial and temporal resolution. The principles of conservation of mass, momentum and energy form are reflected in the basic equations of 3-dimensional fluid dynamics, the Navier-Stokes equations (Durst, 2006). This system of partial differential equations contains a continuity equation and three momentum equations which have to be solved numerically. With improved computational prospects the development of high-resolution numerical models is enhanced and more and more sophisticated models are developed on small scale (Lane, 1998). Although flow conditions could theoretically be calculated for every place at every time by solving the Navier-Stokes-equations, the practical use of these equation for whole river basins is limited due to computational restrictions and to lacking knowledge of appropriate boundary and initial conditions (Lane, 1998).

To elude the problem of parameterising three-dimensional models, approaches accounting for fewer dimensions have been developed. The Saint-Venant equations, for example, ignore lateral and vertical variations in the hydraulic variables, as they are not crucial for many practical purposes (Chow *et al.*, 1988). However, even in a simplified form of these equations initial and boundary conditions have to be known as well as information on channel geometry (Moussa & Bocquillon, 1996), which usually is not the case on catchment scale.

These approaches based on theories of fluid dynamics are helpful to understand the small-scale processes that influence flow behaviour. They are thus widespread in engineering sciences. However, limited data availability and computational constraints impede their practical use especially for applications in natural channels. An investigation of average conditions in larger river basins demands approaches which are aggregated.

A possibility to obviate the difficulties of parameterising hydrodynamic approaches, is the investigation of river hydraulics (Leopold & Maddock, 1953) which allows for an understanding of the relationships between channel form and discharge. The approach by Leopold & Maddock (1953) forms the basis of a tremendous number of approaches addressing channel hydraulics and especially flow velocity. Enhancements of this approach also exist. For instance Singh & Zhang (2008) doubt that average exponent values are reasonable. They thus investigate different configurations of hydraulic geometry relations (i. e. combinations of contributions of different variables to change in stream power) both at-a-station and downstream (Singh & Zhang, 2008).

Widely used equations linking average flow velocity to slope and roughness for uniform turbulent open channel flow are the Darcy-Weisbach and the Manning-Strickler equations. Flow velocity can be calculated according to Darcy-Weisbach by

$$v = \frac{1}{\lambda}\sqrt{8 \cdot g \cdot R \cdot S} \tag{2.20}$$

with the dimensionless Darcy-Weisbach friction factor λ, acceleration due to gravity g, hydraulic radius R and slope S. The Manning-Strickler equation is

$$V = k_{St} \cdot r_{rh}^{2/3} \cdot I_S^{1/2} \tag{2.21}$$

with k_{St} as Strickler-coefficient representing river bed roughness, r_{hy} as hydraulic radius (cross section divided by wetted perimeter) and I_S as bed slope. In anglophone literature often the inverse of the Strickler-coefficient $n = 1/k_{St}$ denoted as Manning-coefficient is used.

The Manning equation is based on empirical considerations and is commonly used (Jirka & Lang, 2005). It is both applied on a small spatial scale (Hessel *et al.*, 2003) and in large scale models (Schulze *et al.*, 2005). The main problem with regard to practical applicability is the estimation of the roughness factor n (Dingman & Sharma, 1997). Several tables with typical n-values can be found in literature (e. g. in (Thompson, 1999), (Chow, 1964), (Naudascher, 1987) and (Chow *et al.*, 1988)). However, channel bed surface cannot be assumed to be homogeneous over larger distances and time periods (Leonard *et al.*, 2000). Additionally, roughness changes with water level (LfU Baden-Württemberg, 2002b).

Another obstacle to the application of the Manning equation is the estimation of the wetted perimeter because the cross-sectional area of a natural channel is very irregular. Detailed data on river profiles might only be available for larger rivers which are of special interest concerning flood protection and waterway transport capacities. The Federal Institute of Hydrology uses high resolution laser scan data to calculate water levels dynamically in individual cases (Rademacher, 2004). However, this data only exists for larger waterways and is not publicly available. Previous studies simplified this problem by assuming rectangular, triangular or trapezoidal river profiles (e. g. (Schulze *et al.*, 2005; Shang, 2008)).

Assuming these simple and regular river profiles and homogeneous roughness coefficients introduces uncertainty in the calculation of flow velocities and channel forms (Dingman & Sharma, 1997).

The difficulty of finding realistic parameters for the Manning equation remains and thus a methodology to derive corroborated estimates for average flow velocity and channel geometry is still missing.

Up to now, for data processing in GREAT-ER a regression approach from the software package Micro LOW FLOWS is used. Micro LOW FLOWS is applied in order to describe the natural variability of river flows in ungauged rivers (Young *et al.*, 2000). The approach used in Micro LOW FLOWS is based on the relations between velocity, width, depth and discharge by Leopold and Maddock (1953). By means of a large number of observed values from British river basins and regression analysis the relation

$$v = 10^{-0.583} \cdot MQ^{0.283} \cdot \left(\frac{Q}{MQ}\right)^{0.495} \tag{2.22}$$

has been established. Q denotes discharge, MQ mean discharge and Q/MQ is the standardised discharge allowing for comparisons between catchments of different sizes (Round & Young, 1997).

Since the river network is parameterised with flow rates for each river segment from data on effective precipitation, velocity can be derived by this regression analysis. However, the relation is based on data from small natural channels (Round & Young, 1997). In absence of a more sophisticated model or adequate data this relation is also applied to larger streams in GREAT-ER.

In the following it is first scrutinised whether this regression equation yields realistic flow velocity values by comparing them to velocity values from the ATV river water quality model.

Additionally, the question of missing data to parameterise the Manning-Strickler equation is addressed by using river structure data and deriving slope, roughness coefficients and hydraulic radius from digital elevation data, and information on bed substrate, river profile and depth, respectively.

2.3.3.2 Estimation of Effects of Flow Velocity on surface water substance loads

It is first tested to what extent flow velocity influences simulation results, before an appropriate approach (i. e. based on available data, addressing areas where uncertain flow velocity values poses problems) to parameterise flow velocity is developed.

To assess the quality of simulated in-stream concentrations against the background of an uncertain parameterisation of flow velocities, flow velocity estimates are compared to verified velocity data from the ATV water quality model. For some river sections in the Main river basin data on discharge, flow velocity and river profile is available from this model (Christoffels, 2001). The waste water engineering association (ATV) developed this model, which is a powerful tool employed for water management. The model consists of 17 modules based on a water flow modul. This means that flow behaviour has to be modelled which includes flow velocity. For simulation with the ATV model a geo-referenced river network has to be compiled which is segmented at interesting points (such as emission points, confluences etc.). It is possible to conduct stationary and instationary model simulations whereupon at the network's nodes either a constant discharge value or a discharge hydrograph has to be available. Usually such information originates from observation. By dint of river cross sections and coefficients of roughness the flow velocity can be derived at any node. The ATV model is capable of modelling additional hydrodynamic processes as e. g. longitudinal dispersion or sedimentation (Christoffels, 1998).

Data is available for the Main river, the Red main (one of the headwater streams of the Main River), for the Wern river, for parts of Rednitz, Pegnitz and Regnitz. Except for river Wern velocity estimates are verified. As ATV velocities for the Main river are only available from river kilometre 384 to 212, flow velocities downstream to the mouth are derived by extrapolation. This extrapolation is underlain by exponential decline of flow velocity behind a water gate that escalates at the next water gate

$$v(L) = v(0) \cdot d^{-k \cdot L} + v_{min} \tag{2.23}$$

v_{min} denotes a constant minimum flow velocity.

The question regarding the impact on different flow velocities and hence residence times on degradation ensues. Hypothetical substances denoted by half-lives are used to compute degradation capacity of rivers with different flow velocities. This analysis aims at identifying those combinations of flow velocity inaccuracy and substance's half-lives for which significant differences concerning eliminated load are observed. The practical relevance is investigated by applying the GREAT-ER model with velocities based on the regression analysis and based on ATV model data, respectively.

As only first-order degradation with an aggregated degradation rate is considered, hypothetical substances are used that are only characterised by their half-lives. Results of this analysis can then be translated to real substances. Half-lives with which degradation is calculated are 1 hour, 12 hours, 24 hours, 5 days, and 30 days.

Discharge values from the ATV model are used to derive velocities by means of equation 2.22. Velocity profiles for the two approaches can then be compared in order to obtain an impression of the discrepancies between the two approaches. To calculate degradation of hypothetical substance for different residence times, a standard river segment of 2 km length is defined in which 1 unit of substance is emitted. First-order degradation is assumed with a fixed degradation rate k. The load at the end of a segment is hence

$$Phi_{out} = Phi_{in} \cdot e^{-k \cdot HRT} \tag{2.24}$$

with the initial load Phi_{In}. The percentage which is left of the initial load of 1 unit substance is then calculated according to the different residence times calculated by formula 2.18.

Besides the consideration of a single segment also degradation on a longer flow distance of 100 km (equating to 50 successive standard segments) is examined. The residence times are correspondingly longer. There are no emissions in between, but only at the beginning of the segment.

2.3.3.3 Estimation of Flow Velocity

A methodology to derive adequate average flow velocities for different kinds of rivers (small creeks, larger streams, etc.) is developed because flow velocity plays a significant role for surface water concentrations of some substances. River structure will be taken into account because it mainly controls flow velocity.

According to the Manning-Strickler equation 2.21 flow velocity is a function of slope, river bed roughness and hydraulic radius. These parameters have to be derived from remote sensing elevation data and river structure survey records

Slope. Elevation information is available for each river structure survey point with a distance of approximately 100 m from DGM5. By spatially joining this information to the river segments, which are used for GREAT-ER simulations, a slope value can be calculated from elevation difference and length of the segment.

Roughness. Discharge capacity of a river can be quantified by means of roughness coefficients. Higher k_{St} values indicate a smooth the river bed (LfU Baden-Württemberg, 2002a). According to the Manning-Strickler equation 2.21 the roughness coefficient is the factor influencing flow velocity most. An appropriate estimation of it is therefore fundamental for flow velocity estimation with the Manning-Strickler approach. However, this value cannot be measured directly (LfU Baden-Württemberg, 2002a).

Empirical roughness coefficients can be found in many hydrological works. A summary can be found in (LfU Baden-Württemberg, 2002b). According to these tables roughness coefficient values for natural channels range from approximately 19 $m^{1/3}/s$ to 42 $m^{1/3}/s$ (LfU Baden-Württemberg, 2002b). Mapping of tabulated river types and river segments from the GREAT-ER river networks is ambiguous and uncertain as the coefficient has to mirror effects of multiple characteristics (river bed roughness, channel profile, riparian vegetation, meanders, bed load and vegetal invasion) (LfU Baden-Württemberg, 2002a).

An approach directly accounting for different aspects that influence discharge capacity was introduced by Cowan (1956). According to him the Manning-coefficient n is composed of partial coefficients referring to bed material (n_0), irregularity of bed structure (n_1), changes in cross-section profile (n_2), effect of obstructions (n_3), vegetation (n_4) and degree of meandering (m_5) (Cowan, 1956).

$$n = (n_0 + n_1 + n_2 + n_3 + n_4) \cdot m_5 \tag{2.25}$$

For this approach the different partial coefficients can be mapped more easily because for the most part river structure survey parameters directly correspond to the parameters used in Cowan's approach. Table 2.3 shows which parameters are used.

Hydraulic Radius. The hydraulic radius is defined as ratio between cross-section area and wetted perimeter of a river (German IHP/HWRP National Committee, 1998). As cross section profiles are not available, actual profiles are substituted by standard river cross section types. River structure survey data differentiates between 6 or 7 profile types for medium to larger streams and small rivers, respectively (LUA, 1998; LUA, 2002).

To compute cross-section area and wetted perimeter, depth and width have to be known. Here, trapezoidal river cross sections are used to approximate actual river

Table 2.3: Mapping of adjustment factors for Manning's n according to Cowan (1959)

Factor	**Classification**	**Value**	**Parameter**	**Parameter value**
n_0 Bed material	concrete firm soil fine gravel coarse gravel rock cut coarse sand cobble boulder	0.011 0.02 0.024 0.026 0.025 0.031 0.04 0.055	bed stabilisation alluvium, clay, org. material fine gravel coarse gravel rock cut sand stones, rubble boulder	3.1 bed material
n_1 Effect of surface irregularities	smooth minor moderate severe	0 0.003 0.008 0.015	none minor moderate severe, very severe	3.3 substrate diversity
n_2 Change in channel cross section	gradual alternating occasionally alternating frequently	0 0.003 0.0125	none, minor modest severe, very severe	4.4 width variance
n_3 Obstructions	negligible minor appreciable severe	0.002 0.01 0.025 0.045	none minor moderate severe, very severe, artifically elevated	2.5 flow diversity
n_4 Vegetation	small medium large very large	0.006 0.0175 0.0375 0.075	none grassland herbs, tall forbs cane brake	5.1 riparian vegetation
m_5 Meandering	minor appreciable severe	1 1.15 1.3	straight, prolate, poorly winding moderately winding meandering, severely winded	1.1 course developing

cross sections. As for medium and larger streams depth is not recorded in the river structure survey larger rivers are not considered at this stage.

Cross-section area and wetted perimeter for a trapezoidal profile with depth d, bottom width bw and surface width sw, are

$$A = \frac{sw + bw}{2} \cdot d \tag{2.26}$$

$$P = bw + 2 \cdot \sqrt{\left(\frac{sw - bw}{2}\right)^2 + d^2} \tag{2.27}$$

, respectively.

Resulting flow velocity estimates are compared to flow velocity values which are currently used and which depend on equation 2.22.

2.4 Exemplary GREAT-ER Scenarios

On the one hand substance concentrations in a river network are determined by substance load that reach surface water and by loss processes that affect this substance and on the other hand by characteristics of the surface water.

Discharge quantity directly controls surface water concentrations by dilution of substance loads. The differences in concentrations are thus reciprocal to discharge. When considering discharge distributions (instead of single average discharge values), the relation between discharge and concentrations might be more complex because different probabilities for different discharge values have to be taken into account. As the methodology for parameterising discharge distribution is developed anew and is based on completely different and often only recently available geodata and processing methods, no comparable river basins with an “old” parameterisation are available. Especially river network delineation and streamflow quantification were not based on consistent data and standardised methodologies. A direct comparison between simulation results in an “old” catchment and a “new” catchment thus turns out to be impossible.

In spite of this, two exemplary model runs are performed to illustrate the influence of streamflow parameterisation within GREAT-ER for both substances that enter rivers via point discharge only and that enter rivers diffusively. For a typical "down-the-drain" chemical emissions are discharged into surface water via waste water treatment plants. Assuming a more or less constant per-capita-consumption leading to a constant emission rate temporal variations of surface water concentrations can mainly be ascribed to streamflow variability. This is different for substances that enter surface water via runoff additionally. The attribution of a drainage area to each river segment’s outlet point allows for incoporation of site-specific watershed information (e. g. land use or runoff composition). If substance loads are determined by the composition of runoff into a fast and a delayed part, analysis of runoff separation might be beneficial to represent substance input into river networks in the GREAT-ER model.

Additional scenarios focus on the influence of hydromorphological river network parameterisation with respect to depth and flow velocity because substance removal by degradation and loss from the water phase (by volatilisation and net deposition) and also substance transport are influenced by hydromorphological conditions in the water bodies. By means of model simulations with GREAT-ER the effect of changes in flow velocity and river channel depth are analysed in detail. The former determines the water's residence time within a river segment and thus time which is available for degradation. Depth influences sedimentation, volatilisation and photodegradation since these are depth-dependent processes.

2.4.1 Point Discharges

Typical substances that reach surface waters mainly via waste water treatment plants are pharmaceuticals (Ternes *et al.*, 2004). During the last decade, pharmaceuticals and metabolites in river waters have been detected ubiquitously (e. g. (Ternes, 1998; Heberer, 2002). Among these substances the anti-inflammatory pharmaceutical diclofenac is one of those with a high prescription amount of 75 tonnes per year in Germany (Ternes, 1998).

Simulations are carried out in the Saale river basin. Emission assumptions base on the prescribed amount of 75 tonnes per year which is divided by a population of 82057000 inhabitants (DESTATIS, 2009). An average per-capita consumption of 0.914 g/(cap a) results. Approximately 15 % of the substance are excreted unmetabolised by humans (Ernesti, 2008). It is assumed that emissions take place from waste water treatment plants only. Further emission from e. g. hospitals or via surface wash-off from disposed sludge are neglected due to unavailable information. Physico-chemical parameters are mainly taken from the PHYSPROP database (see table 2.4) (Syracuse Research Corporation, 2009). Photodegradation is the only degradation type which is significant for diclofenac. An average degradation rate of 2.62 d^{-1} is assumed (Ernesti, 2008).

2.4.2 Non-point Discharges

A group of substances that enter surface waters not only via point discharges but also via runoff are metals. Beside potential background concentration from ore-containing bedrock and soils, many metals are both emitted from household wastewater, from industrial processes, from corrosion of metal materials, by atmospheric deposition, or by agriculturally use.

The metal nickel e. g. is used in multiple applications (see (Fuchs *et al.*, 2002)) and therefore a good example to demonstrate emission by various pathways in the GREAT-ER model. Apart from point emission sources like household and industrial waste water and abandoned mining, nickel is predominantly emitted from diffusive sources such as from groundwater, urban surfaces, eroded unpaved area or topsoil (Fuchs *et al.*, 2002). The amount of nickel (and also other metals) from urban stormwater runoff depends on the sewer system and if stormwater is either treated in a sewage treatment plant or drained untreated into surface waters at discharge points (Hüffmeyer, 2010). Not only in urban paved areas but also from unpaved area

Table 2.4: Chemico-physical parameters and emission assumptions for diclofenac

Parameter	**Value**	**Unit**	**Reference**
CAS	15307-86-5		(Syracuse Research Corporation, 2009)
Molar Mass	296.16	g/mol	(Syracuse Research Corporation, 2009)
$log(K_{OW})$	4.51		(Syracuse Research Corporation, 2009)
Vapour pressure	$8.19 \cdot 10^{-6}$	Pa	(Syracuse Research Corporation, 2009)
Water solubility	2.37	mg/L	(Syracuse Research Corporation, 2009)
Henry Coefficient	$4.73 \cdot 10^{-12}$	$\frac{Pa \cdot m^3}{mol}$	(Syracuse Research Corporation, 2009)
Domestic consumption	0.913999	$\frac{g}{cap \cdot a}$	calculated from (Ternes, 1998; DESTATIS, 2009)
Per-capita emission	0.1371	$\frac{g}{cap \cdot a}$	15 % of domestic consumption (Ernesti, 2008)
Photodegradation rate	0.109	$1/h$	(Ernesti, 2008)
WWTP removal	0.35		(Ernesti, 2008)

Table 2.5: Chemico-physical parameters and emission assumptions for LAS

Parameter	**Value**	**Unit**	**Reference**
CAS	68411-30-3		(HERA, 2009)
Molar Mass	342,4	g/mol	(HERA, 2009)
$log(K_{OW})$	3.32		(HERA, 2009)
K_{OC}	2500		(HERA, 2009)
Vapour pressure	$(3-17)\cdot 10^{-13}$	Pa	(HERA, 2009)
Water solubility	250	mg/L	(HERA, 2009)
Henry Coefficient	$6.35 \cdot 10^{-3}$	$\frac{Pa \cdot m^3}{mol}$	(HERA, 2009)
Domestic consumption	1.2	$\frac{g}{cap \cdot a}$	(Holt *et al.*, 1998; Price *et al.*, 2009)
Instream removal	0.06	$1/h$	(HERA, 2009)
WWTP removal Primary Activated Sludge Trickling filter	. 0 0.99 0.93 - 0.97		(Matthijs *et al.*, 1999)

nickel is washed off from the ground by surface runoff and erosion. By baseflow and interflow nickel from geogenic background is washed out from bedrock or soils and reaches surface water. In regions with elevated nickel ore deposits often abandoned mines exist that still emit mine water with elevated nickel concentrations. This also is the case in the Sieg river basin which is chosen for an exemplary GREAT-ER simulation. In the western part of the basin a settling pond (Grünewaldteich) discharges former mining water with considerable metal loads into the Sülz river (LUA, 2002). Emission assumptions and physico-chemical parameters are defined according to Fuchs et al. (2002).

2.4.3 Effect of Flow Velocity Parameterisation

An effect of flow velocity on substance concentrations is anticipated for substances which are degraded fast in-stream. The surfactant linear alkylbenzene sulphonate (LAS) which is primarily used as ingredient of household detergents is a typical example for fast degrading substances (HERA, 2009).

Physico-chemical parameters are taken from previous GREAT-ER simulations and from the HERA-Risk Assessment Report (HERA, 2009). They are summarised in table 2.5. For simulations the Main river basin is chosen because here data from different flow velocity parameterisations is available for the main river course (see chapter 2.3.3.2).

2.4.4 Effect of River Depth Parameterisation

For volatilisation, sedimentation and photodegradation river depth is a required parameter because in the GREAT-ER model these processes are described dependent on depth (Boeije & Koormann, 2003). If there is a difference in simulated concentrations when parameterising the river network with different depths, then it is anticipated to emerge for substances that underlie these processes in the river.

The substance diclofenac is degraded by photolysis and therefore used to analyse the effect of different depth parameterisations. In the Ruhr river basin, different depth parameterisations are available. On the one hand river depth values are calculated from discharge values as suggested by Round and Young (1998). On the other hand data from the river structure survey are used to parameterise river depths (see chapter 2.3.2.2). Scenario analyses are performed for these two versions of the Ruhr catchment. As river structure data does not contain information about depth variation with variations in discharge, deterministic simulations with mean values of the hydrological and hydromorphological parameters are run.

Chapter 3

Results

3.1 River Network Hydrology

Analyses of streamflow gauging data as described in chapter 2.3 provide information on streamflow variability which is used to parameterise hydrological characteristics of every river segment of a river network. Likewise analyses of river structure build up a toehold for a morphological parameterisation. Results from these analyses and emanated development of parameterisation strategies are presented in the following sections.

3.1.1 Streamflow Representation

Estimating streamflow distribution comprises analysis of gauged streamflow time series and development of a methodology to handle ungauged areas of a basin. Results from parameter estimation based on gauging data, goodness-of-fit assessment, comparison of estimated and observed flow duration curves, deriving mean discharge for every river segment by implementing a simple water balance model, and analysis of low flow to describe streamflow variability are presented with full details.

Parameter estimations. To test whether observed daily mean streamflow values follow a lognormal or a gamma distribution, distribution parameters μ and σ for lognormal or β and λ for gamma distribution are estimated first. From 500 bootstrapped samples maximum likelihood estimators are computed and averaged

Goodness-of-fit. For a first impression of accordance of streamflow data with a theoretical distribution function QQ-Plots are valuable. Figure 3.1 illustrates the comparison between quantiles derived directly from observed data and quantiles of the derived theoretical distribution functions at some of the analysed gauging stations. It is eye-catching that for larger percentiles the difference between observed and theoretical values is larger for the gamma distribution where observed values are remarkably higher. For the majority of the analysed gauging stations the 1-1 line between observed and theoretical quantiles is approximated at least for lognormal distribution. Exceptions can be found among gauging stations with a large drainage area. There some of the highest observed quantiles are considerably larger than theoretical ones.

A more objective picture on agreement with theoretical distribution functions can be drawn from statistical goodness-of-fit tests.

Results from X^2-tests - in spite of a graphical resemblance with a lognormal distribution - do not reveal accordance with either lognormal nor with gamma distribution. The picture is different when testing with the Kolmogorov-Smirnov test.

To not reject the null hypothesis p-values for the Kolmogorov-Smirnov test have to be higher than the significance level. For the X^2-test critical values are 3.94 and 4.87 at a significance level of 5 % and 10 % and 10 degrees of freedom, respectively (d'Agostino & Stephens, 1986).

For testing the lognormal distribution a workaround of testing the logarithm of observed streamflow values for normality is performed additionally because here critical values are known. Then for a sample of size 100 the critical value is 0.089 for $\alpha = 0.05$ and 0.103 for $\alpha = 0.01$.

The comparison between p-values for lognormal and gamma distribution tests reveals that the null hypothesis for compliance with a lognormal distribution is only rejected in one case with a significance level of 5 %, while the goodness-of-fit test for gamma distribution rejects its null hypothesis in 8 out of 38 cases. When increasing the significance level, which diminishes the probability of a type II error, the gamma distribution hypothesis is more often rejected than the lognormal distribution hypothesis. While at a 10 % significance level the hypothesis that streamflow follows a lognormal distribution still holds at 36 analysed gauging stations, the gamma-distribution-hypothesis is rejected in 18 out of 38 cases.

When testing the logarithms of recorded streamflow against the hypothesis of a normal distribution, the critical values are slightly higher than 0.089 for most gauging station, but are in accordance with the 1-percent significance level for more gauging stations.

The X^2 test yields very high values which claim for rejecting the null hypothesis for both lognormal and gamma distribution. The values from the test for the gamma distribution are roughly 2 to 9 orders of magnitude higher than values from the test for lognormal distribution or the normal distribution. For the Saale river basin X^2 test statistics are significantly higher than for Sieg and Ruhr.

These results hint at preferring the choice of a lognormal distribution to describe streamflow variability. In the following analysis are therefore carried out with the assumption that streamflow follows a lognormal distribution.

Flow duration curves. Cumulative distribution functions of streamflow data are equivalent to flow duration curves. For a comparison between observed flow duration curves and (by parameterisation of streamflow distribution) derived flow duration curves it is important to find out to what extent a conventional FDC differs from a mean annual FDC (cf. (Vogel & Fennessey, 1994)). At first sight the different flow duration curves are similar, especially in the middle part. However, for the low and the high flow part, differences between the curves can be observed. The discharge values that are exceeded most of the time are much lower when considering the whole period-of-record. For the flood values the flow duration curve for the complete period-of-record is as well higher than for the flow duration curve

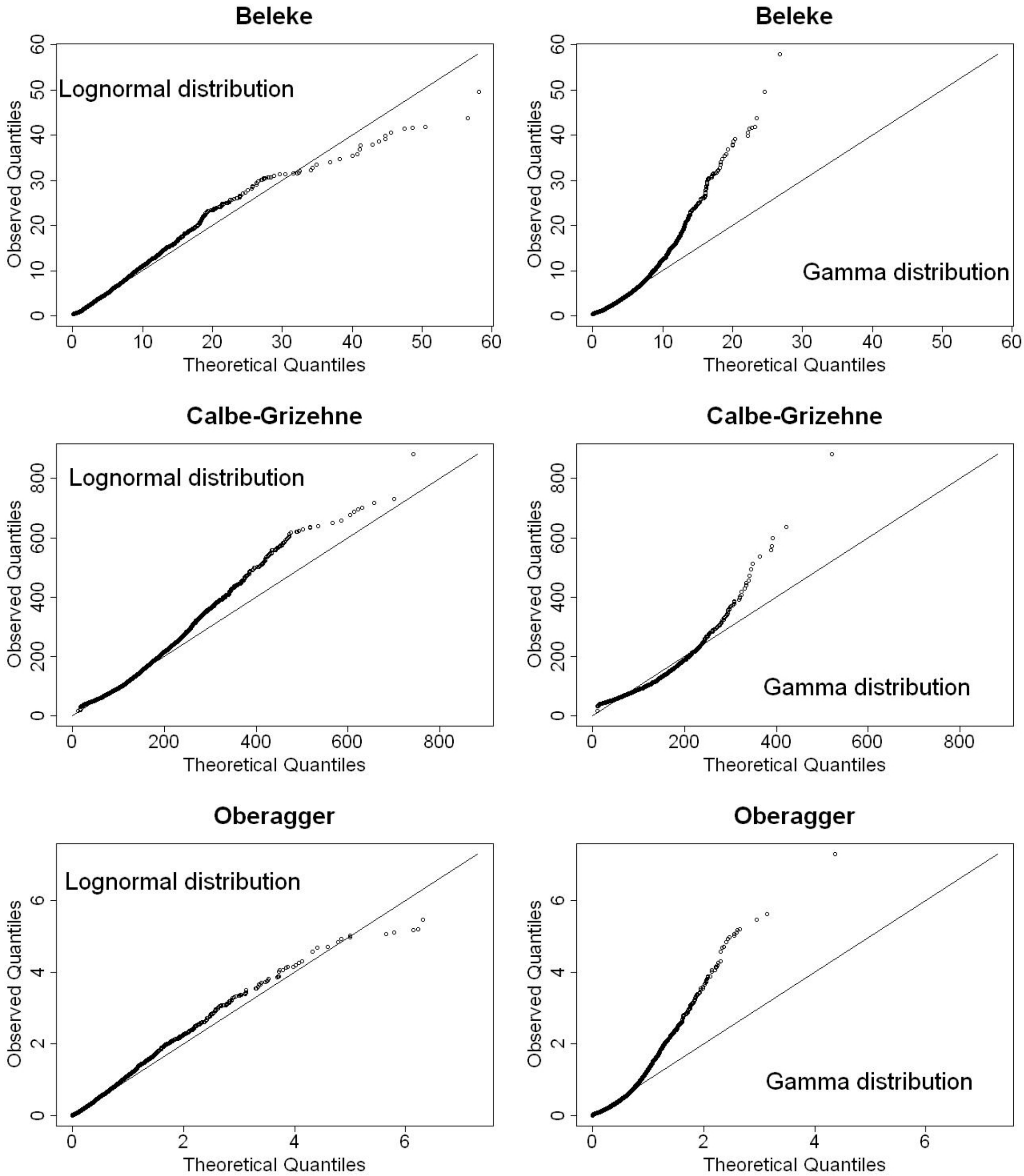

Figure 3.1: QQ-Plots for three different gauging stations: lognormal distributions (left) and gamma distributions (right)

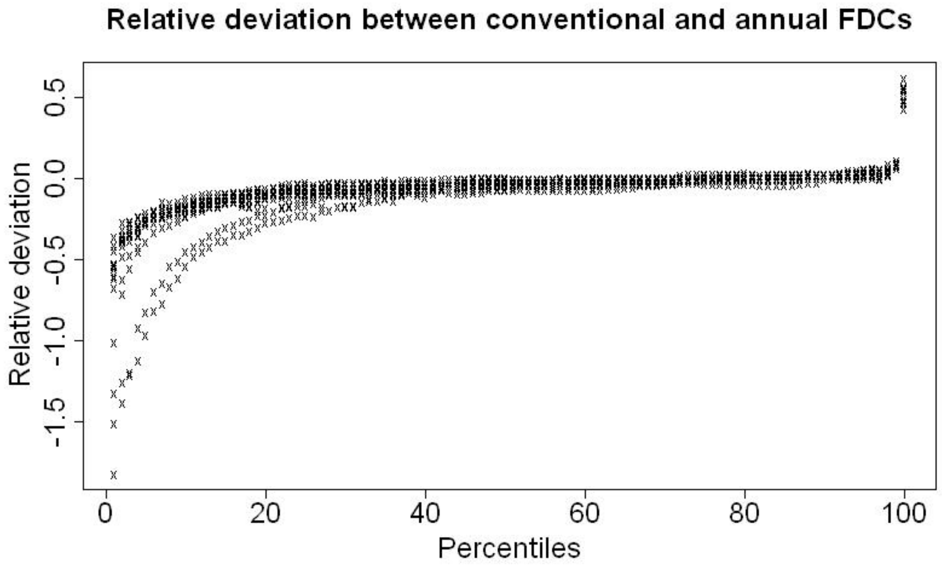

Figure 3.2: Relative deviations between conventional and annual FDCs for gauging stations in the Sieg river basin

of a typical year. Up to the 15-percentile those percentiles referring to entire time series deviate more than 10 % from percentiles that are calculated as mean values of annual percentiles at the analysed gauging stations on average. These relative deviations are displayed exemplarily for the Sieg river basin in figure 3.2.

A visual comparison between a theoretical lognormal distribution, which is parameterised by maximum likelihood estimators from observed streamflow data, and a flow duration curve constructed from empirical quantiles reveals that in general the form of the graphs resemble each other much, although there are some smaller differences especially for the higher percentiles. An analysis of the coefficient of determination r^2 yields very high values for both comparisons with conventional and mean annual FDCs. The lowest r^2-value occurs for gauging station Zöllnitz for comparisons with both types of FDC. For this gauging station also the visual comparison shows perceivable differences between the curves (see figure 3.3). Highest values can e. g. be found for gauging station Morsbach (Sieg) for the conventional FDC and for Mylau (Saale) for the mean annual FDC. These results are also mirrored in the graphical comparison (figure 3.3). The majority of r^2-values is above 0.99 for both conventional and mean annual FDCs.

To obtain information about statistical significance of the linear interrelation a Wilcoxon rank-sum test is performed. P-values are between 0.3 and approximately 1. In most cases p-values are higher when comparing mean annual FDCs to the theoretical probability distribution function.

Mean discharge. Results indicate that representing streamflow by a lognormal distribution is reasonable. The next step is to address the question if such a probability function can be parameterised for every point of the river network. Comparisons

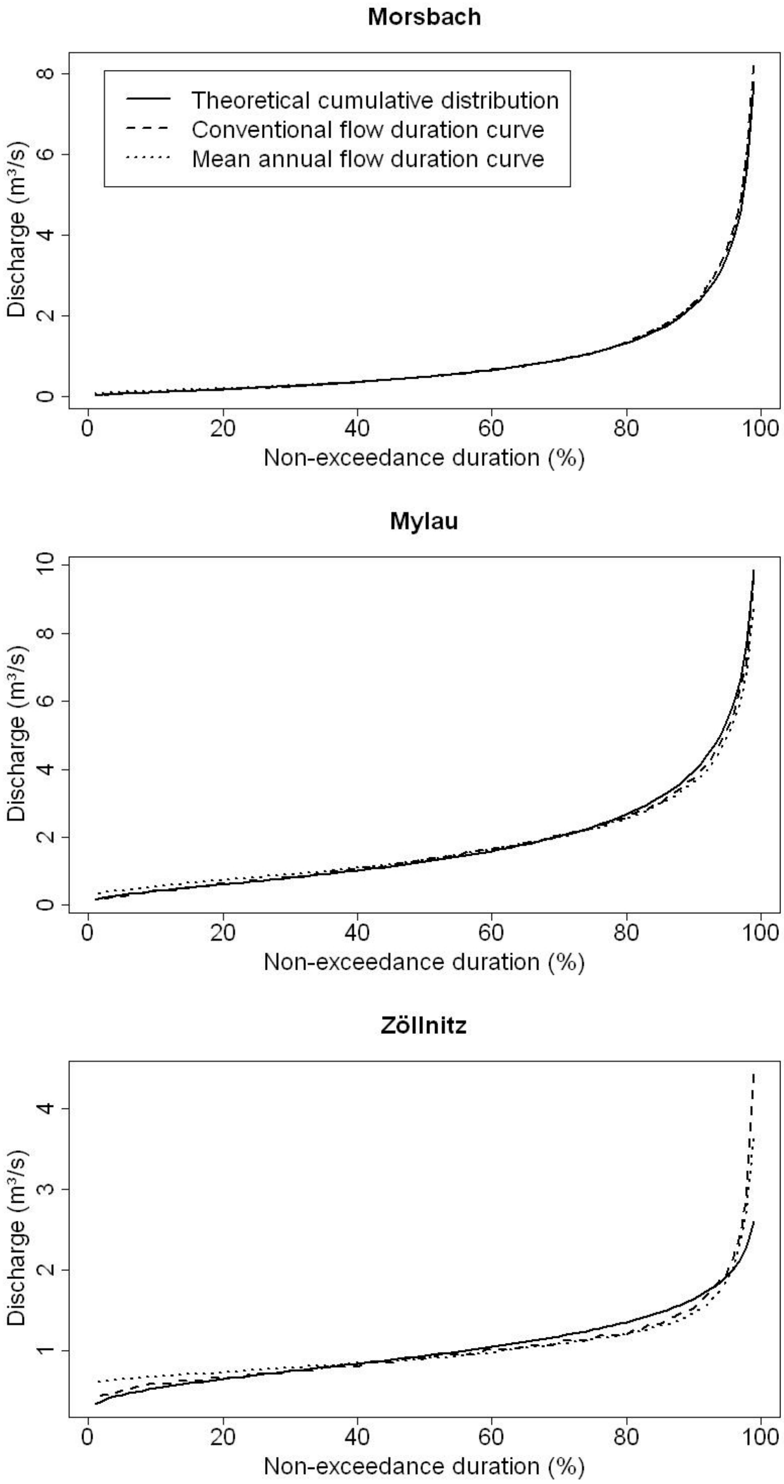

Figure 3.3: Flow duration curves for gauging station Zöllnitz (Saale), Morsbach (Sieg) and Mylau (Saale); conventional FDC (solid), annual FDC (dashed), and theoretical distribution (dashed)

between observed long-term mean discharge values and computed mean discharge values from the effective precipitation map yield the following results:

From 44 gauging stations for which daily mean discharge values for the period 1976 - 2005 are available and which are investigated in detail, calculated mean discharge at 18 stations differs less than 10 %, at 17 stations between 10 and 20 % and at the remaining 9 between 20 and approximately 50 %.

Long term mean discharge is one of the characteristic hydrological values which is also available for those gauging stations for which daily values for the reference period 1976 - 2005 are not available. An additional comparison with these stations provides a more complete picture of the goodness of the implemented simple water balance model to compute mean discharge on the basis of effective precipitation. Additionally to Sieg, Ruhr and Saale basins, such a comparison is carried out for Main river basin (see figures 3.4, 3.5, 3.6, and 3.7). Green polygons represent those areas where computed and observed mean discharge deviate less than 10 %, blue polygons denote overestimations by more than 10 % and yellow polygons indicate underestimation by more than 10 %.

Main. Mean discharge values derived from effective precipitation deviate less than 10 % from observed mean discharge in almost the whole Main river basin (see figure 3.4). Larger scale deviations only occur near the Main's mouth to the Rhine around Frankfurt, in the upper Nidda basin (gauging station Ilbenstadt), near the regulated Brombach reservoirs in the south of the basin and in the Pegnitz drainage area (gauging station Hohenstadt) in the eastern part of the basin. There are some smaller mostly headwater sub-basins where estimated discharge values are too low.

Ruhr. In the Ruhr river basin small deviations between observed and derived values can clearly be found along the Ruhr itself and along the Lenne river, except for their headwaters. In the sub-basins of Volme, Hönne and Möhne mean discharge values derived from HAD overestimate observed mean streamflow, whereas they are underestimated in the Wenne sub-basin (see figure 3.5).

Saale. In the Saale river basin a north-south gradient from under- to overestimation of mean discharge can be observed (see figure 3.6). In the sub-basin of the Bode river (gauging station Hadmersleben), which originates in the Harz mountain range, observed mean streamflow values are higher than those calculated on the basis of the hydrological atlas. In the lower course of the Saale river and its tributaries in the middle of the catchment deviations are small (less than 10 %), while in the southern part upstream of gauging station Naumburg-Grochlitz computed MQ-values are between 10 and approximately 30 % higher than the observed ones at gauging stations. Larger deviations can be found only in small headwater streams.

Sieg. The comparison between observed and derived mean discharge in the Sieg river basin is displayed in figure 3.7. Especially in the northern part of the catchment in tributaries Agger, Sülz and Bröl computed mean discharge deviates less than 10 % from gauging measurements, likewise in headwaters of the Sieg river itself, and in the Nister. In the lower course of the Sieg river, mean discharge is overestimated slightly more than 10 %. At the river's mouth mean discharge is overestimated by 11 % compared to gauging measurements at the station Menden 1. Larger deviations both upwards and downwards can be found in smaller headwater streams.

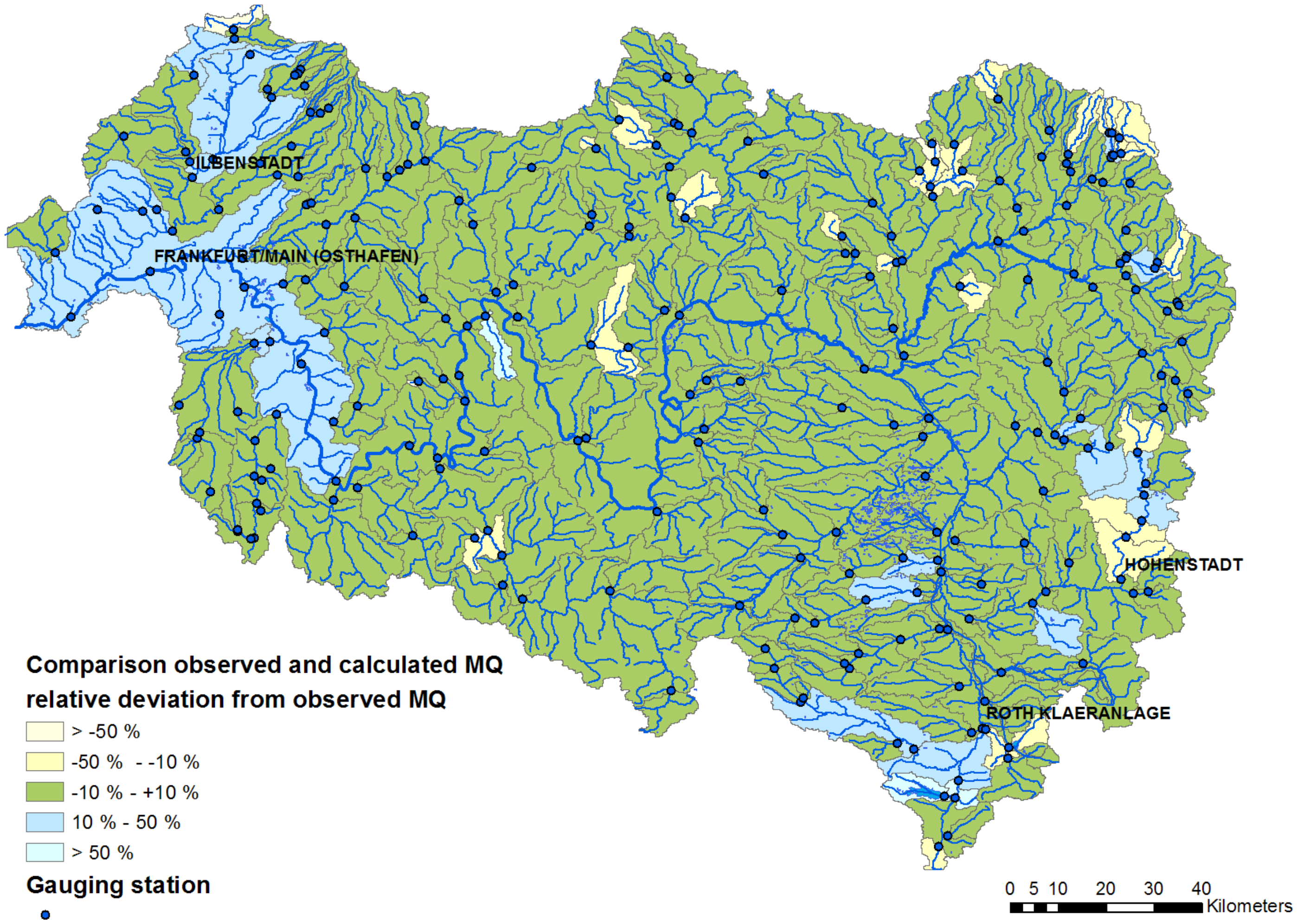

Figure 3.4: Comparison of observed and computed mean discharge values for gauged drainage areas in the Main river basin

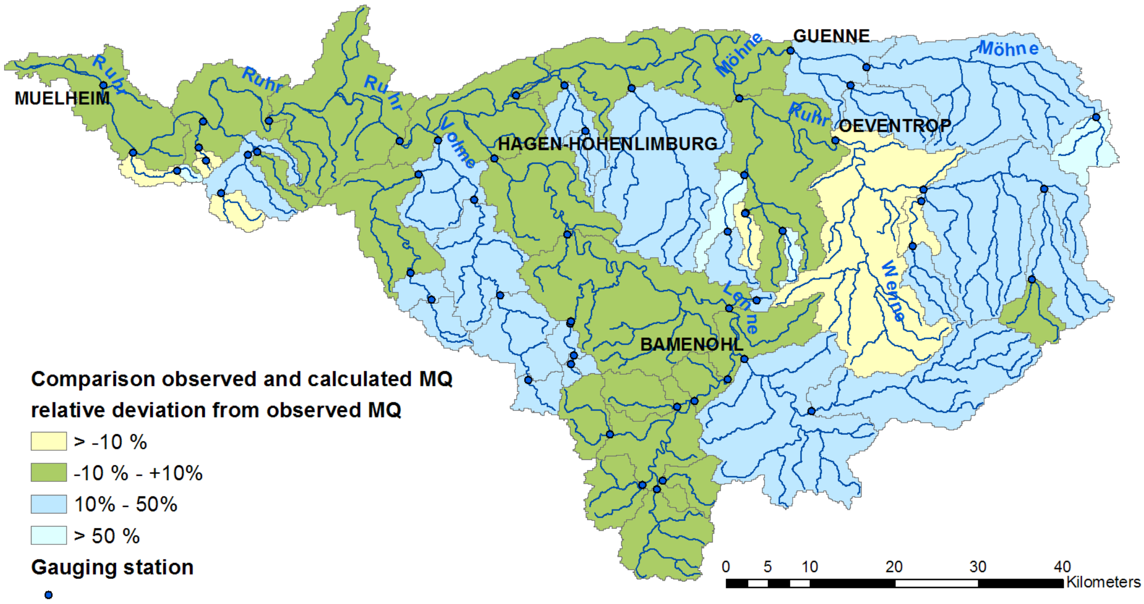

Figure 3.5: Comparison of observed and computed mean discharge values for gauged drainage areas in the Ruhr river basin

A direct comparison between observed and simulated mean discharge values can be seen in figure 3.8.

Streamflow variability. To parameterise streamflow variability, low flow is analysed in the four basins Main, Ruhr, Saale and Sieg by means of comparing observed and computed MAM(10)-values. Results are summarised in table 3.1. It includes characteristic values describing both inter-annual variability (minimum, maximum, variation coefficient) and the differences of average values of MAM(10) with respect to the data source (daily data from 1976 - 1989, daily data from the complete 30 year period-of-record and hydrological atlas).

A comparison of the average values of MAM(10) for the two different periods shows that the deviations are between 4 % and 46 %. Mean MAM(10)-values relating to the 14-year period are slightly higher except for 3 gauging stations.

The annual values of MAM(10) are not constant and in part they vary up to several m^3/s which can be seen at the minimum and maximum values. The interval between the lowest and the highest value of MAM(10) for the 14-year reference period covers - depending on the drainage area size - a range between 50 l/s and 60 m^3/s in the Saale basin. In the Ruhr and the Sieg basin the differences are smaller as the absolute values of MAM(10) are smaller, too. The intervals are higher for some gauging stations when considering the longer time-series due to a larger downwards deviation. The lowest value of MAM(10) differs in average 50 % (Ruhr), 44 % (Saale) and 63 % (Sieg) from the average value. The average upwards deviations are 65 %, 61% and 95 %, respectively. For the complete 30 year period-of-record both the intervals and the deviations are larger. Again the absolute deviations are largest in the larger river basins. The deviations downwards are 51 % (Ruhr), 70

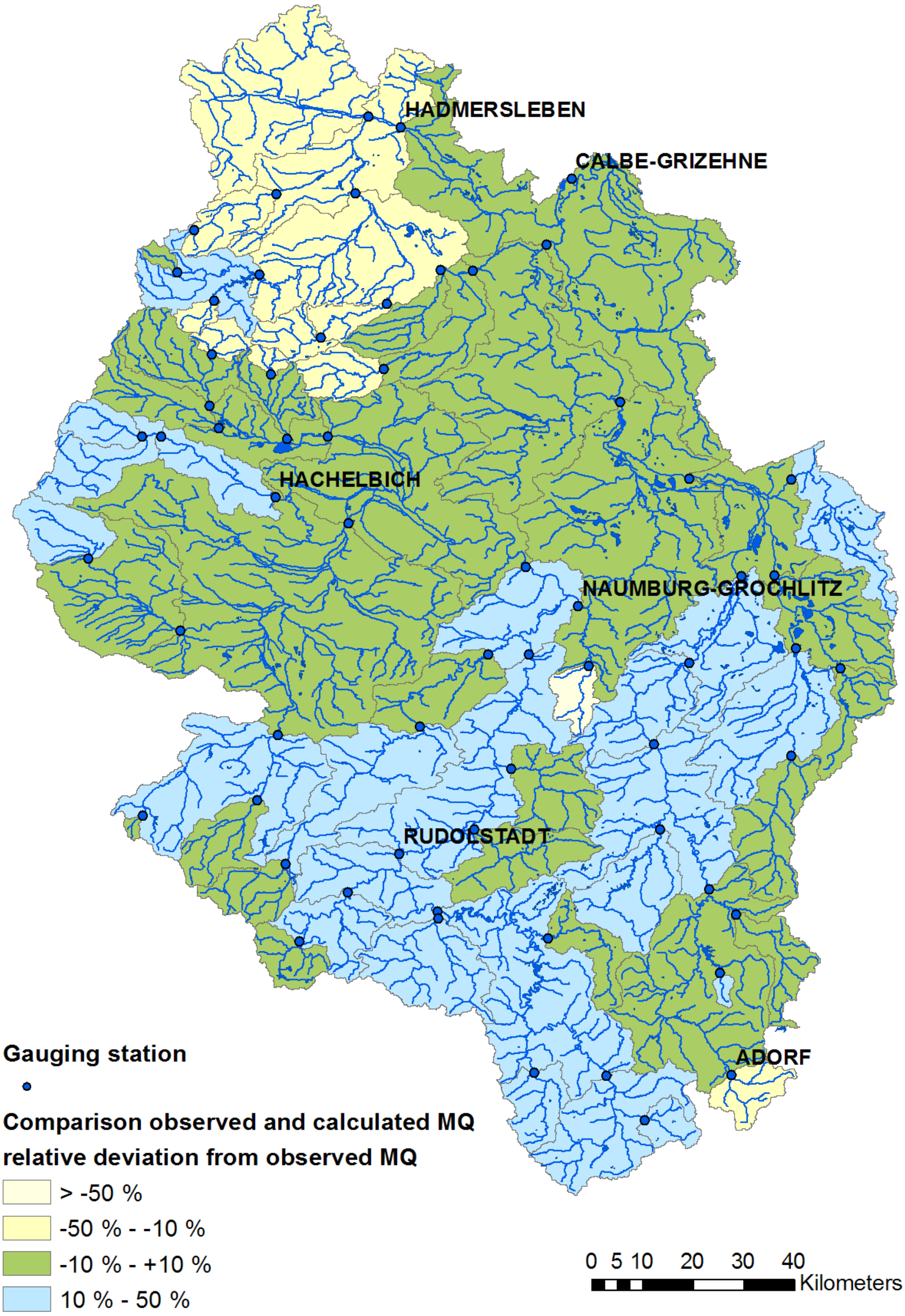

Figure 3.6: Comparison of observed and computed mean discharge values for gauged drainage areas in the Saale river basin

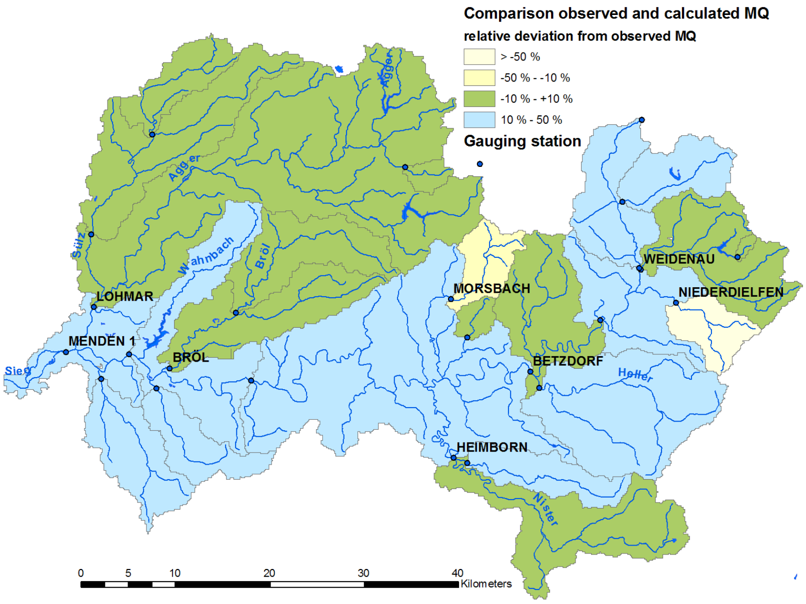

Figure 3.7: Comparison of observed and computed mean discharge values for gauged drainage areas in the Sieg river basin

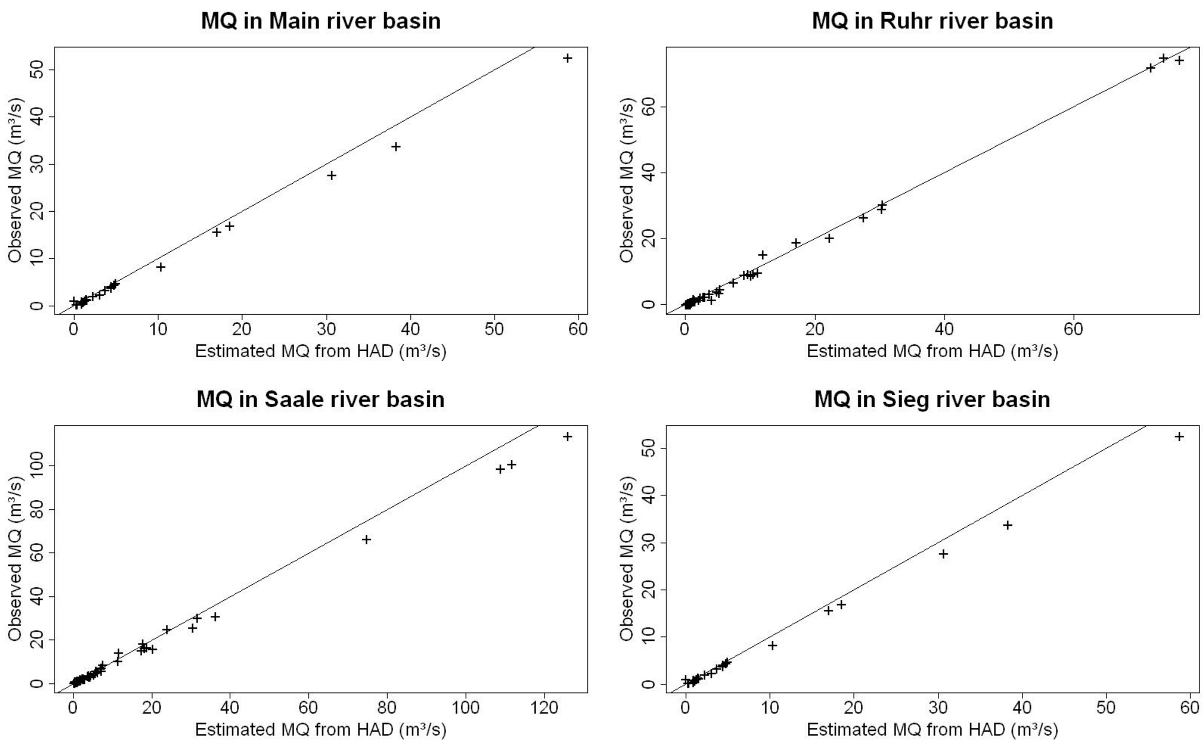

Figure 3.8: Comparison of observed and computed values for mean discharge plotted against each other

% (Saale), and 62 % (Sieg), whereas the deviations upwards are 87 %, 85 % and 127 %, respectively. The variation coefficients range from approximately 9 to 90 % within the 14 year reference period. Taking into account the longer time series variation coefficients are between 11 and 81 %. Average variation coefficients are 33 %, 34 % and 44 % in Ruhr, Saale and Sieg, respectively for the period from 1976 to 1989. For the longer periods the average variation coefficients approximately the same, viz. 34 %, 40 % and 44 %.

The variability in the Main river basin where the time series only cover ten years the variation coefficients are similar to those in the Saale and the Ruhr.

The comparison of average values of MAM(10) which are calculated from daily discharge data of years 1976 - 2005 on the one hand and of those that are based on the specific low flow discharge of drainage areas on the other hand shows differing results for the analysed river basins (figure 3.12).

Main. Gauging stations where the HAD overestimates values of MAM(10) have different drainage area sizes ranging from approximately 90 to 460 km^2. As only small and single gauging stations have been analysed, a spatial illustration of deviations is omitted. For the better part of the catchment no information is available.

A correlation analysis shows a significantly higher correlation between drainage area and low flow derived from the specific low flow discharge map (0.9) than between drainage area and the measured streamflow data (0.6).

Ruhr. A comparison between average MAM(10)-values shows good agreement (deviations of less than 25 %) along the Ruhr river and the Möhne river while the HAD underestimates MAM(10) in the southern part of the basin. In the drainage areas of gauging stations Stephansohl and Kickenbach, however, MAM(10) is overestimated. In all but 4 considered gauging drainage areas, however, derived values of MAM(10) lie within the range of observed MAM(10)-values from the period-of-record. At Altena and Roenkhausen estimated MAM(10)-values are lower than observed values. The magnitude of low flow strongly correlates to the drainage area size. The correlation is stronger for the values of MAM(10) based on the HAD (0.995) than for those based on observed gauging data.

Saale. In almost the whole river basin estimated MAM(10)-values deviate less than 25 % from average observed MAM(10)-values. Overestimation is observed most clearly at gauging stations Weida and Mylau. At 13 of 15 analysed gauging stations estimated low flow values lie within the range of annual MAM(10)-values. An analysis of the relative deviations of the map-based values from the average of annual MAM(10) values with respect to the drainage area size shows a decreasing deviation with increasing drainage size. This relation holds for both the longer and the shorter period-of-record.

Sieg. The picture in the Sieg river basin is similar to the comparison with mean discharge values. Good agreement can be found in the Agger sub-basin, while derived values overestimate observed values along the Sieg river itself. Deviations between observed and derived values of MAM(10) are on average 40 %. When comparing average MAM(10)-values from the 30-year period-of-record and the 14-year period-of-record to map-based values, respectively, comparisons with the longer period exhibit larger relative deviations. However, for most of the gauging stations the derived value lies within the range of observed MAM(10)-values. Inter-annual

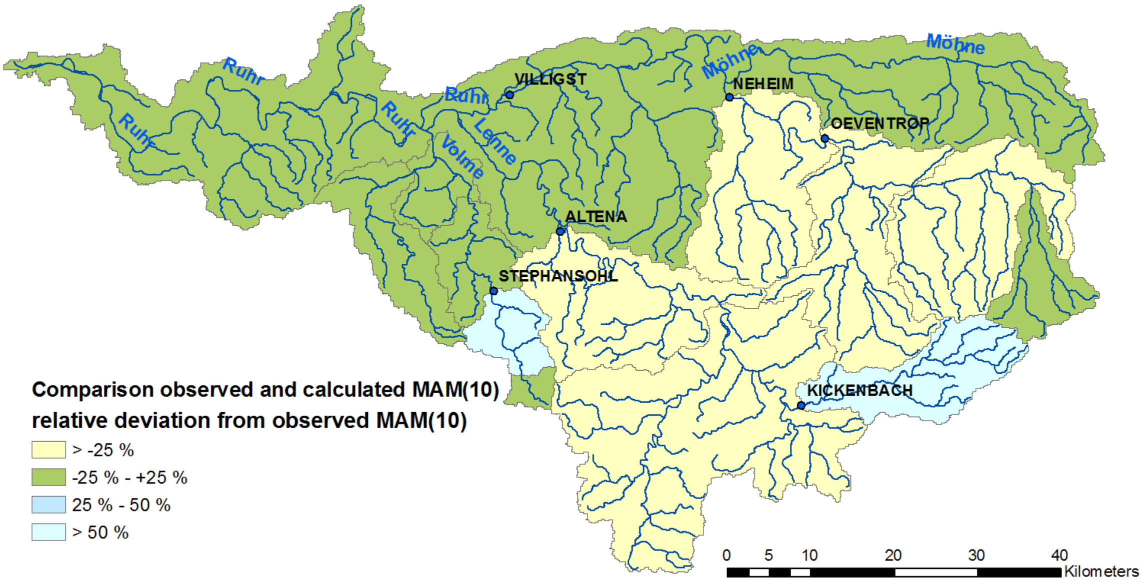

Figure 3.9: Comparison of observed and computed MAM(10)- values for gauged drainage areas in the Ruhr river basin

variability is larger than in the other basins.

The correlation between drainage area size and magnitude of low flow is comparable for both the observed values and the map-based values of MAM(10).

Similar to comparison between observed and computed mean discharges low flow discharges results are displayed as maps (figures 3.9 - 3.11) and plotted against each other (figure 3.12).

In order to use MAM(10) for parameterising the streamflow distribution, the standard deviation has to be derived from them, i. e. it has to be checked if there is some kind of regularity concerning which percentile MAM(10)-values correspond to. Therefore, at gauging stations derived MAM(10)-values (based on intersecting specific low flow discharge and drainage areas) are compared to theoretical lognormal distribution functions (based on parameter estimates from observed streamflow time series). Results can be found in table 3.1. Percentiles vary from 3 percentile up to 88 percentile at which 88 percentile is an outlier. Mean percentiles are 9, 18 and 17 for Ruhr, Saale and Sieg, respectively. Relating percentiles to drainage area size shows that with increasing drainage area the range of percentiles becomes smaller. The differences in lognormal probability distribution functions do not vary considerably when being derived from the 10th, 15th or 20th percentile, respectively. In general, deviation are larger for higher exceedance durations. Average discharge deviations are between approximately 30 m^3/s in small drainage areas and 8 m^3/s for large drainage areas.

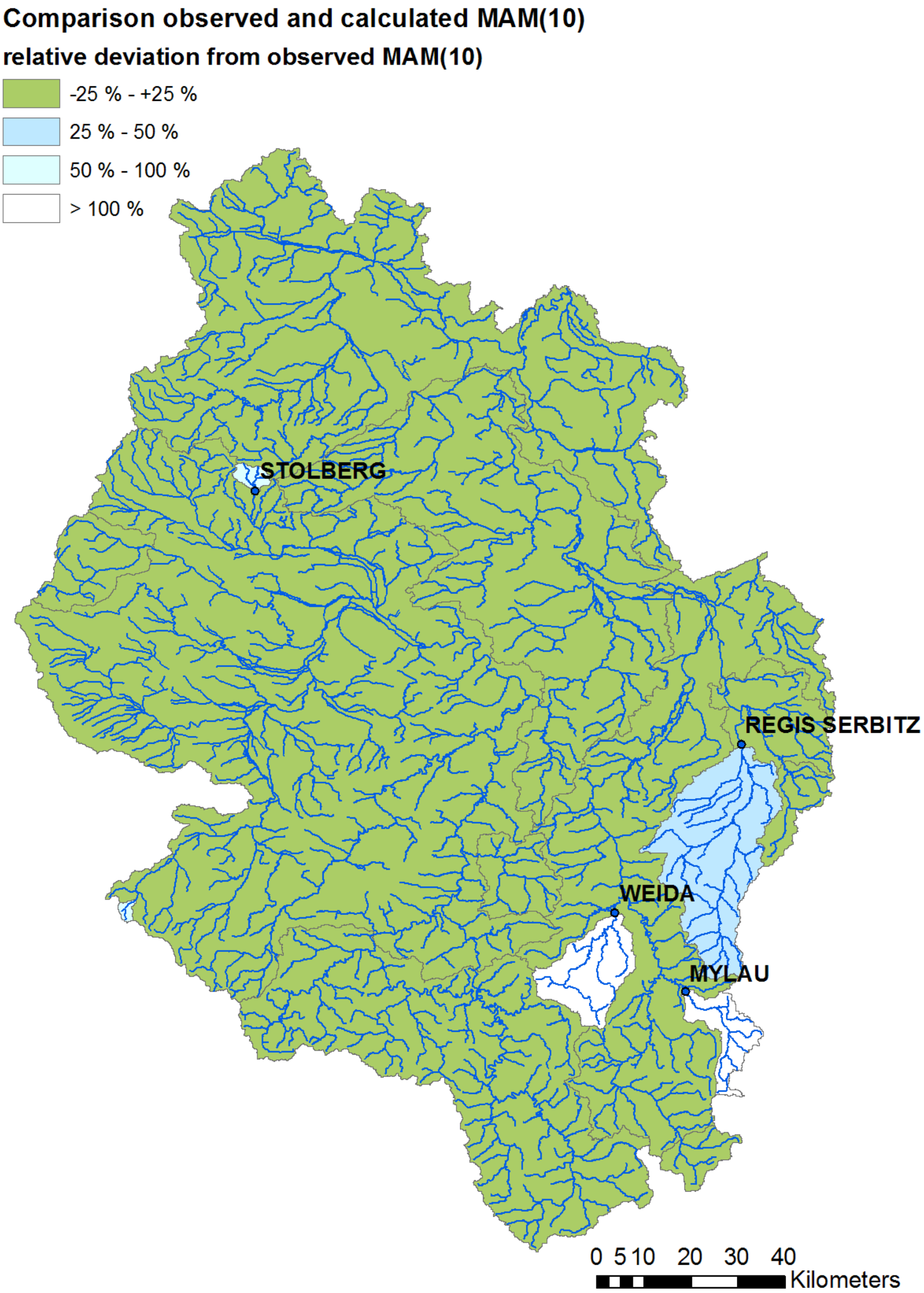

Figure 3.10: Comparison of observed and computed MAM(10)- values for gauged drainage areas in the Saale river basin

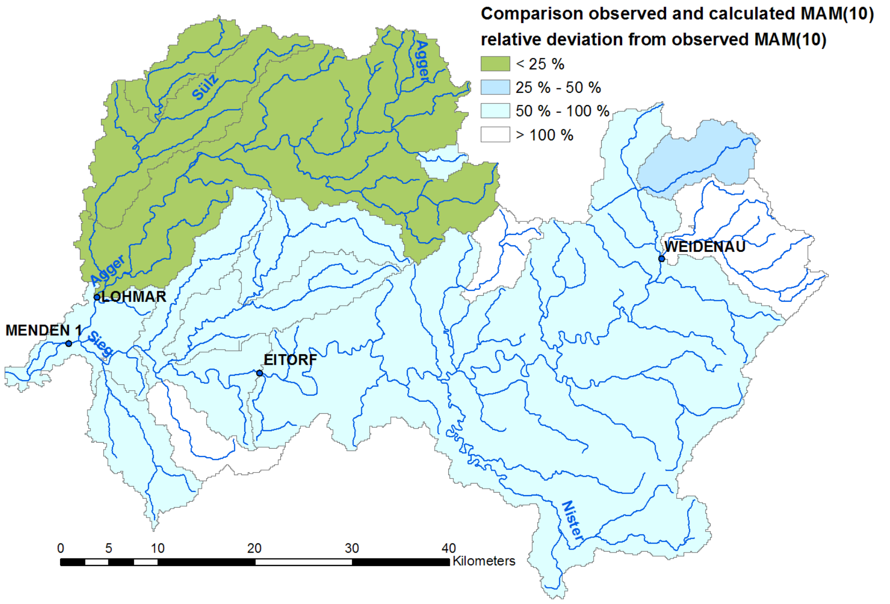

Figure 3.11: Comparison of observed and computed MAM(10)- values for gauged drainage areas in the Sieg river basin

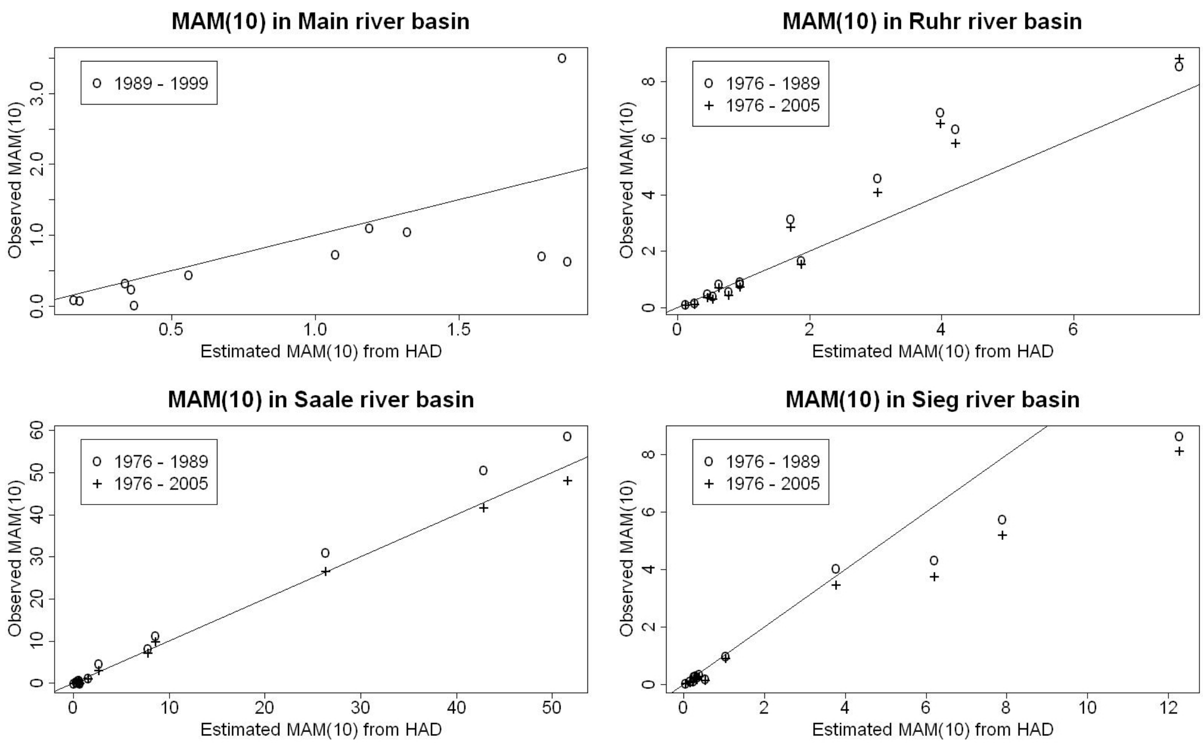

Figure 3.12: Observed and estimated values of MAM(10) plotted against each other

Table 3.1: Results from MAM(10) analysis

	Drainage area size (km^2)	1976 - 1989				1976 - 2005				Hydrological Altas	
		Average MAM(10)	Variation Coefficient	Min	Max	Average MAM(10)	Variation Coefficient	Min	Max	MAM(10)	Percentile
Altena	1190	8.44	0.16	5.41	10.35	8.06	0.15	5.04	10.35	5.33	2
Beleke 1	252	0.93	0.4	0.49	1.63	0.77	0.43	0.37	1.63	0.95	20
Hagen-Ambrock	197	0.87	0.31	0.45	1.3	0.77	0.32	0.4	1.3	0.95	10
Hagen-Eckesey	425	1.7	0.35	0.91	2.76	1.56	0.29	0.91	2.76	1.88	11
Hagen Haspe	156	0.85	0.34	0.48	1.47	0.73	0.33	0.41	1.47	0.63	4
Kickenbach	187	0.58	0.54	0.23	1.13	0.47	0.55	0.2	1.13	0.78	16
Kierspe	23	0.13	0.28	0.08	0.18	0.11	0.33	0.03	0.18	0.13	14
Meschede	426	3.16	0.2	1.86	4.47	2.88	0.2	1.86	4.47	1.72	1
Neheim	1045	6.34	0.2	4.44	8.25	5.85	0.2	3.39	8.25	4.21	2
Oeventrop	760	4.61	0.25	2.49	6.44	4.12	0.24	2.49	6.44	3.03	1
Olsberg	110	0.5	0.6	0.18	1.06	0.39	0.62	0.11	1.06	0.46	13
Roenkh.	884	6.94	0.09	5.73	8.02	6.54	0.11	4.51	8.02	3.98	3
Ruethen1	70	0.19	0.59	0.08	0.43	0.15	0.69	0.01	0.43	0.27	18
Stephansohl	96	0.43	0.33	0.23	0.73	0.35	0.38	0.15	0.73	0.54	20
Villigst	2013	8.58	0.28	4.85	13.56	8.87	0.2	4.85	13.56	7.6	5
Adorf	171	0.42	0.57	0.02	0.8	0.41	0.45	0.02	0.8	0.49	15
Bernburg	19660	50.68	0.22	31	69	41.86	0.31	18.1	69	42.85	7
Böhlen	1359	4.63	0.12	3.64	5.48	3.17	0.49	0.92	5.48	2.68	6
Calbe	23719	58.81	0.29	28.9	89	48.33	0.36	16	89	51.65	12
Mylau	155	0.25	0.74	0.07	0.63	0.28	0.59	0.07	0.63	0.6	22
Naumburg	11449	31.19	0.28	17.9	49.4	26.65	0.34	2.9	49.4	26.39	7
Oberthau	4939	11.37	0.18	8	15.8	9.98	0.24	5.12	15.8	8.55	

Results from MAM(10) analysis

	Drainage area size (km^2)	1976 - 1989				1976 - 2005				Hydrological Altas	
		Average MAM(10)	Variation Coefficient	Min	Max	Average MAM(10)	Variation Coefficient	Min	Max	MAM(10)	Percentile
Regis	769	1.21	0.3	0.73	1.88	1.13	0.31	0.5	1.88	1.56	13
Rudolstadt	2678	8.3	0.17	5.9	11.6	7.24	0.28	0.96	11.6	7.77	1
Stolberg	32	0.06	0.57	0.02	0.1	0.04	0.78	0.01	0.1	0.06	7
Streitwald	178	0.34	0.34	0.12	0.51	0.28	0.43	0.03	0.51	0.31	9
Tambach		0.03	0.46	0.01	0.06	0.03	0.42	0.01	0.06	0.66	
Weida	297	0.2	0.4	0.11	0.4	0.23	0.33	0.11	0.42	0.59	38
Wippersdorf	318	0.81	0.31	0.49	1.46	0.75	0.32	0.46	1.46	0.63	8
Zöllnitz	255	0.67	0.23	0.33	0.96	0.56	0.33	0.14	0.96	0.51	1
Broel	216	0.75	0.39	0.38	1.22	0.67	0.41	0.29	1.22	0.86	14
Broeleck	101.4	0.35	0.41	0.11	0.59	0.3	0.39	0.11	0.59	0.4	14
Eitorf	1468	4.34	0.38	1.83	8.38	3.77	0.37	1.83	8.38	6.21	19
Geisbach	48.9	0.12	0.45	0.04	0.23	0.1	0.42	0.04	0.23	0.24	38
Hoffnungst.	219	1	0.35	0.44	1.66	0.93	0.32	0.44	1.66	1.05	9
Hommerich	63.7	0.3	0.38	0.13	0.51	0.27	0.33	0.13	0.51	0.31	10
Kreuztal	63.4	0.27	0.24	0.16	0.43	0.22	0.35	0.06	0.43	0.26	12
Lohmar	785	4.05	0.26	2.07	5.88	3.47	0.28	2.07	5.88	3.78	9
Menden	2825	8.65	0.45	2.63	17.91	8.13	0.38	2.63	17.91	12.28	17
Morsbach	43.12	0.12	0.76	0.02	0.35	0.09	0.81	0.02	0.35	0.17	18
Niedersch.2	86.9	0.24	0.39	0.08	0.38	0.19	0.45	0.08	0.38	0.34	30
Oberagger	12.5	0.05	0.43	0.02	0.08	0.04	0.44	0.01	0.08	0.06	19
Siegburg-Kaldauen	1885	5.75	0.47	1.89	11.72	5.21	0.43	1.89	11.72	7.89	18
Weidenau	134	0.19	0.87	0.02	0.63	0.16	0.77	0.02	0.63	0.54	28

A comparison between estimated theoretical lognormal distributions which are parameterised by means of the maps of effective precipitation and specific low flow discharge and drainage areas on the one hand and lognormal distributions which have been used hitherto in GREAT-ER (cf. (Wissing, 2006)) is exemplarily drawn for some river segments shown in figure 3.13. In Ruhr and Saale distribution functions which base on the newly developed approach of taking MAM(10)-values as 11- or 18-percentile are steeper than the hitherto existing distribution functions. Differences are not pronounced. In the Sieg river basin the derived distribution functions are less skew. Their mode value is significantly larger.

3.1.2 Runoff Separation

To separate the fast and the slow runoff components and to derive base flow index (BFI) the two approaches by Gustard et al. (1992) and Demuth (1993) are compared. By means of mean flow total runoff volume at gauging stations can be computed, and as BFI denotes base flow fraction of total runoff base flow can be calculated. Table 3.2 shows computation results for the Gustard and the Demuth-methods, respectively. Base flow values from the Demuth method are significantly smaller (between 20 % and 60 %), which can be ascribed to differences in the approaches. Gustard's approach is based on MAM(5)-values whereas Demuth's method rests upon monthly minimum values. Comparing resulting base flow values to the gauging station's flow duration curves yields likewise smaller corresponding percentiles for the second method. While the method suggested by Gustard et al. (1992) yield base flow values that almost constantly correspond to approximately 50th percentile, Demuth's base flow values cover a larger range of corresponding percentiles. It is remarkable that there are no outliers for the percentiles corresponding to base flow discharges derived by Gustard's approach. For the stations Böhlen and Calbe base flow discharge derived by the Demuth-approach is lower than the 1-percentile of the corresponding discharge time series.

Average baseflow values are 0.73 (Gustard) and 0.46 (Demuth) for the Main, 0.61 and 0.35 for the Ruhr, 0.74 and 0.42 for the Saale and 0.56 and 0.31 for the Sieg river basin, respectively. Differences between BFIs within a catchment are small when BFI is derived by the Gustard-approach. Variation coefficients range from 0.06 to 0.13. When using the Demuth-approach derived BFI values within one catchment show larger differences. Here, variation coefficients are between 0.18 and 0.32.

Table 3.2: Base flow index (BFI) values derived by the method of Gustard et al. (1992) and Demuth (1993), average base flow discharges (BFQ) derived on basis of mean discharge and corresponding percentiles from a comparison with FDCs

	Gustard et al. (1992)			Demuth (1993)		
	BFI	BFQ	Percentile	BFI	BFQ	Percentile
Ansbach	0.67	0.47	54	0.39	0.27	21
Bad Berneck Ölschnitz	0.76	1.14	53	0.49	0.74	30
Bayreuth	0.69	2.07	54	0.37	1.12	21

Base flow index (BFI) values derived by the method of Gustard *et al.* (1992) and Demuth (1993), average base flow discharges (BFQ) derived on basis of mean discharge and corresponding percentiles from a comparison with FDCs

	Gustard et al. (1992)			Demuth (1993)		
	BFI	BFQ	Percentile	BFI	BFQ	Percentile
Berneck Weisser Main	0.74	0.75	51	0.49	0.49	25
Friedberg	0.64	0.67	56	0.34	0.36	23
Geldersheim	0.77	0.20	56	0.46	0.12	34
Groß Biberau 2	0.75	0.23	54	0.47	0.14	27
Harreshausen	0.73	1.95	51	0.46	1.23	27
Hohenstadt	0.92	4.53	54	0.80	3.96	30
Niederflorstadt	0.7	1.90	56	0.42	1.13	26
Sachsenheim	0.87	2.11	56	0.64	1.54	38
Steinberg	0.56	0.23	55	0.20	0.08	28
Weilbach	0.69	2.28	56	0.42	1.39	25
Altena	0.65	16.91	54	0.38	9.76	18
Beleke1	0.65	2.29	51	0.36	1.28	27
Glinge	0.53	57.65	49	0.27	29.25	24
Hagen Ambrock	0.55	2.65	51	0.31	1.51	25
Hagen-Eckesey	0.58	5.29	50	0.30	2.75	21
Hagen-Haspe	0.64	2.20	51	0.45	1.56	32
Kickenbach	0.56	2.30	50	0.35	1.42	31
Kierspe	0.51	0.34	50	0.28	0.19	25
Meschede	0.69	6.27	51	0.45	4.12	23
Mueschede	0.73	2.49	47	0.38	1.31	11
Neheim	0.66	12.69	51	0.46	8.77	29
Oeventrop	0.64	9.60	51	0.38	5.65	18
Olsberg	0.61	1.53	53	0.32	0.8	27
Roenkhausen	0.64	13.17	52	0.33	6.72	9
Ruethen1	0.62	0.71	49	0.31	0.35	22
Stephansohl	0.52	1.23	51	0.26	0.61	22
Villigst	0.65	18.73	51	0.39	11.35	21
Adorf	0.76	1.26	52	0.36	0.6	14
Bernburg	0.87	91.32	56	0.48	50.25	3
Bohlen	0.83	6.13	52	0.37	2.7	
Calbe	0.85	98.52	55	0.40	46.67	
Mylau	0.66	1.25	48	0.44	0.84	28
Naumburg	0.85	57.32	54	0.44	29.63	2
Oberthau	0.79	20.76	54	0.52	13.77	13
Regis	0.75	2.66	47	0.57	2.01	23
Rudolstadt	0.78	20.35	51	0.49	12.83	13
Stolberg	0.65	0.28	51	0.37	0.16	28
Streitwald	0.68	0.60	51	0.39	0.34	4
Tambach	0.57	0.17	47	0.33	0.1	27
Weida	0.57	1.00	52	0.19	0.34	12

Base flow index (BFI) values derived by the method of Gustard *et al.* (1992) and Demuth (1993), average base flow discharges (BFQ) derived on basis of mean discharge and corresponding percentiles from a comparison with FDCs

	Gustard et al. (1992)			Demuth (1993)		
	BFI	BFQ	Percentile	BFI	BFQ	Percentile
Wipperdorf	0.73	1.65	53	0.36	0.82	12
Zöllnitz	0.83	1.09	46	0.62	0.81	11
Bröl	0.57	2.38	50	0.25	1.04	16
Bröleck	0.54	1.16	52	0.26	0.56	22
Eitorf	0.56	15.91	50	0.27	7.64	23
Geisbach	0.56	0.32	49	0.35	0.2	29
Hoffnungsthal	0.59	2.87	50	0.31	1.5	21
Hommerich	0.59	0.85	49	0.31	0.44	19
Kreuztal	0.54	0.73	51	0.30	0.4	26
Lohmar	0.62	10.53	49	0.36	6.15	23
Menden	0.59	31.25	51	0.28	14.94	21
Morsbach	0.52	0.55	50	0.39	0.41	40
Niederpleis	0.61	0.52	49	0.44	0.37	32
Oberagger	0.51	0.18	49	0.20	0.07	17
Siegburg-Kaldauen	0.58	19.77	51	0.32	10.88	26
Weidenau	0.52	1.28	51	0.24	0.6	28

3.1.3 River Depth Parameterisation

It is questionable if equation 2.13 which derives depth values from discharge is appropriate for all river segments in current GREAT-ER river basins. The North Rhine-Westphalian river structure survey provides recorded actual depth values. They are analysed and compared to the current GREAT-ER parameterisation in order to find an adequate description of river bed depth.

Analysing variability of depth from river structure data shows that it is rather small. Data from the river structure survey is available for approximately 1645 km of flow length in the Ruhr river basin. 1455 km belong to small and medium rivers, i. e. water depth has been surveyed. Lengths of river segments belonging to this group for which depth values do not vary within one segment sum up to 638 km. For another 783 km standard deviation is less than 0.5 m. Only for a few segments river depth varies more. Locations of sites where the variation coefficient is larger than 50 % are illustrated in figure 3.14. A spatial pattern of higher variability cannot be identified.

The comparison of river bed depths in the Ruhr river basin shows that depth derived by equation 2.13 are higher by trend. Figure 3.15 plots river bed depth derived from river structure survey against depth derived by the regression approach in dependency with discharge. From 970 pairs of variates 477 lies within the range of factor 2 around exact compliance. For the majority of 499 pairs, however, estimated river depths are larger than 2 times the surveyed river depths. Only for 4 river segments the power relation between discharge and depth from Young and Round

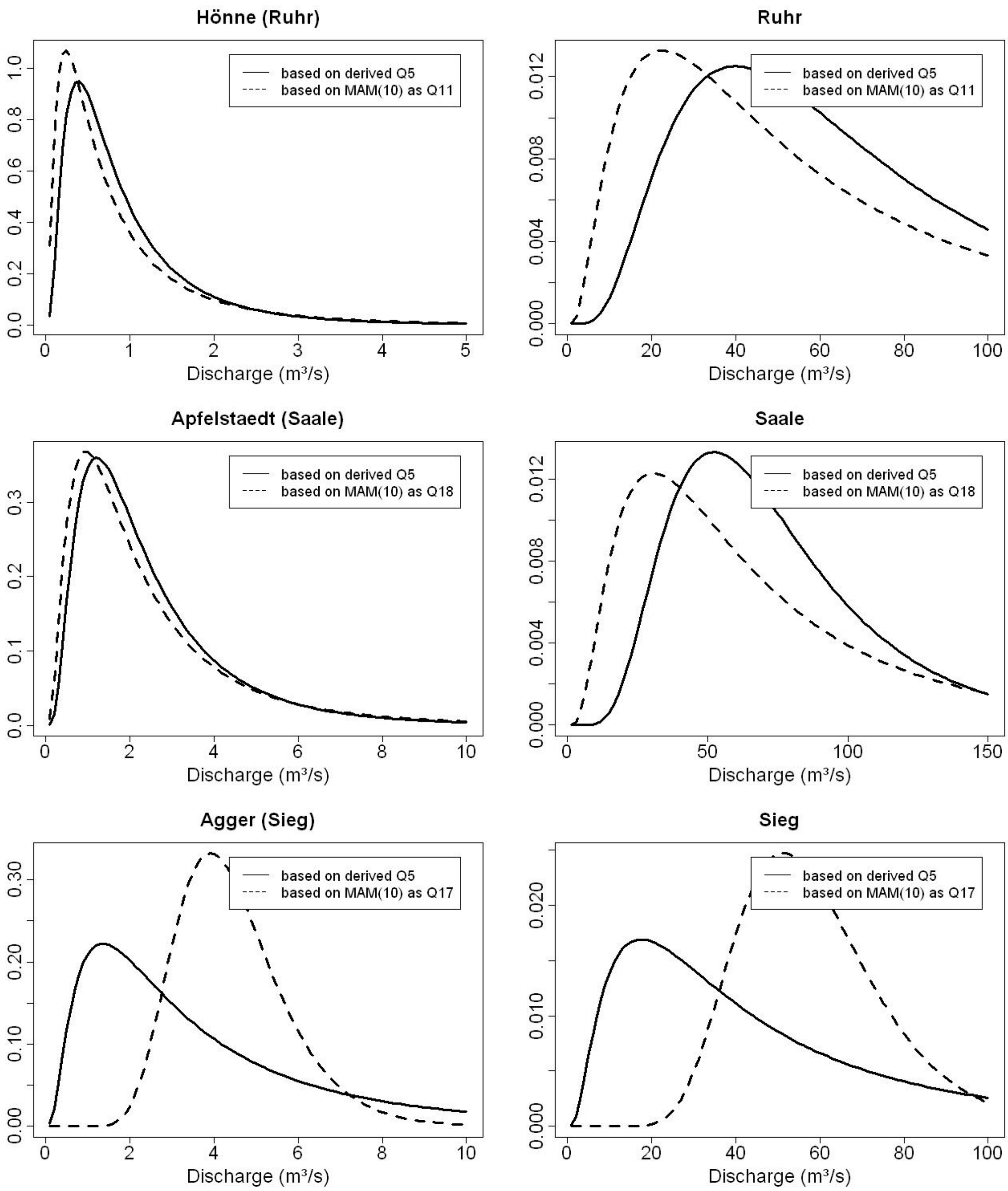

Figure 3.13: Exemplary comparisons of "former" (solid lines) and "new" (dashed lines) streamflow distribution

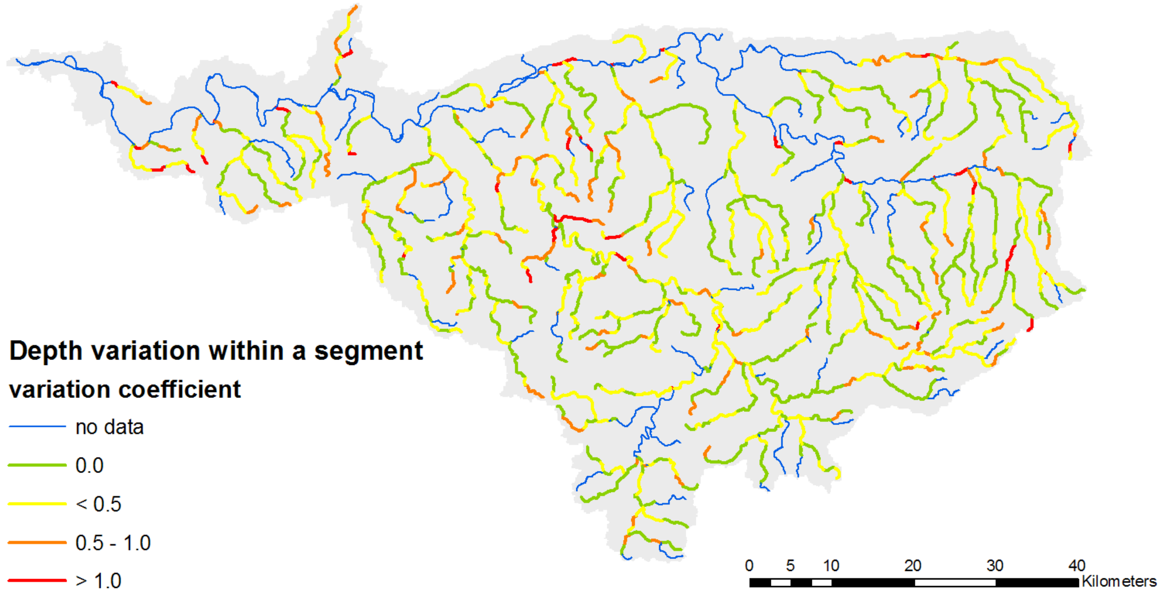

Figure 3.14: Variation of depth values from the river structure survey in the Ruhr river basin within one GREAT-ER river segment (variation coefficient)

yields smaller depth than surveyed in river structure data. A spatial analysis of deviations shows no regular pattern. Coherence between deviations and river size cannot be observed.

The Lenne river is one of the largest rivers for which river structure data contents information on depth. Its depth profile is illustrated in figure 3.16. Depth values derived from equation 2.13 are significantly larger compared to those depth recorded within the scope of river structure survey. Except for some peaks the latter reports depth which are approximately half as deep as the hitherto used values.

As river structure data might not be of avail for every river basin a secondary approach to derive depth has been developed. It is based on stage-discharge relationsships.

Stage-Discharge curves sometimes hint at very unambiguous relations and sometimes resemble point clouds. The latter are especially stations with rather small drainage areas. Power transformations of stage actually yield approximately linear relationships to discharge (cf. (Gawne & Simonovic, 1994). Optimal power values are listed in table 3.3. Also intercept and slope of the optimal regression are itemised. From these values zero-flow stage is derived. A negative zero-flow stage means that the gauge datum is above the river ground while a positive zero-flow stage indicates that the gauge datum lies below the river ground.

Most of the exponents lie between 2 and 3. The average exponent is 2.4. Zero-flow stages are except for some outliers very small (below 0.1 m). The regression equations, however, differ considerably. Slopes range from 2 to 50.

From the optimal exponent, regression coefficients, zero-flow stage and mean discharge stage and depth are derived. A comparison between these depth values

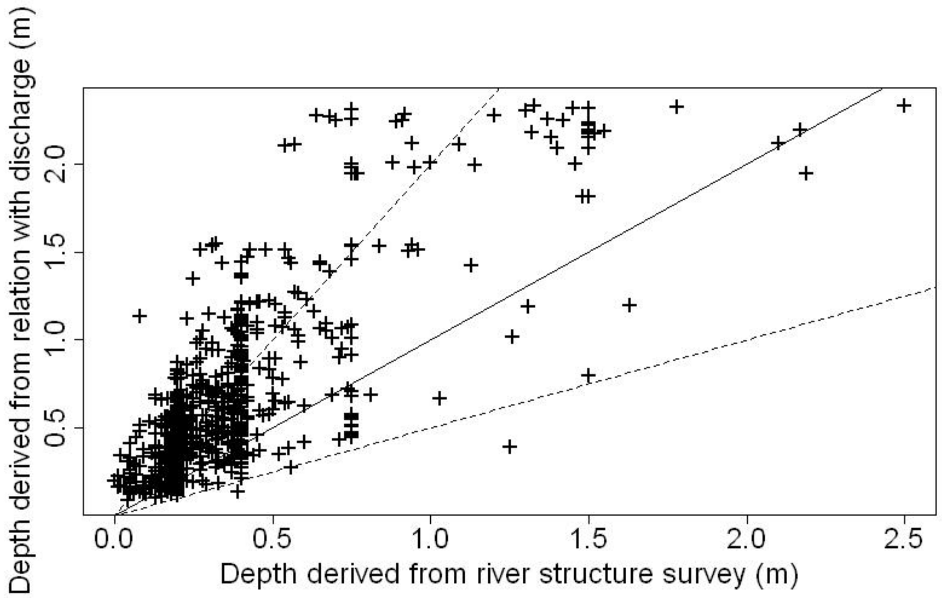

Figure 3.15: Comparison of average river depth values from two different approaches in the Ruhr river basin: the hitherto used approach based on a power relation with discharge (Round & Young (1997)) (y-axis) and aggregated values from the river structure survey (x-axis)

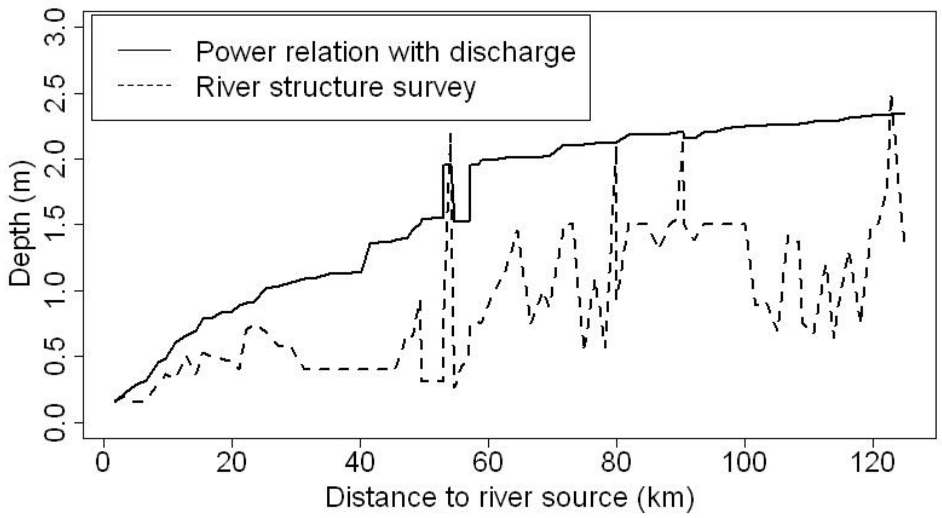

Figure 3.16: Comparison of depth profiles for the Lenne river: Depth values derived by equation 213 (solid line) and derived by river structure survey data (dashed line)

Table 3.3: Linear relationships between discharge and transformed stage

	TE	Intercept	Slope	Zero-flow stage
Ahausen	2.35	1.477	3.136	-0.2006
Amecke	2.15	-0.097	8.486	0.0055
Attendorn	1.8	-0.311	12.843	0.0134
Bahmenohl	2.85	-3.584	5.111	0.2458
Börlinghausen	2.25	-0.394	7.462	0.0232
Brilon	2.05	-0.014	5.102	0.001
Endorf	1.75	-0.113	6.832	0.0092
Fürwigge	2.45	0.004	12.327	0
Günne	2.75	0.159	2.034	-0.0287
Hagen-Hohenlimburg	1.5	-2.862	50.526	0.0377
Hattingen	2.1	8.291	11.323	-0.3487
Hüppchenhammer	2.1	0.037	10.247	-0.0019
Kraghammer	2.45	-0.024	11.363	0.0007
Langscheid	3.4	-0.198	2.357	0.0249
Meschede 2	2.15	-0.125	2.957	0.0204
Möhnesee-Neuhaus	3.2	-0.091	6.657	0.0042
Neue Mühle 2	2.65	-0.050	5.830	0.0032
Nichtinghausen	2.3	-0.022	12.060	0.0007
Nieder-Buschhausen	2	0.0270	6.658	-0.0023
Olpe	2.2	-0.645	6.060	0.0488
Remblinghausen 2	3.2	-0.009	4.303	0.0007
Rüblinghausen	2.2	-0.220	12.726	0.0079
Seidfeld 3	1.8	0.005	3.196	-0.0017
Siedlinghausen 2	3.05	-0.022	4.611	0.0014
Sundern	1.65	-0.028	4.354	0.0042
Treckinghausen 1	3.45	-0.084	2.661	0.0087
Voellinghausen	2.3	-2.759	8.301	0.1446
Walkmühle	3.45	0.083	2.219	-0.0104
Wetter	1.75	-43.349	28.583	0.8667

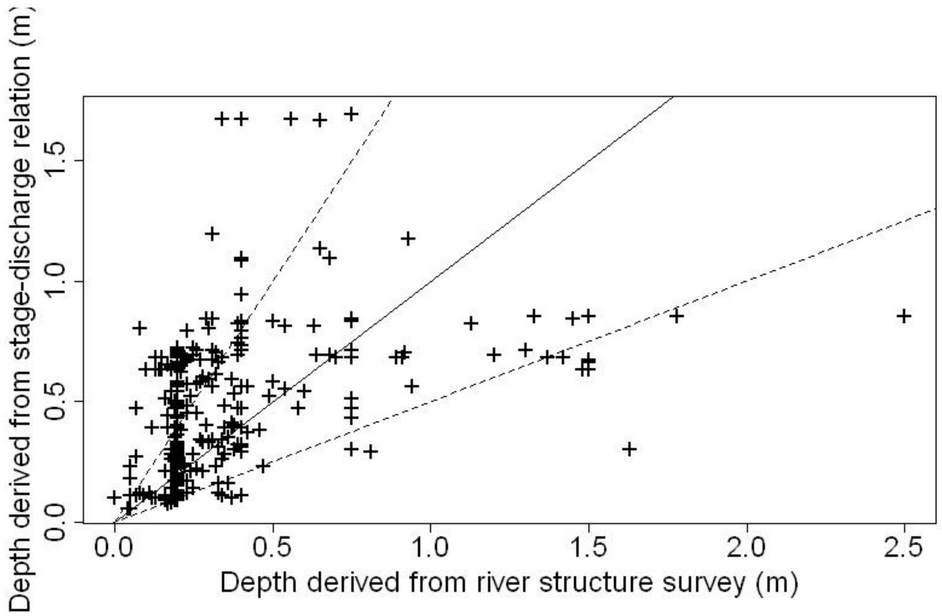

Figure 3.17: Comparison of average river depth values from two different approaches in the Ruhr river basin: stage-discharge relationship (y-axis) and aggregated values from the river structure survey (x-axis)

and river depth data from the river structure survey can be carried out for those gauge drainage areas for which stage-discharge relations are available. Figure 3.17 shows such a comparison. The majority of depth value pairs deviates less than factor 2 from each other. Maximum depth values from stage-discharge relations are much lower than those from the IH-regression approach.

As depth derived from stage-discharge relations only is available for smaller sub-basins, a spatial comparison of the two values for river depth (from river structure survey and from stage-discharge-relation) can only covers smaller parts of the Ruhr river basin. Clusters of river segments where the stage-discharge-relation depth deviate more than factor 2 from depth surveyed occur in the north-western part of the catchment in the Möhne River sub-basin and in headwaters of the Lenne river in the south-western part.

3.1.4 Flow Velocity Estimation

An analysis of the impact of different flow velocity parameterisations on substance concentrations in surface waters is exemplarily carried out at selected river sections of the Main river. The intention is to identify those combinations of flow velocity differences and substances half-lifes for which significant differences in estimated concentrations occur.

Similar to river depth parameterisation river structure data is used to derive flow velocity values. Results based on the Manning-Strickler approach are presented.

3.1.4.1 Investigation of Flow Velocity Differences

Flow velocity profiles for velocity values from the ATV model and derived flow velocities from equation 2.22 are shown in figure 3.18. Velocity values from the ATV model oscillate in all river sections except for the Wern, but also there a larger variability than for the calculated velocity values can be observed.

For the Red Main, the Pegnitz and the Rednitz derived flow velocities seem to represent an average ATV velocity. For the Regnitz, the Wern and the Main derived velocities are larger than average ATV velocities. For the Main river, e. g. derived values are to average 140 % of ATV velocities. At some locations velocities are estimated lower with the regression, namely at the locations of water gates where the river cross section abruptly changes. In figure 3.18 locations of water gates are additionally plotted. Behind each water gate the velocity gradually increases towards the next water gate.

Near river kilometre 300 the Main is canalised.The canalised section is recognisable in the velocity profile. Embankments regulate discharge within the canal. Both approaches predict almost constant flow velocity. However, the ATV model velocity is again lower than the velocities derived from discharge.

For the other rivers partly artificial structures but also natural river structure might cause velocity deviations. In the following only velocity differences observed in the Main river itself are considered.

Effect of flow velocity on degradation. The theoretical considerations on the relation between flow velocity and remaining load after a given river length for different half-lives lead to some qualitative conclusions:

- The faster water flows the more load is left at the end of the segment.
- The lower half-life is the lower is the remaining load.
- The graphs showing the relation between flow velocity and remaining load first have a gradient of more than 1 and with increasing velocity the gradient decreases, i.e. for lower velocities the fraction of remaining load shows larger differences for different flow velocities and for higher flow velocities the differences become less.
- In front of this "inflexion point" the increase of remaining load is steeper with increasing velocity for higher half-lives.
- Behind the "inflexion point" the increase in remaining load is flatter with increasing flow velocity for higher half-lives.
- For very high flow velocities the percentage of remaining load converges to 100 % for all half-lives.

Figure 3.19 illustrates this relation quantitatively. Owing to the short length of 2 kilometres and the corresponding small residence time, only a few percent of the substances are eliminated. For substances with a half-life of more than 12 hours the percentage of load left at the segment's end is above 90 % for flow velocities of more than 0.4 m/s. Only substances degrading rapidly (represented by a substance with half-life of 1 hour) are eliminated to a substantial extend within such a short river section.

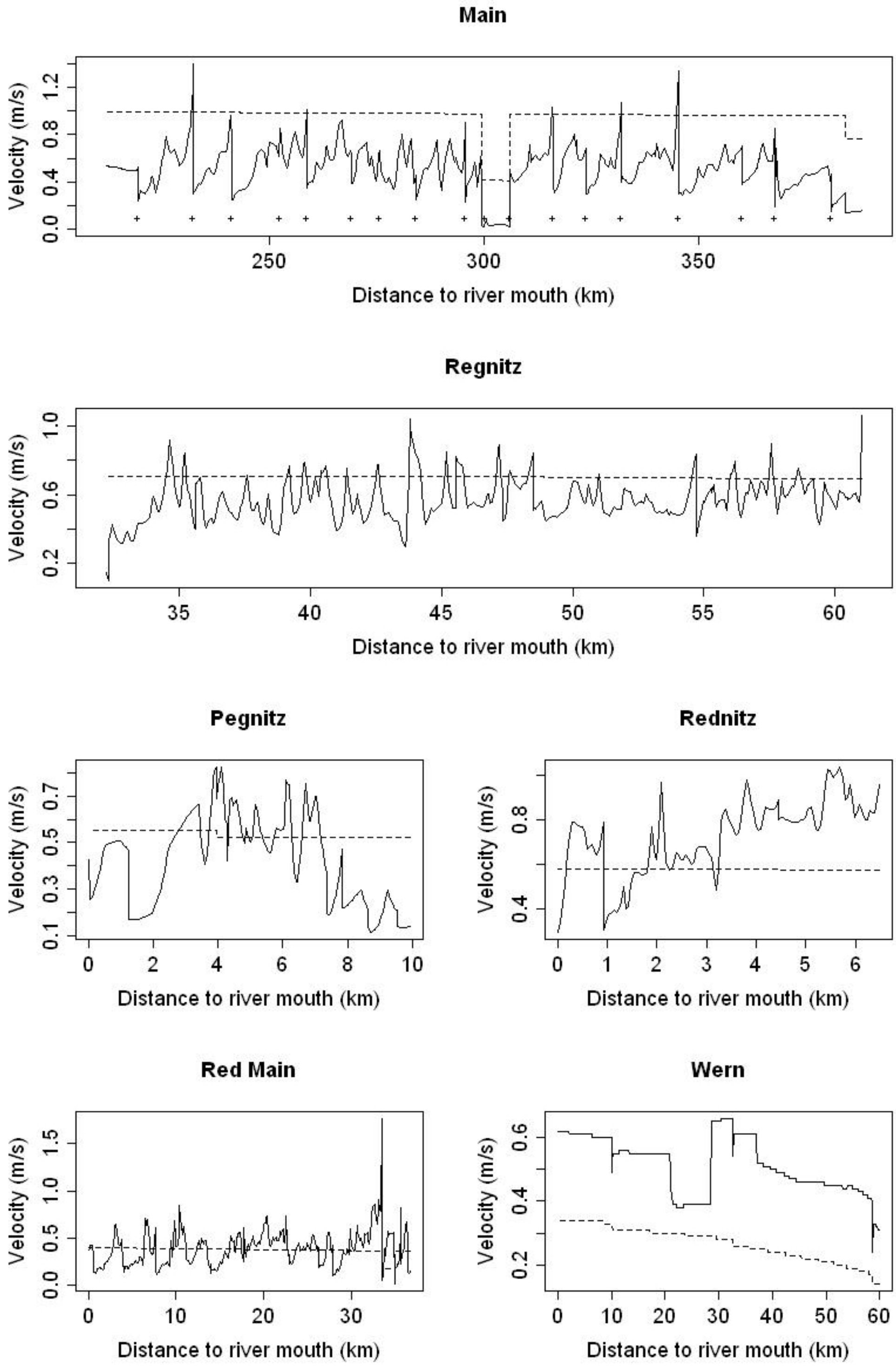

Figure 3.18: Velocity profiles based on ATV data (solid lines) and the hitherto used approach based on power relations with discharge (dashed lines), locations of water gates are plotted for the Main (crosses)

For a half-life of 1 hour the "inflextion point" is at approximately 0.6 m/s flow velocity, whereas it is lower for longer half-lives, viz. ca. 0.25 m/s for a half-life of 12 hours and below 0.1 m/s for higher half-lives. The velocity range for which significant differences in remaining load at a river segment's end can be observed is larger for low half-lives. Of a substance with a half-live of 1 hour 2 percent is left after it has flown through a 2 kilometre long river segment with a flow velocity of 0.1 m/s. If it flows faster with 0.3 m/s 28 % is left. The remaining load for these flow velocities for a substance with half-life of 1 day is 85 % and 92 %, respectively. Comparing flow velocities of 0.3 and 0.5 m/s 28 % or 46 % is left of a substance with 1 hour half-life, whereas the difference for a substance with 1 day half-life is much smaller, namely 2 % (95 % and 97 %).

For a 100 km long river section the general behaviour of the relation does not change, but a more considerable amount of load is eliminated (Figure 3.19). The differences in flow velocity are more momentous regarding the fraction of load that is eliminated. A substance with a half-life of 1 hour has practically completely vanished. Only for very high flow velocities of more than 6.5 m/s, which might rarely occur in natural rivers, more than 5 % of the load is left.

Considering a maximum flow velocity of 2 m/s after a flow length of 100 km (i. e. residence time of scantily 14 hours) approximately 45 % of a substance with the half-life of 12 hours is left. For substances with longer half-lives the percentage is higher, viz. 67 % for half-life of 1 day, 92 % for a half-life of 5 days and 99 % for a half-life of 30 days.

Practical relevance of these considerations can be investigated by transferring these results to realistic average flow velocities and range in which these velocities vary, as available for the Main river basin. With average flow velocities of 0.52 m/s (ATV) and 0.95 m/s (equation 2.22) differences for substances with half-lives of 1 hour, 12 hours, 1 day, 5 days and 30 days are 0 %, 13 %, 22 %, 11 % and 2 %, respecitively.

3.1.4.2 Flow Velocity Estimation

River structure data records are not complete for all river segments in the Ruhr river basin. Therefore, for more than 400 of 1400 river segments Manning-Strickler parameters could not be estimated. For this reason resulting velocity value is compared to the value derived by equation 2.22 only for those river segments for which all parameters (roughness coefficient, hydraulic radius and slope) could be estimated. Results are displayed in figure 3.20. Largest differences occur in headwaters while differences decrease downstream.

A graphical comparison between velocity values derived by equation 2.22 according to an approach developed by Round & Young (1997) on the one hand and velocity values derived by the Manning-Strickler equation (2.21) which is parameterised on the basis of river structure survey data is shown in figure 3.21. Most Manning-Strickler values are significantly higher. While the velocities according to Round & Young (1997) are mainly between 0.1 and 0.4 m/s, the Manning-Strickler values largly accumulate between 0.2 and 0.7 m/s. Good agreement between different velocity values can be found in medium streams like the Möhne or the Lenne.

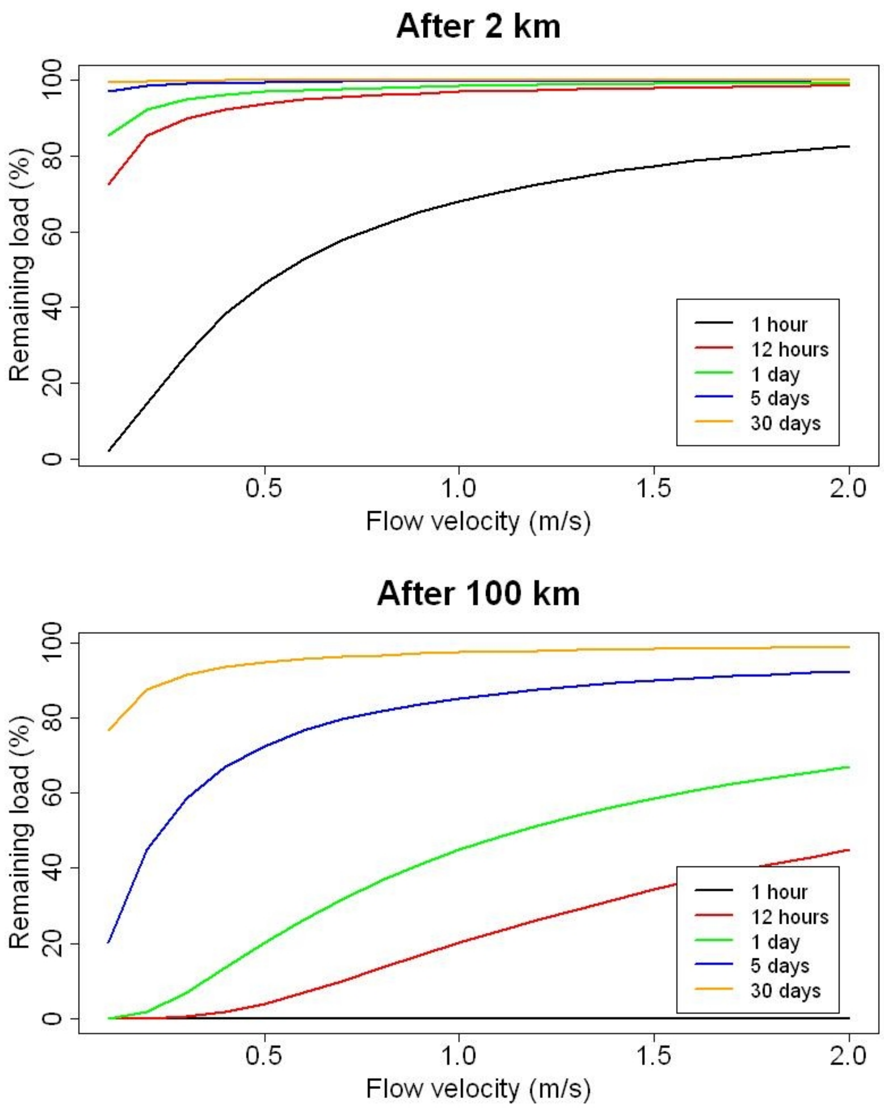

Figure 3.19: Percentage of remaining load after a flow length of 2 km (top) and 100 km (bottom) depending on flow velocity for different half-lifes

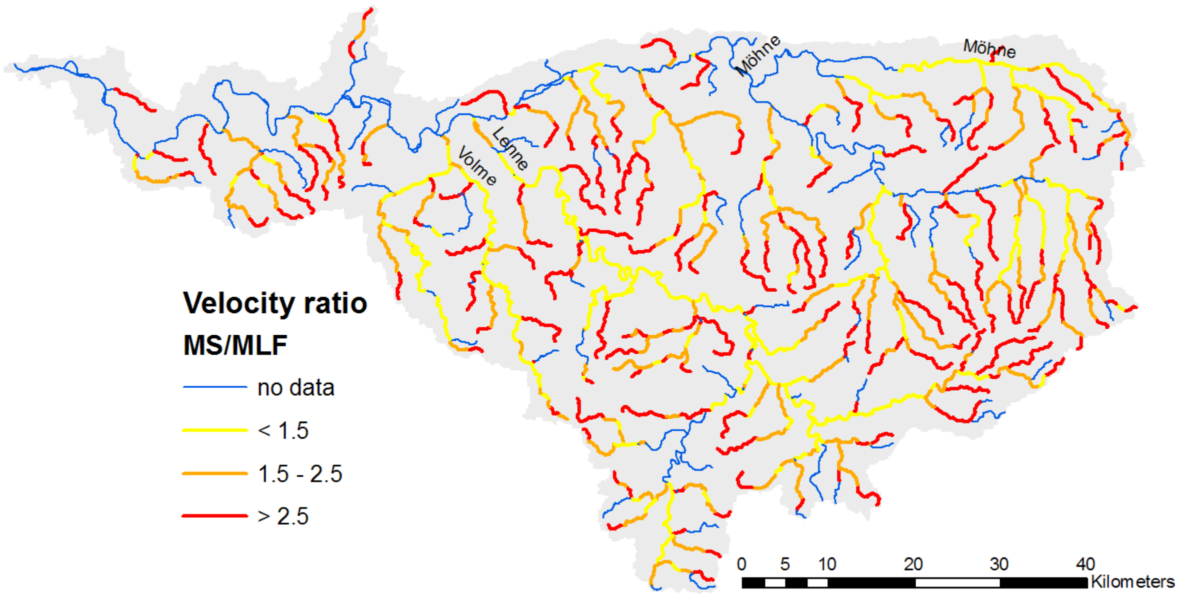

Figure 3.20: Ratios of flow velocity values from the two different approaches: Flow velocity values derived by the Manning-Strickler equation which is parameterised by dint of river structure survey data divided by values derived by a power relationship with discharge

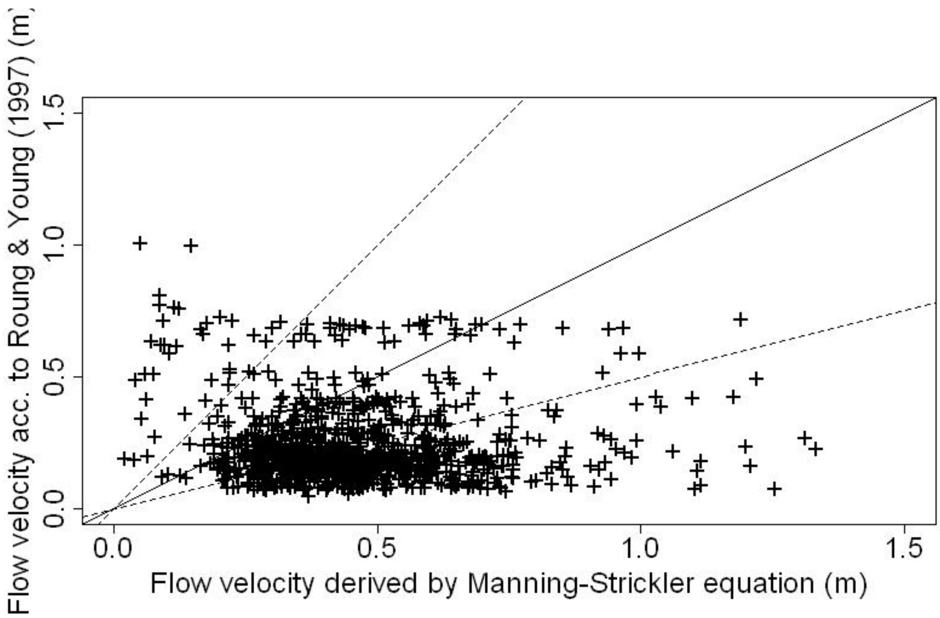

Figure 3.21: Comparison of different flow velocity estimations in the Ruhr river basin: Flow velocity values derived by the Manning-Strickler equation which is parameterised by dint of river structure survey data (x-axis) and values derived by a power relationship with discharge (y-axis)

3.2 Simulation of Surface Water Concentrations with GREAT-ER

The four exemplary simulations of surface water concentrations of diclofenac, nickel and LAS cover the range from a very fast degrading (LAS) over a substance with medium half-life (diclofenac) to a conservative (nickel) substance. The GREAT-ER model is applied in all four river basins with respect to the questions arisen in chapter 3.

3.2.1 Point Discharges - diclofenac in the Saale river basin

As example for a substance that enters surface water bodies via point emissions (waste water treatment plant effluents) only, chemical fate of the pharmaceutical diclofenac is predicted with the GREAT-ER model in the Saale river basin.

The calculated spatial distribution of diclofenac concentrations in the river network is displayed in figure 3.22. Due to emissions only from municipal waste water treatment plants it is plausible that headwaters do not contain diclofenac. However, in many cases the first emission into (small) rivers yields high concentrations which are diluted further downstream. In most parts of the river network concentrations are below 50 ng/l, but near larger cities (Erfurt, Leipzig and Halle) elevated concentrations above 100 ng/l can be found because of higher total emissions due to a large number of inhabitants.

The concentration profile of diclofenac in the Saale river is shown in figure 3.23. In the most upstream segments no diclofenac is discharged, and thus no surface water concentrations are predicted. At the confluence with the tributary Lamitz, into which an emission already proceeded, very low surface water concentrations can be found. The waste water treatment plant Hof with approximately 100000 connected inhabitants causes a strong concentration increase from 3 ng/l to more than 160 ng/l. The mean flow rate at this point is only ca. 6 m^3/s which explains poor dilution. Along the Saale river discharge accumulates and as there are no large emissions the concentration peak declines, especially due to the Bleiloch reservoir with a volume of 215 million m^3. The further course of the Saale shows smaller peaks with subsequent dilution. Further emissions are apparently balanced by substance loss and increasing dilution. Mean simulated concentration at the river's mouth is 25 ng/l. Observed concentrations from monitoring by ARGE-Elbe (2003) are much higher (figure 3.23). They range between approximately 20 ng/l and 400 ng/l. Similarities between concentration profiles of observed and estimated concentration profiles cannot be identified except for the area near the Bleiloch reservoir. Observed concentrations at several sequent sampling sites are below 100 ng/l downstream of the reservoir, but still higher than calculated concentrations. At the Saale's mouth measured surface water concentration is approximately 300 ng/l.

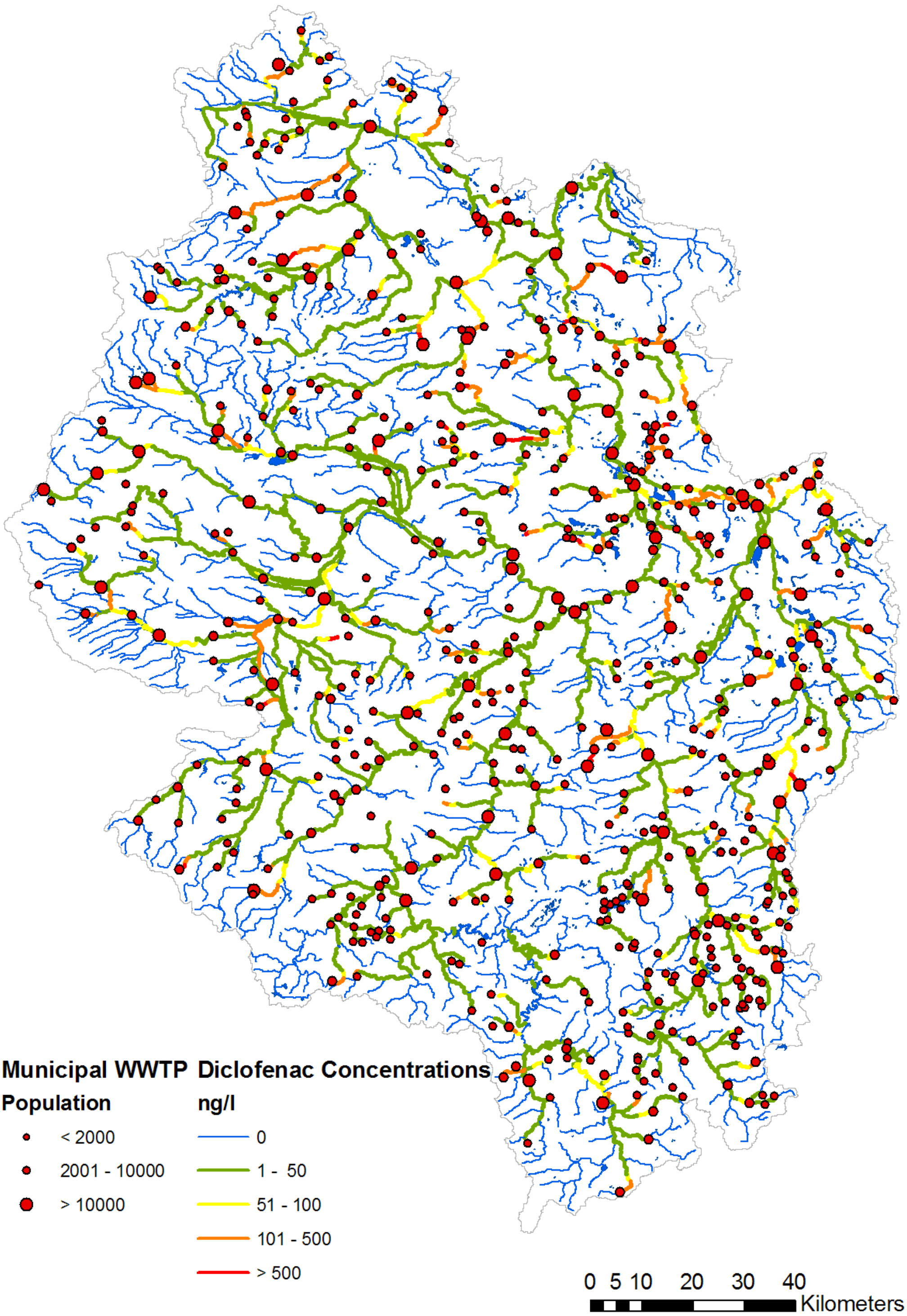

Figure 3.22: Calculated spatial distribution of diclofenac concentrations in the Saale river basin

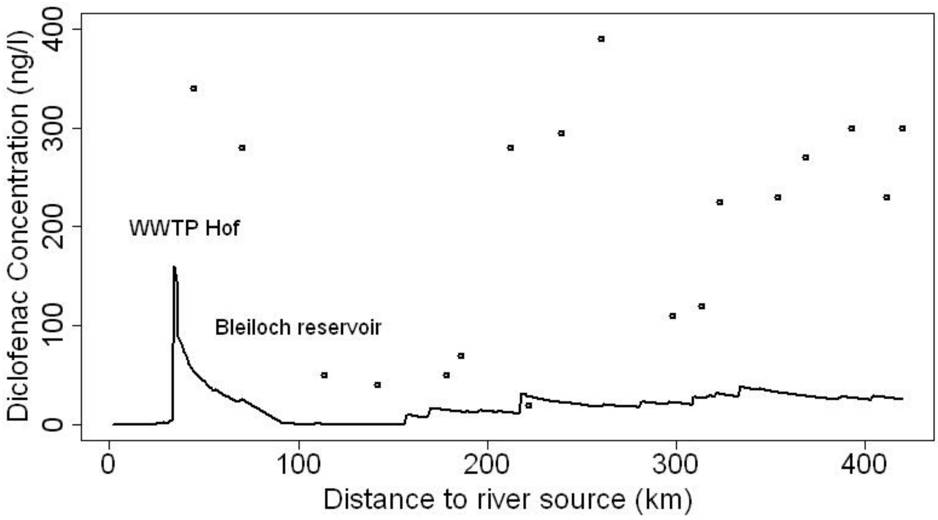

Figure 3.23: Predicted concentration profile of diclofenac concentrations along the Saale river and observed concentrations by ARGE-Elbe (2003)

3.2.2 Point and Non-point Discharges - nickel in the Sieg river basin

To illustrate the influence of surface and subsurface runoff separation on non-point emissions in GREAT-ER nickel concentrations in the Sieg river basin have been estimated. Aside from a base scenario in which all emission sources are considered, a scenario with point discharges only is shown (see figure 3.24).

Due to the high relative fraction of nickel emissions via groundwater infiltration and erosion a ubiquitous background surface water concentration can be observed in the base scenario. Emissions from agricultural drainage, wash-off from urban paved surfaces as well as waste water effluents from municipal sewage treatment plants elevate surface water concentrations additionally in agriculturally used or urban areas.

By only considering point discharges the influence of municipal waste water treatment plants is in evidence. In this scenario headwater rivulets are unaffected by nickel emissions. At some sites where waste water is discharged into smaller rivers concentrations steeply increase due to a small flow rate. They are diluted further downstream. In the Sieg river itself concentrations are elevated downstream of the city of Siegen where waste water from more than 100000 inhabitants is emitted. Emissions from former mining activities along the Sülz river can clearly be identified. Loads discharged from the Grünewaldteich also influence nickel concentrations at the mouth of the Sieg river.

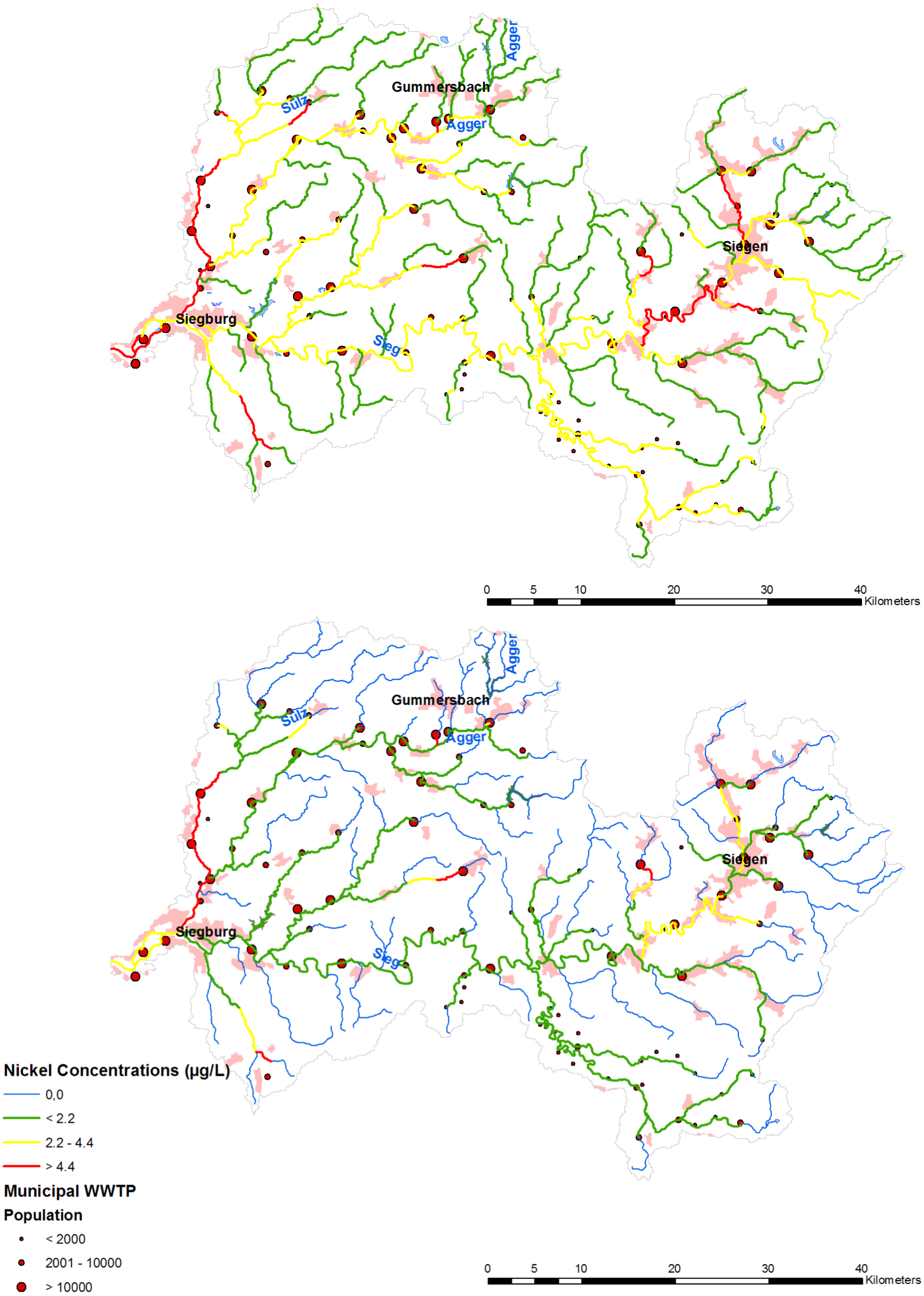

Figure 3.24: Estimated nickel concentrations in the Sieg river basin: base scenario (top) where all emission sources are considered and scenario with point discharges (WWTP effluent, mining water) only (bottom)

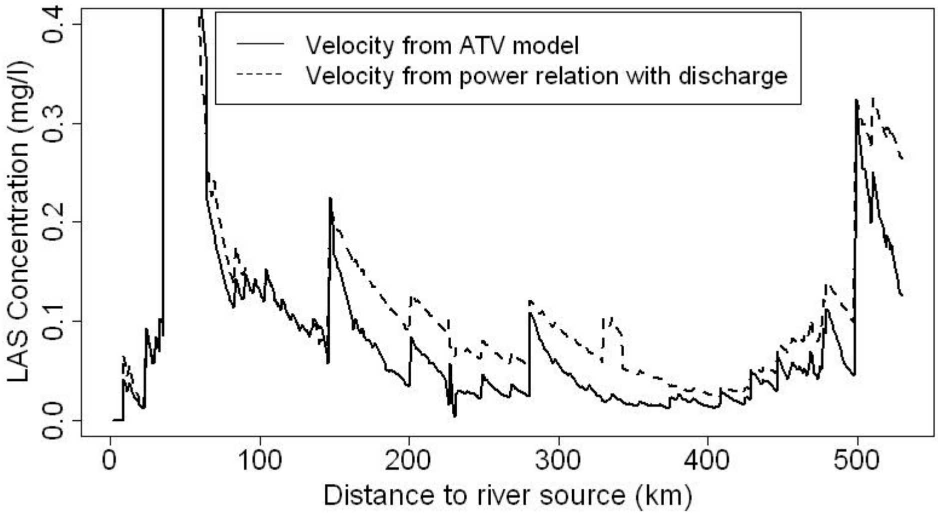

Figure 3.25: Predicted concentration profile of LAS concentrations along the Main river with velocity values from the ATV model (solid line) and those from equation 2.22 (dashed line)

3.2.3 Effect of Flow Velocity - LAS in the Main river basin

LAS is a substance for which different concentration estimates resulting from different flow velocities is anticipated (see chapter 3.1.4). Simulations of LAS in the Main river basin with different flow velocity parameterisation actually shows remarkable concentration differences along the Main river. Figure 3.25 shows the concentration profile for simulations with flow velocity values from the ATV model (solid line) for the Main and from equation 2.22 (dashed line), respectively. Along the first 150 km simulated concentrations resemble each other. For this upper part of the Main river flow velocity parameterisation is the same. Differences in simulation results arise from probabilistic Monte Carlo simulations. Differences become more perceivable at the confluence with the Regnitz river. LAS concentration rises due to the large amount of waste water which is carried by the second largest tributary of the Main from the congested urban area Nürnberg/Fürth. Assuming the (smaller) ATV flow velocities concentrations decline more due to higher residence times. Therefore, the concentrations simulated with ATV-velocities remain smaller than those from simulations with the higher velocities. At the Main's mouth the difference is more than factor 2 (12.6 mg/l vs. 26.4 mg/l).

3.2.4 Effect of River Depth - diclofenac in the Ruhr river basin

The effect of depth variations is considered by analysing diclofenac concentrations because in-stream loss of the pharmaceutical is governed by photolysis which is

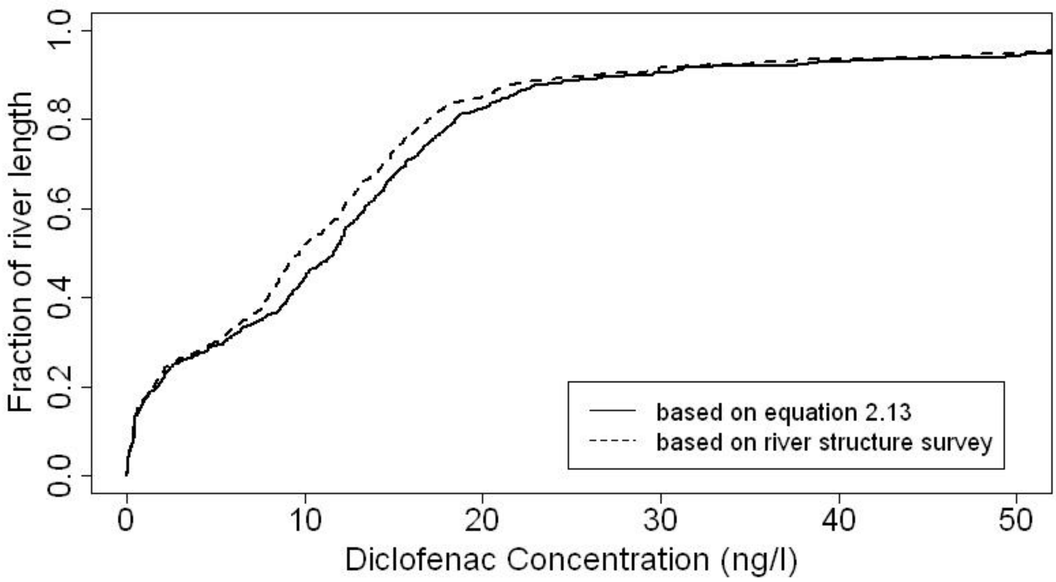

Figure 3.26: Cumulative distribution for river length within the Ruhr river basin below a certain calculated diclofenac concentration; depth derived by equation 2.13 (solid line) and depth from river structure survey (dashed line)

influenced by river depth. Two scenarios with depth values from equation 2.13 and from river structure survey are analysed, respectively.

The dependence between loss and depth triggers differences in estimated surface water concentrations based on different depth parameterisations. In medium and larger tributaries like e. g. the Volme or the Lenne differences sum up to several ng/l. A cumulative distribution of river length below a certain diclofenac concentration is shown in figure 3.26. Concentrations calculated with higher depth values from the river structure survey are comparatively larger. Estimated average diclofenac concentrations that are e. g. exceeded in only 20 % of the rivers are approximately 17 and 18.5 ng/l for the scenarios with depth from river structure survey and from equation 2.13, respectively. Especially in a concentration range between 5 and 25 ng/l given average concentrations are predicted for different fractions of the river network.

Concentration differences do not appear in the whole river basin. Especially in the Ruhr river where alternative river depth values are not available concentrations are very similar. Concentration differences from tributaries are thus not propagated through the river network to the Ruhr's mouth.

Differences in concentration developing can be observed in the Lenne river by analysing the concentration profile (figure 3.27). Along the first roughly 20 km concentrations are very similar. Between river kilometer 25 and 45 the concentration gap increases. This gap is propagated and expands till the confluence with the Ruhr river. At this point the concentration difference is approximately 4 ng/l.

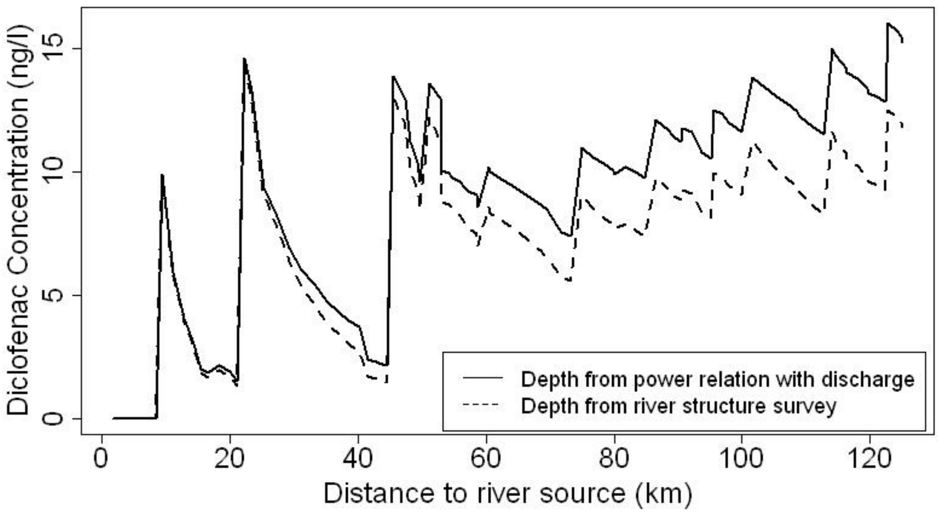

Figure 3.27: Predicted concentration profiles for diclofenac concentrations along the Lenne river which are calculated with depth values derived by a power relatioon with discharge (solid line) and by river structure data (dashed line)

Chapter 4

Discussion

4.1 Steady-State Exposure Modelling with GREAT-ER

From a variety of exposure assessment approaches the geo-referenced steady-state model GREAT-ER is chosen to estimate surface water concentrations on catchment scale. It allows for predicting and analysing surface water concentrations at the catchment scale. The steady-state assumption yields stationary concentration conditions. It is chosen due to continuous substance input into surface water and continuous output from the considered surface water bodies (via transport or because of loss).

The spatial scale on which GREAT-ER operates are river basins of a size of up to 30000 km^2. River basins are the hydrological unit which is typically addressed by integrated river basin management approaches which take into account interrelations between different basin characteristics. For prediction of surface water concentrations at each point of a river network substance loads from tributaries and from upstream segments of the river are important. Such connections which enable e. g. transport of a substance through a river network have to be considered. To incorporate whole river basins is thus reasonable for a tool which can be used within the scope of integrated river management.

The spatial resolution of GREAT-ER is defined by its river segment length (of at the utmost 2 km). In spite of the spatious approach of whole river basins this resolution enables the identification of locally elevated concentrations. By spatially linking emission sources and immission concentrations understanding of environmental fate of substances can be gained. Information on spatially distributed catchment characteristics like runoff composition, slope or river structure is assigned to each river segment. In this way spatial heterogeneity of a basin can be represented by the river network. Although geo-referenced approaches exhibit considerably larger data demands, observed spatial heterogeneity of river basin characteristics justifies such approaches.

River channels are represented one-dimensionally in GREAT-ER. Although there might be streamflow and river structure gradients within a river section this simplification still is commensurate at this spatial scale. Loss processes which are represented in GREAT-ER can sufficiently be parameterised with one parameter for each river segment. If e. g. loss or transport processes have to be considered at a smaller scale or if their three-dimensionality is of interest, other approaches are recommended.

If information of average surface water conditions is required, emission assumptions have to mirror average conditions. Even if emissions of many substances remain nearly constant temporal variability of hydrological conditions provokes concentration variability. As in the long term sequence of hydrological events is beside the point, the probabilistic approach of GREAT-ER neglects it. It instead accounts for occurrence probabilities of certain conditions. These occurrence probabilities can well be represented by probability distributions even though they fail at certainly predicting single hydrological events. Especially extreme events are not in the focus of this study.

Diffusive input of substances that is transported via runoff has recently been integrated into the GREAT-ER model (Hüffmeyer, 2010). Correlating the influence of emission pathways and discharge amount also is a simplification. Comparisons between observed and predicted concentrations, however, indicate that these assumptions are reasonable (cf. (Hüffmeyer, 2010)).

In summary, surface water concentration prediction is advisably carried out at the catchment scale because the river network topology influences loads and concentrations in the lower river reaches. Representing temporal variability by a probabilistic approach is reasonable if temporal sequence of concentrations is not considered. GREAT-ER is a suitable modelling tool for prediction of long-term average surface water concentrations on the catchment scale.

Quality of its estimates significantly depends on the description of the hydrological conditions whose parameterisation is discussed in the following.

4.2 Assessment of River Network Parameterisation

Results of river network parameterisation are discussed in order to generally assess if the developed methods are adequate for describing river networks for the GREAT-ER model. Besides this the methods and their data (processing) requirements have to be traded off against enhanced model result with respect to spatial heterogeneity.

4.2.1 Streamflow

The amount of discharge is the variable influencing surface water concentrations in any case because it determines the dilution of emitted substances. Parameterisation of each river segment with specific streamflow values has therefore been investigated in detail.

Parameter estimation. When drawing sub-samples from the daily discharge time series, maximum likelihood estimators by and large deviate only marginally for each sub-sample. Estimators for the lognormal distribution exhibit smaller average values than those estimated from the complete time series which can be ascribed to the probably smaller number of extreme flood events in the sub-sample. Maximum

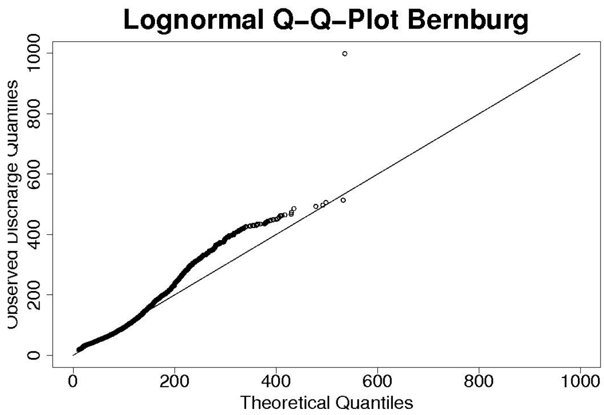

Figure 4.1: QQ-Plot for gauging station Bernburg (drainage area size: 19639 km^2)

likelihood estimators for shape β and rate λ parameters for the gamma distribution are larger for sub-samples. This leads to a larger mode value of the distribution and a steeper increase of cumulative probabilities, respectively. The higher β, the lower is the distribution's skewness.

Goodness-of-fit tests. QQ-plots indicate good agreement between a theoretical lognormal distribution which is based on estimated mean and standard deviation and observed streamflow data. Deviations between empirical and theoretical quantiles which can be found at some gauging stations for very high percentiles can be traced back to extreme flood events which occurred during the 30-year period-of-record. One example is the QQ-plot for the gauging station Bernburg which has a drainage area size of 19639 km^2 (figure 4.1). Such outliers might influence test results. For the GREAT-ER model single extreme flood events are not in the centre of interest. Therefore, good accordance with low and medium flow conditions is emphasised. The first impression given by the QQ-Plots is corroborated by test results from the K-S tests. In case of the X^2-test large samples pose the problem that the test statistic becomes large because in each class a large number of realisations occurs. Even if the relative deviation from the expected number of realisations is small, in absolute numbers the difference is big, although the differences to the theoretical distributions are not that large according to the K-S-test. It is thus questionable if the test provides usefull information, and therefore the X^2 test emerges as rather unuseful. This findings coincide with the statement of Sachs & Hedderich (2006) that the X^2 test is not as powerful as other goodness-of-fit tests.

Sufficient agreement with lognormal distribution could be proofed for almost all gauging stations. The only gauging station for which p-values for both lognormal and normal test (applied to logarithms of streamflow data) is lower than 0.05 is Roenkhausen in the Ruhr river basin. Discharge exceedance probablities here are characterised by a steep decrease for higher discharge values, i. e. high discharge values occur seldomly, but if they occur they are remarkable high. Diminutive exceedances of critical values for the normality test can be found for most of the Saale and Ruhr gauging stations and for some of the gauging stations in the Sieg river basin. Results from the normality test for which both p-values and critical values are available show that deciding upon the p-value is a weaker criterion than deciding upon exceedance of critical values. The K-S-test is consistent, i. e. critical values become very small with increasing sample size because it is expectable that large samples resemple a theoretical distribution to great extend.

When interpreting test results some characteristics of streamflow records like seasonality, the occurrence of extreme events and in general the high spatial variability of river basin characteristics have to be borne in mind (Borgman *et al.*, 1970). Representing streamflow by a simple concept of a probability distribution can only approximate real streamflow. By and large the assumption of lognormally distributed streamflow seems to be reasonable.

Flow duration curves. Results from comparisons between empirical flow duration curves and the theoretical cumulative distribution functions show that accordance with mean annual flow duration curves is slightly higher compared to conventional flow duration curves. The differences, however, are very small.

Flow duration curves are not only used to inspect if derived lognormal probability distribution functions are parameterised appropriately, but also to link exceedance durations with low flow indices. It was found that differences between conventional and mean annual flow duration curves are remarkable for high and low percentiles. In chapter 3.1 average percentiles corresponding to MAM(10)-values for each of the analysed river basins have been identified as 9-, 17- and 18-percentile for Ruhr, Saale and Sieg, respectively. Within this range differences can be significant. By construction of mean annual flow duration curves extreme floods or low flow periods become less important because they are balanced. A probably more typical year is thus represented by mean annual flow duration curves. When mapping percentiles from these curves to e. g. MAM(10)-values it might be supposed that the exceedance of MAM(10)-values then also is not as much influenced by extreme events as it would be the case for using a conventional flow duration curve. Therefore, it is recommended to use mean annual flow duration curves for this mapping. However, there is a pragmatic constraint as regards data availability. While conventional flow duration curves can be found in German Hydrological Yearbooks by default, mean annual flow duration curves have to be derived from long time series of daily streamflow data. Even if this data is available for many gauging stations within a catchment, it has to be handled which is laborious.

Mean discharge estimation. When assessing the goodness of mean discharge value estimation from intersecting effective precipitation and drainage area uncertainty in the input data has to be taken into consideration. The map of effective precipitation has been evaluated (BMU, 2005a), and this evaluation showed good agreement for a comparison between gauged streamflow data and derived streamflow data on the basis of the map. Deviations in general were below 5 % except for anthropogenically shaped areas. This is considerably less than explored in this study.

The comparison of results from the water balance model and observed mean discharge values for the four river basins yields good agreement for large parts of the basins, even though deviations are larger than those discovered by BMU (2001). At most locations where mean discharge is overestimated or underestimated differences can be explained.

In the water balance model it is assumed that precipitation which does not evaporate flows to the watersheds outlet either as surface or subsurface runoff. Any artificial abstractions or discharges of water out of or into the watershed or alterations in natural runoff regime because of land use changes are not considered. Therefore, the estimation of mean discharge values is difficult where artificial water transitions (like near the Brombach reservoir in the southern part of the Main river basin) or storages (like in the Ruhr river basin and in the Sieg river basin) are present.

Besides, disagreement in small headwater rivers can be attributed to the general higher variability of streamflow in smaller (often mountain) torrents and to the smaller drainage area size. Data of effective precipitation is based on a 1 km x 1 km raster. This spatial resolution reqires spatial aggregation. The data basis for delineation of drainage areas has a higher resolution, but in spite of this elevation of a 90 x 90 m cell is an average and aggregated value. Additionally the assumption that the surface drainage area corresponds to the sub-surface watershed is a simplification which in reality might not be true in any case. While these factors are probably balanced in larger drainage areas they appear in smaller watersheds.

By and large deviations between observed and estimated mean discharge values are sufficiently small. However, deviations do not seem to be purely random but the water balance model overestimates by trend.

Low flow estimation. Additionally to analysis of exceedance durations in form of quantiles of the streamflow probability distribution, low flow has been analysed by means of the index MAM(10) which makes allowance for the duration of a low flow period. The Hydrological Atlas of Germany indicates that specific low flow discharge which corresponds to MAM(10) is rather homogeneous in space. Also over- and underestimations according to gauged values of MAM(10) shows a rather homogeneous pattern.

Locally confined deviations can be traced back to similar reasons as deviations in mean discharge estimation (e. g. regulation by reservoirs, anthropogenic impact on runoff regime, etc.).

The comparison also reveals that the longer time series in many cases cover a larger range of values. However, when averaging MAM(10) extreme years are balanced. Thus the coefficients of variation are smaller. Schreiber & Demuth (1997) state that MAM(10) is a temporally very stable index with coefficients of variation below 69 % in the southwest of Germany. In this study coefficients of variation are higher only in a very few cases. Findings of Schreiber & Demuth (1997) can thus be corroborated for further parts of Germany.

Relating inter-annual variability of MAM(10) with drainage area size shows decreasing variability with larger drainage area sizes. This relation seems to be reasonable as within a larger drainage area streamflow variability can be buffered. The fact that the correlation between drainage area size and derived MAM(10)-values is higher than the correlation between drainage area size and observed MAM(10)-values is plausible against the background of wide-ranging spatial homogeneity of specific low flow discharges and a direct linear relation to drainage area, when intersecting drainage area polygons with one (homogeneous) value for MAM(10).

Streamflow distribution. The derived values for mean discharge and low flow discharge are used to describe the lognormal probability distribution. By assuming that MAM(10) represents on average the 9-, 17- and 18-percentile for the different river basins the relation between low flow values and low flow duration is spatially aggregated. Although specific low flow values are rather homogeneous in space streamflow in general is subject to many spatially very variable factors like precipitation, evapotranspiration, topography, or land use. The same amount of low flow forms a different part of total streamflow at different locations.

If there are systematic and considerable differences in observed values of MAM(10) and corresponding exceedance durations it might be reasonable to subdivide a basin and assume that MAM(10) corresponds to different percentiles in each part.

In this study large differences could only be observed for the Main river basin. There, however, only short time series of 10 years are available only for very small drainage areas. It is presumed that these time series do not represent the full range of low flow in the Main catchment for these reasons.

For Ruhr, Saale and Sieg it can reasonably be assumed that the above mentioned percentiles are sufficient to parameterise streamflow distribution.

4.2.2 Runoff Separation

Runoff separation by means of the two cited approaches produce very different results. BFI as well as base flow discharge are significantly higher when separating base flow according to Gustard et al. (1992). Demuth's approach (1993) explicitely takes into account that occurring low flow might in some cases be influenced by other sources than groundwater, e. g. surface runoff or interflow. To separate pure base flow from ulterior influenced low flow the approach based on ranking low flow values according to their magnitude has been developed by Demuth (1993) (see chapter 2.3.1.4). These influences are not explicitely considered in Gustard's approach. Therefore, it is plausible that both approaches entail very different results.

For GREAT-ER emission pathways it is important to separate between fast overland runoff and runoff that flows through soil layers because transported components are different. Surface runoff might cause erosion and washes off substances that deposited on the ground. Sub-surface runoff is influenced by its passage through the soil matrix and/or aquifers and might transport substances from there. As information on location of aquifers and geohydrology is not available, sub-surface runoff processes cannot be separated within the GREAT-ER model at the moment. It is therefore sufficient to only separate between (fast) surface and (delayed) subsurface runoff. A differentiation between interflow and baseflow is not required.

The runoff separation approach by Gustard et al. (1992) consequently is commensurate. The amount of this delayed flow meets with exceedance of approximately 50 % properly. Emission assumptions make use of this relation. Emissions occurring from surface runoff are only active if the median discharge is exceeded. Further information on emission estimation can be found in Hüffmeyer (2010).

4.2.3 River Depth

To relate river depth to streamflow amount leads to strictly monotonic increasing depth along the river because streamflow increases with increasing drainage area. Analysis of river structure data, however, shows that the depth profile of a river is diversified. An alternative parameterisation procedure might therefore reflect this variablity more adequately.

River structure data. River structure survey data origins from an in-situ data aquisition. Depth parameters from the river structure survey within one river segment show that for such short distances depth differences are in many cases not significant. To describe depth of a river segment by just one average value hence seems to be reasonable. There are also segments in which variation among depth value records are pronounced. These segments are mainly situated at confluences with other rivers (see figure 3.14). The points for which river structure is recorded have to be spatialised to the river segments used for GREAT-ER. This procedure is automised and might lead to mismatches in some cases which could also be one reason for high variability. To eliminate such potential problems data processing has to be analysed and probably refined.

A major drawback for using depth from river structure survey is that only mean values can be drawn directly from the survey and a probability distribution cannot be parameterised directly.

Stage-discharge relation. The secondary approach to parameterise river depth is the usage of stage-discharge relations. Discharge can than be used to derive stage and finally river depth (stage minus zero-flow-stage). This relation could theoretically also be applied for other discharges than mean discharge and could therefore produce depth values corresponding to the full range of streamflow.

However, this approach exhibits other shortcomings. The relations are based on the situation at gauging sites and is transferred to the gauges' drainage areas. It is doubtable if this river profile is representative.

It is not recommended to use this approach for large basins because the assumption that stage-discharge-relations at one place are representative for large and spatially heterogeneous drainage areas is unlikely to hold. However, this approach might be applied at gauging stations to investigate plausibility of depth values derived by other data. For spatially limited areas and small natural drainage areas such an approach might be helpful to estimate depth values. One of its disadvantages, however, is its high data requirements. Time series on both stage and discharge have to be available.

4.2.4 Flow Velocity

The approach to derive flow velocity hitherto is similar to that for deriving depth values. In consequence flow velocity values slowly increase along the river course. Flow velocity variability caused by changes in river bed structure or slope alterations is not considered. For computation of substance degradation by the GREAT-ER model residence times of water within a river segment is important. Flow velocity merely is an auxiliary quanity to calculate this residence time. If residence time within a river section remains the same no matter how flow velocity varies within this section, estimated concentrations at the end of the river section remain the same, too. The spatial resolution of GREAT-ER is determined by a river segment length of at the utmost 2 km. Flow velocity parametersation has to follow the same spatial resolution.

Flow velocity comparison. The comparison with flow velocity values from the ATV water quality model reveals a systematic overestimation of flow velocity by equation 2.22 for larger rivers. Since the regression analysis on which equation 2.22 is based is derived from data from small natural channels in the UK (Round *et al.*, 1998) it is not astonishing that the equation is not adequate for larger, often artificially modified rivers as e. g. the Main. For smaller rivers a comparison of currently used flow velocity values with (from river structure) derived flow velocity values reveals that often the first are slower. Analysis of river structure data and derivation of flow velocity values from these data show that many flow velocity values are within the interval of 0.2 and 0.7 m/s. Round et al. (1998) report measured flow velocity values between 0.2 and 0.8 m/s. This range hence is lifelike.

Effect of velocity differences. It could be shown that within a flow velocity range between 0.2 and 0.7 m/s the fraction of remaining load significantly changes for substances that are degraded rapidly (half-life below one day). This means that for such substances flow velocity is a sensitive parameter.

As a consequence of this sensitivity there is demand of an appropriate flow velocity parameterisation. The presented approch of parameterising the Manning-Strickler equation (2.21) is an attempt of relating flow velocity to river structure. Results show higher variability of flow velocity. It can not be assessed if the derived flow velocity values are more realistic because of lacking velocity measurements. However, it can be concluded that results from application of the Manning-Strickler relation are plausible (Round *et al.*, 1998). Ratios of Manning-Strickler flow velocity values and formerly used flow velocity values are highest in headwater streams. According to equation 2.22 flow velocity is low there because discharge is low there, too. However, at these sites e. g. slope is higher which leads to higher flow velocity. Ratios are thus particularly high if the denominator (in this case formerly used flow velocity value) is very small.

By and large the approach is promising as it enables for accounting for river structure. To enhance estimation of Manning-Strickler parameters evaluation of flow velocity values would be beneficial. Then also a more sophisticated approach accounting e. g. for different profile types or incorporating impoundment of river water by weirs or dams.

4.3 Impacts of Hydrological Conditions on Predicted Concentrations

The GREAT-ER model is exemplarily applied for some substances in the four analysed basins. These scenario calculations do not in the first instance aim at predicting realistic surface water concentrations but rather intend to illustrate the effect of hydrological river network parameterisation. They indeed provide merely small insight of the possibilities of GREAT-ER because they focus on the hydro(morpho)logical background. An in-depth evaluation of predicted surface water concentrations by means of monitoring data is not performed due to absence of comprehensive monitoring data.

The four presented applications of GREAT-ER aim at showing different aspects. While the first two cases address the representation of discharge and runoff separation and resulting surface water concentrations estimates, the latter two illustrate how differences in the hydromorphological parameterisation propages in terms of surface water concentrations.

A direct comparison between GREAT-ER model runs in "old" and in "new" river basins not meaningful because no comparable "old" river basin is available. For the Ruhr river basin and parts of the Main river basin "old" versions exist, but their underlying river network data is based on different data sources and is partly higher and partly lower spatially resolved.

4.3.1 Point and Non-point Discharges

Estimated diclofenac concentrations in the Saale river basin show reasonable results. Local concentration elevation can be explained by either high emissions (in densely populated regions) or poor dilution (in smaller rivers). However, monitoring data which is available along the Saale river and for some of its largest tributaries from ARGE-Elbe (2003) are severalfold higher. These measurements are based on single sampling, i. e. they only represent the situation at sampling time which have been taken between 29th November and 1st December 2000. At gauging station Calbe-Grizehne, for instance, daily mean discharge values were between 52.3 and 54.5 m^3/s during this period. Mean discharge in comparison is 115 m^3/s. When assuming diclofenac emissions only origin from household wastewater, its emission into the rivers is independend from streamflow magnitude. During low flow situations consequently dilution is smaller. This does not explain the whole extend of deviations between observed and estimated concentration. Sampling uncertainty plays a decisive role for such samples (Rode & Suhr, 2007). As single measurements are probably not very representative, further monitoring would be needed to properly evaluate model results.

Results of the two scenarios for nickel concentrations in the Sieg river basin can be explained by different emission assumptions (point and non-point discharges vs. point discharges only). Nickel is an example of substances that can ubiquitously be found in river basins. Such substances are either naturally contained in pedosphere or lithosphere (like e. g. metals) or they have been emitted into the environment by humans and can be found on the ground (e. g. due to atmospheric deposition or disposal of sludge). Estimating surface water concentrations of such substances requires the incorporation of "background" concentrations. Instead of adding one aggregated background concentration for the whole basin, spatially distributed information on subsurface runoff, surface runoff and land use (to identify areas from which certain substances are typically washed off) is integrated into the hydrological framework for GREAT-ER.

For predicting nickel concentrations in the Sieg river basin the influence of subsurface runoff is crucial and effects all river segments (see figure 3.24). It is therefore important to adequatly estimate groundwater and interflow contribution. Another important nickel source consists of former mining activities. Their identification and integration into emission assumptions requires additional information on spatial nickel application patterns within a basin.

For other substances other discharge pathways might be more important. Concentration estimations of substances that are e. g. washed off from agricultural used areas require information on the amount and location of such area. The spatial distribution of cropland might be very different depending on the basin considered. The same applies to wash-off from paved urban area. Compared to ubiquitious contribution of subsurface runoff containing nickel load, these emissions are probably spatially more variable in many basins.

It can thus be concluded that knowledge of basin characteristics especially with respect to emission and occurrence of the substance of interest is beneficial for performing GREAT-ER simulations.

4.3.2 Hydromorphological Parameterisation

Prediction of LAS in the Main river basin is one of those cases which have been identified as being sensitive towards flow velocity estimation in section 3.1.4.1. Model results thus corroborate the analysis of the effect of flow velocity on concentration prediction against the background of different average flow velocities.

Concentration differences resulting from different underlying flow velocity parameterisation depend on the substance's half-life and on flow velocity differences. The Main river is the largest river for which GREAT-ER is currently applied. Flow velocity values derived in dependence with discharge by equation 2.22 are therefore at the head of velocity estimates. Residence times of a substance within this river is hence rather short. Consequently, concentrations remain higher due to lacking time for degradation. The example of LAS in the Main river is thus a kind of worst case. It illustrates that there is a perceivable effect of flow velocity parameterisation but in most parts of the river network (especially in smaller rivers) differences resulting from different flow velocity parameterisation are probably smaller.

In general, the fact that differences in flow velocity parameterisation provoke different concentration estimates militates in favour of a flow velocity parameterisation approach which incorporates spatially distributed river structure information and which probably predicts flow velocity more approapriate.

Predictions of diclofenac concentrations in the Ruhr river basin locally show different results when taking different river depth values as a basis. Concentration differences from tributaries, however, do not necessarily bear on concentrations at the mouth. It can be concluded that locally there is a relevant impact of river depth parameterisation on concentration predictions although it might not be visible at the basin's outlet. Because of dilution concentration differences from tributaries are decreased then. Presumably a difference would be remarkable if also in the larger Ruhr river depth values were different.

In the presented scenarios in-stream diclofenac losses are only effected by photodegradation. This is only one of three processes (photodegradation, sedimentation and volatilisation) represented in GREAT-ER which depend on river depth. Depending on the substance and its physico-chemical properties differences in concentration estimates based on different river depth parameterisation might be more distinctive.

Even though differences in estimated concentrations might be small and locally confined a parameterisation of river depth which is based on local river channel structures is advocated because it particularly effects local concentration estimates. Prediction of local concentrations is one of GREAT-ER's most relevant features. It is thus reasonable to enhance the estimation of those factors that influence local concentration predictions.

Chapter 5

Conclusions and Outlook

Geo-referenced assessment of surface water concentrations of various substances is beneficial for current demands on river basin management. Development and operation of geo-referenced approaches for chemical fate modelling in surface water has to cope with the challenge of developing adequate approaches which allow for describing relevant processes and of parameterising these approaches.

Therefore, a sound hydrological framework for steady-state exposure assessment in surface water is developed. Against the background of distinct spatial heterogeneity of river basin characteristics a description of the hydrological and hydromorphological conditions has to account for the impact of this heterogeneity on streamflow regime and river channel morphology.

Major findings of this work are summarised in the following:

- Streamflow variability can be described by a lognormal probability distribution. The distribution functions can sufficiently well be parameterised at ungauged locations within a river basin with spatial data of effective precipitation and specific low flow discharge.

- Delineation of drainage areas for each river segment enables consideration of site-specific basin characteristics like land use or runoff. This information is essential to understand a substance's pathways to surface water bodies and to estimate input loads.

- Composition of runoff pathways impacts both variability of streamflow and emission of substances transported by runoff. By application of a runoff separation method (Gustard *et al.*, 1992) in the analysed river basins a stable relation between subsurface runoff and 50 % exceedance duration of streamflow could be shown. Results from runoff separation analyses are crucial to describe substance transport with surface and subsurface runoff, respectively.

- River depth and flow velocity parameterisation which account for spatially distributed information of river morphology yield values that differ from hitherto used values.

- Exemplary application of GREAT-ER illustrates significant differences in estimated concentrations in connection with different depth and velocity parameterisation. Estimated surface water concentrations hence depend on appropriate river structure parameterisation, since estimation of river depth and flow velocity are sensitive parameters for substances with short half-lives or substances that are significantly affected by sedimentation, volatilisation or photolysis.

These findings lead to the following recommendations concerning prospective integration of additional river basins into the GREAT-ER model suite:

- It is advisable to analyse long-term discharge records of the basin's gauging stations to find out how MAM(10) corresponds to exceedance durations because this relation might vary from basin to basin.

- The quantification of streamflow by means of effective precipitation and specific low flow discharge is advocated because it is proved that this approach yields reasonable discharge distribution descriptions.

- Incorporation of river structure information is a promising approach to account for spatial heterogeneity of river structure which significantly influences concentration predictions. Improved spatial concentration predictions is worth the increased data demand.

Analysis and application of methods to describe streamflow and river channel characteristics (see section 2.3) both point out enhancements and shortcomings for the description of river networks on catchment scale. While the parameterisation of streamflow variability works sufficiently well, the hydromorphological parameterisation still has room for improvements. Especially two issues have to be addressed: i) incorporation of temporal changing river depth and flow velocity and ii) the influence of impoundment dams on flow velocity.

Representation of temporal changing river depth and flow velocities can be handled by probability distributions. Besides the type of probability distribution also the relation to streamflow has to be adapted to methods accounting for river structure.

Locations and characteristics of weirs and dams are not considered at the moment due to limited data availability. However, it is expected that they have a severe influence on flow regime, depending on their size and their operation. Incorporation of such effects into hydrological parameterisation is data intensive. For this reason it should be deliberated well about whether the cost-benefit ratio is advantageous.

In summary, the presented work provides a methodology and a hydrological framework for geo-referenced surface water exposure modelling with the GREAT-ER model or other models which operate on a similar spatial and temporal resolution. Basic methods to describe hydrologcial and hydromorphological conditions on catchment scale are propounded. They make use of geo-referenced data and account for local and regional characteristics of the watershed more than hitherto used methods do. Resulting hydro(morpho)logical descriptors bear comparison with observed conditions and are plausible. Analysis of exemplary GREAT-ER simulations show that the integration of additional information affects predicted surface water concentrations.

The developed framework builds a basic theoretical background for hydrological parameterisation of geo-referenced steady-state exposure modelling in surface waters. There is, however, still ample scope for further meliorations and extensions.

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Erklärung über die Eigenständigkeit der erbrachten wissenschaftlichen Leistung

Ich erkläre hiermit, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe. Die aus anderen Quellen direkt oder indirekt übernommenen Daten und Konzepte sind unter Angabe der Quelle gekennzeichnet.

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