WATER AND BIOGEOCHEMICAL FLUXES IN THE RIVER RHINE CATCHMENT

With 28 figures, 8 tables and 2 photos

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Zusammenfassung: Wasser- und biogeochemische Flüsse im Einzugsgebiet des Rheins

Aus gemessenen Niederschlags-, Klima- und Abflussdaten werden in einem konzeptionellen Modell die Komponenten des Wasserhaushaltes in ausgewählten Teileinzugsgebieten des Rheins für den Zeitraum 1961–1990 berechnet. Hierauf basierend werden die Wasservolumina und unterschiedlichen hydrologischen Regime im Rheineinzugsgebiet diskutiert. Eine Analyse hundertjähriger Zeitreihen hydrologischer Parameter zeigt, dass in den letzten Jahrzehnten Änderungen eingetreten sind. Selbst wenn diese regionalen Veränderungen nicht anthropogenen Klimaänderungen zugeschrieben werden können, zeigen statistische Analysen, dass die Annahme stationärer Verhältnisse in den Zeitreihen nicht länger gegeben ist.

Zur Quantifizierung der Auswirkungen möglicher Klimaschwankungen auf den Abfluss im Rhein und seiner Zuflüsse sind umfangreiche Berechnungen regionaler Klimaszenarios für das gesamte Einzugsgebiet des Rheins auf der Basis von Wasserhaushaltsmodellen und Abflussmodellierungen notwendig. Für diese Untersuchungen stehen drei regionale Klimaszenarien aus dem Projekt "Klimaveränderungen und Konsequenzen für die Wasserwirtschaft" (KLIWA) für Süddeutschland zu Verfügung. Ein Klimaszenario, entwickelt vom Max-Planck-Institut (MPI) für Meteorologie in Hamburg, basiert auf dem regionalen Klimamodell REMO und berücksichtigt das Gesamteinzugsgebiet. Dieses Szenario ist unter Anwendung der hydrologischen Modelle LARSIM und HBV-SMHI in Abflusswerte überführt worden, wobei für ausgewählte Pegel der Einfluss möglicher Klimaänderungen analysiert wurde. Die Ergebnisse werden vorgestellt und diskutiert.

Eine kurze Übersicht biogeochemischer Stoffflüsse an ausgewählten Messstationen entlang des Rheins wird präsentiert. Die vorgestellten Kenntnisse zur Biogeochemie des Rheins veranschaulichen die Bedeutung des Wissens um Stoffquellen und ablaufende Prozesse im Rheinsystem.

Summary: By combining measured precipitation and climatic data as well as observed discharge data with a conceptual hydrological model the water balance components for the time period 1961–1990 are calculated for selected sub-basins of the River Rhine. Based on this the water volumes and the various hydrological regimes, which are occurring in the River Rhine basin are discussed. An analysis of 100-year hydro-meteorological and hydrological time series have shown that changes arose in the past decades. Even if these regional changes cannot be assigned to anthropogenic induced climate changes with the highest statistical security in the mathematical sense, the assumption of stationarity of hydro-meteorological and hydrological time series is no longer valid.

For the quantification of the effects of possible climate change on the discharge of the River Rhine and its tributaries extensive computations using regional climate scenarios for the entire Rhine basin are necessary using water balance and/or river basin models. For these investigations three regional climate scenarios were available, which were provided in the context of project "Klimaveränderung und Konsequenzen für die Wasserwirtschaft" (KLIWA) for southern Germany. The climate scenario provided by the Max-Planck-Institute (MPI) for Meteorology in Hamburg, based on the regional climate model REMO, takes the entire River Rhine basin into account. This climate scenario is converted with the help of the hydrological models LARSIM and HBV-SMHI into discharges and the model results of selected gauges are analysed in view of the impact of possible climate change. The results are presented and their maximum stress is discussed.

A short review of the biogeochemical fluxes estimated at selected measuring stations along the Rhine is given. The described knowledge available on the biogeochemistry of the Rhine illustrates the importance of understanding sources and processes of the biogeochemical important parameters in the Rhine system.

Introduction

The international research programme "Land Use and Climate Impacts on Fluvial Systems During the Period of Agriculture" (LUCIFS) aims to explore past to present responses of fluvial systems to climate change and human activities, thus providing a basis for the understanding of the long-term "memory" of fluvial environments. The system research focuses on questions of variable sensitivity, thresholds and non-linear

responses on different spatial and temporal scales. Within the RhineLUCIFS project, these issues are considered for the basin of the Rhine, which is one of the largest rivers in Europe.

Water fluxes form in all sub-systems of a river basin, e.g. biomass, soil, floodplain and water bodies, one of the main driving forces of weathering processes, soil loss, erosion and sediment dynamics as well as for biogeochemical fluxes. A wide range of temporal and spatial scales has to be considered here. Furthermore, the processes are interacting in various manners but concentrate and accumulate through the drainage network. Due to these facts, it is important to note that besides these regional aspects these processes participate in the global cycles via the oceans and atmospheric pathways. Additionally, it has to be pointed out that element fluxes in the landscape as well as in the aquatic environment are an integrating measure describing ecosystem functions.

In order to describe the water and element fluxes from one functional unit (or storage) to another, one common approach is the calculation of budgets. In recent times the modelling of the processes and of the interactions of the different sub-systems has become common practice in scientific research as well as in water resources management. Models are superficially similar to budgets, with the exception that they use equation systems instead of purely descriptive data to simulate the time course of water and material fluxes. Both approaches often gain additional insights by the simultaneous examination of fluxes of several interrelated materials (e.g. C, N, P) through the system. The advantage of models is that the interchanges between the processes can be (i) studied under defined external conditions, (ii) to test the results in comparison with observations and (iii) to improve the models, and (iv) to dare to make predictions about future system states.

In Part 1 of this study, the water budget of the River Rhine is described by longitudinal sections of annual means of the main water balance components, namely precipitation, evapotranspiration, runoff and streamflow. Furthermore, the wide variety of hydrological regimes within the Rhine basin is highlighted. Part 2 considers the interannual and decadal variability of the hydrological variables, which can be studied on the basis of 100- year time series. Another subject of study are the impacts of an anticipated climate change induced by the emissions of the so-called greenhouse gases on the hydrology of the Rhine and its main tributaries. Regional climate-change scenarios in combination with two macroscale hydrological models are used here.

In Part 3 a short review of some of the knowledge available on the biogeochemistry of the Rhine is given. It illustrates the importance of knowing the sources and understanding the processes of the biogeochemical important parameters. Moreover, the role of water fluxes as a key parameter in understanding the element fluxes from one station to the next one, is used to gain an understanding of the quantitative side of the biogeochemical processes in the river, its tributaries and of the influence of other aspects of global change affecting the basin.

The RhineLUCIFS benefits from earlier studies that are updated and summarised here in this new context.

1 Hydrological regimes in the River Rhine basin

1.1 Hydrography of the River Rhine basin

The basin area of the River Rhine (Fig. 1) represents 185,300 km2 and the 1,320 km long course of the river starting at the outlet of Lake Toma (Photo 1) in Switzerland is divided into six major stretches. Lake Toma, located in the northern high cirque of Piz Badus (2,928 m) is regarded as the source of the Vorderrhein. The Hinterrhein rises from the Paradies Glacier at the Mascholhorn (Adula Range) in the Rhine Forest area. The source rivers join in Reichenau, near Chur. Downstream of the unification up to the outlet of Lake Constance the river course is called the alpine Rhine. This is a high mountain river. The basin area up to the inflow in Lake Constance amounts to $6,122 \text{ km}^2$.

Below Lake Constance, from Stein am Rhein, the river flows west as the Hochrhein over a distance of 142 km until Basel. From the mouth of the Aare onwards, the discharge rate of the Rhine is affected by numerous glacier and high mountain streams, whose unbridled drainage patterns compensate for three alpine fringe lakes. The alpine Rhine and Hochrhein are marked by the influence of more than $16,000 \text{ km}^2$ of high mountain area, of which about 400 km^2 are covered by glaciers.

Downstream of Basel, the Upper Rhine flows through the approx. 300 km long and, on average, 35 km wide Upper Rhine graben, a tectonic rift. The lowland plain with a markedly flatter gradient than the Hochrhein caused over the centuries a network of channels (furcation zone). Numerous river training works have been undertaken there since the beginning of the 19th century. With the exception of the Neckar area, only relatively minor catchment areas follow; however, they have high run-off levels due to the high precipitation and the relief. In Mainz the tributary with the largest surface, the River Main, joins the Rhine after a distance of 524 km. Downstream up to Bingen only small secondary rivers flow into the Rhine.

The section of the Rhine that extends from Bingen to south of Cologne is called the Middle Rhine. Its meanders have cut 200 to 300 m down into the rock (Photo 2), and at the narrowest point the valley bottom is merely 200 m wide. The largest tributaries along this stretch are the Nahe, Mosel, Lahn, and Sieg Rivers, and of these the River Mosel, which is 545 km long and rises on the western slope of the Vosges Mountains, represents the main one.

Fig. 1: The River Rhine basin with catchment borders of main tributaries and interim basins. Gauges for description of hydrological regimes and biogeochemical fluxes are depicted

Das Rheineinzugsgebiet mit den Einzugsgebietsgrenzen seiner größten Nebenflüsse sowie wichtiger Zwischengebiete. Dargestellt sind weiterhin die Pegel, für die eine Beschreibung des hydrologischen Regimes und der biogeochemischen Flüsse erfolgt

South of Cologne the Middle Rhine discharges into the Niederrheinische Bucht. The Lower Rhine flows like a typical lowland river in wide meanders. At the western Lower Rhine the watershed of the Meuse is close to the Rhine. Since the water level of the Meuse

is lower than that of the Rhine, subterranean drainage towards the Meuse is easy.

Immediately after the German-Netherland border, the Rhine delta begins, the area where the Rhine and the Meuse dovetail; that is why the catchment area of

Photo 1: The outlet of Lake Toma in Switzerland $\sim 2,400$ m a.s.l.) is considered as the source of the River Rhine (Photo: KRAHE)

Der Abfluss aus dem Tomasee in der Schweiz (~2.400 m üNN) wird als Rheinquelle betrachtet (Photo: KRAHE)

Photo 2: The Middle Rhine at low water condition in 2003 near Kaub (Photo: DRÖGE) Der Mittelrhein bei Kaub während Niedrigwasser 2003 (Photo: DRÖGE)

the Meuse might also be regarded as belonging to the Rhine. The Ijssel and its main tributary the Vechte, both of which are typical lowland rivers, could also be included in the Rhine area, since Rhine water flows into the Ijssel Lake via the Pannerdensche Canal. Both rivers drain the western part of the Münsterland, a region that is characterised by sandy and marshy landscapes, high ground-water levels, and leisurely-flowing rivers with numerous forks. Because of the slight incline this region is only inadequately drained by the unhurried flow of the rivers Vechte, Dinkel, Berkel, and other tributaries of the Ijssel system. In the natural state of these waters the watersheds in this landscape are variable, depending on the water levels of the rivers.

The various hydrological phenomena within the Rhine basin are caused by meteorological processes acting jointly on the basin characteristics. Generally, within the basin there is a transition from the maritime climate in the north and northwestern part to the more continental conditions in the south and southeastern part. The maritime character of the climate is shown in the dominance of advective (frontal) weather situations, which influence the run-off regime of the Rhine and its tributaries as well as in the continental index after Iwanov considering climate variables. After these the borderline between maritime and continental climate can be drawn on the line Belfort-Stuttgart-Bamberg (BRUNOTTE 1997). From the climate perspective and taking into account orographic effects on meteorological variables the Rhine basin can be subdivided in three main climatic regions namely the pre-Alps and Alps (catchment upstream of Basel), then the medium mountain ranges (between Basel and Cologne) and finally the plains in the North (downstream of Cologne).

The flow regime in the Rhine is dominated by melt water and precipitation run-off from the Alps in summer months and by precipitation run-off from the uplands in winter. Further downstream, the influence of the uplands grows more and more, and over the year the discharge becomes very compensated.

1.2 Observation and determination of water balance components

The water balance of a catchment is composed of the elements areal precipitation (P), areal evapotranspiration (E) areal run-off (R) and change in water storage (δS). Under particular hydrogeological conditions, in particular in karst areas, natural underground inflow and outflow (I) must also be taken into account. The water balance describes the hydrological character of the catchment and provides an overview of the available water resources. The relation between the components is given in the water balance equation, which is expressed by: $P = E + R + \delta S - I$. The term δS encompasses the storage of water in the compartments vegetation cover by interception, surface depressions, snow cover, glacier, saturated and unsaturated soil as well as water bodies. The storage compartments are interconnected by vertical water fluxes such as snow and glacier melt, infiltration, percolation through the soil, groundwater recharge or seepage water and capillary rise as well as lateral water fluxes such as surface runoff, interflow and groundwater discharge (s. Fig. 2). Groundwater discharge can interact with adjacent water bodies in two directions due to ex- and infiltration processes. Those are dependent on the water level in the water body and in the groundwater body.

Whereas estimates of precipitation and run-off are based on measurements, evaporation and the storage compartments as well as the water fluxes between them can be determined by measurement equipment only on a plot or hill slope scale. Therefore, estimates of these quantities on the catchment scale can be made only by use of empirical methods, water balance models and in some cases, e.g. groundwater discharge, by analysing discharge hydrographs.

Precipitation constitutes the central input in hydrological systems. It varies tremendously in space and time (LHG/BWG 2002; BMU 2003). Therefore, it is to be measured with complex observation station networks if reliable statements are to be made. It has to be noted that precipitation measurements are affected by systematic measurement errors. In general the measurement errors lead to an underestimation of annual precipitation totals in the order of \sim 10%. Especially in the mountainous regions the level of unreliability increases. For water balance computations the point measures have to be aggregated to areal mean values. Methodologies of different complexity are used for this. For the estimation of areal means for sub-basins in the Rhine basin this was done by a compilation of different raster based data sets. These data sets are provided by the International Commission for the Hydrology of the Rhine basin (CHR/KHR). The gridded precipitation data (\sim) km x 1 km; 7 km x 7 km) are aggregated by arithmetic average to 134 sub-basins on the first level. The basin sizes range from \sim 500 km² to \sim 2,000 km².

Evaporation is the transformation of water into water vapour at temperatures below the boiling point. Even at temperatures below zero water continues to evaporate, for instance from snow surfaces or ice covers. However, not only water surfaces or wetland surfaces contribute to evaporation, even soils that appear dry evaporate as long as the soil capillaries transport water to the surface. This direct release of water vapour from vegetation-free surfaces is called *evaporation*. Plants release water that was taken up by their roots into the air by *transpiration*. Precipitation and evapotranspiration (evaporation plus transpiration) are the two main components of the global cycle of water.

Evapotranspiration measurements over vegetated surfaces are rather difficult and expensive; only a few stations can boast long time series of such data. That is why the evapotranspiration is determined as an approximation from easily measurable meteorological factors or from soil and vegetation parameters. As a first step, the *potential evaporation* (ET_p) is computed from meteorological parameters. The fact that different ET_p formulas result in different ET_p -estimates led to the definition of the FAO grass reference evapotranspiration (ALLEN et al. 1994). The grass reference evapotranspiration is founded on the Penman-Monteith relation (MONTEITH 1973) and is defined as the evapotranspiration of grass of 12 cm height with a soil water content of at least 70% of the available field capacity. The min-

Fig. 2: Run-off components in a catchment with run-off generation and influencing factors on runoff hydrograph. Numbers indicate duration time of water within the hydrological storages (after BAUMGARTNER a. LIEBSCHER 1990)

Abflusskomponenten im Einzugsgebiet und Faktoren, die die Abflussbildung und den Gerinneabfluss bestimmen. Zahlenangaben geben die Verweildauer der Wasserinhalte in den hydrologischen Speichern wieder (nach BAUMGARTNER u. LIEBSCHER 1990)

imum surface resistance r_c is determined as 70 s/m. The aerodynamic resistance r_a results in 208 s/m for a wind speed of 1 m/s (WENDLING 1995).

By application of the hydrological model HBV-SMHI (BERGSTRÖM 1996) which is calibrated for the whole Rhine basin (EBERLE et al. 2001) the gross reference evaporation is transformed to actual evapotranspiration values. The gross reference evaporation is calculated after the equation of WENDLING (1995) as areal means for 134 sub-basins of the Rhine basin. The sum of these daily amounts yields the annual and monthly evaporation depth in mm, here averaged over the period 1961 to 1990 for further analyses.

The volume of water that flows through a certain channel cross-section per unit of time is referred to as discharge. It is usually measured in m³/s or l/s. If the flow observed at a certain cross-section is applied to the surface of the related catchment area, the resulting entity is referred to as *discharge per unit area* in l/s · km2 or *run-off depth* in mm/unit of time. The latter can be directly compared with the precipitation and evaporation parameters in the water balance equation. From the

Table 1: Surface areas of sub-basins of the River Rhine

Teileinzugsgebiete des Rheins

** Surface area

** Official km–0 is at the Rhine bridge in Constance

water balance components in large river basins only the discharge can be estimated based on observed water levels at gauging stations and measured rating curves (water level-discharge relation).

Viewed over several years, the total run-off indicates the volume of the potential water resources. Its usability is limited by many factors, such as yield, quality, ecological aspects and storage capacity. But the values are relevant for examining the water resources in small areas such as catchment areas of waterworks and reservoirs, for instance.

1.3 Annual means of water balance components in the Rhine basin

The regional distribution pattern of the water balance components especially of the mean annual discharge (MQ) offers valuable basic information on the availability of surface water and on the hydrological background as well. However, the mean volume of discharge varies considerably depending on the region as well as time and duration. During low-frequency, highvolume discharge events (floods), large volumes of water flow through the watercourses without being able to be used for water management purposes. Furthermore, major installations and housing estates which use large amounts of water also need information on whether the water volume they require can be guaranteed without any risk of long interruptions in supply. Because of these dependencies, measurements of flow variability, based on the quotients of main discharge values

(MHQ/MNQ or HHQ/NNQ), are important indicators. Multi-year discharge measurements are required in order to calculate the main values for a gauging station (Tab. 3).

In order to illustrate the hydrological background the mean annual precipitation, evapotranspiration and run-off depths are listed, too (Tab. 4). While the discharge values are deduced from observed data, the runoff depths are calculated by means of the HBV-SMHI model. Therefore, these values represent the natural water cycle within the named basins. Additionally, the run-off coefficient, calculated as the ratio of mean annual run-off depth to mean annual precipitation depth is registered. The standard 30-year reference period (currently 1961–1990), as recommended by the World Meteorological Organization (WMO), is used. Therefore, all figures and tables show mean values for this reference period. Based on daily values long-term means for months, hydrological year and hydrological halfyears has summed up. The importance of the snow cover for hydrological questions cannot be taken into account here. Detailed maps and illustrations, for example duration of snow cover and water equivalent can be found in the Hydrological Atlas of Germany (BMU 2003) and Hydrological Atlas of Switzerland (LHG/BWG 2002).

The discharge in the River Rhine increases as the catchment area and length of the water course increase (Fig. 3). The longitudinal sections show the mean discharge (MQ), the mean lowest discharge (MNQ), the mean highest discharge (MHQ). The mean discharge

River Rhine stretch	Gauge	River	A_{E_0} * $\lceil \mathrm{km^2} \rceil$	P mm	Е mm	R mm	R/P $\lceil\% \rceil$
Alpine Rhine	Diepoldsau	Rhine	6,120	1,475	340	1,135	0.8
Hochrhein	Basel	Rhine	35,920	1,410	495	915	0.6
Upper Rhine	Maxau	Rhine	50,200	1,315	520	795	0.6
Upper Rhine	Worms	Rhine	68,830	1,160	510	650	0.6
Middle Rhine	Kaub	Rhine	103,490	995	500	495	0.5
Middle Rhine	Andernach	Rhine	139,550	965	505	460	0.5
Middle/Lower Rhine	Cologne	Rhine	144,230	960	505	455	0.5
Lower Rhine	Rees	Rhine	159,300	950	505	445	0.5
Hochrhein	Untersiggenthal	Aare	17,630	1,515	500	1,015	0.7
Upper Rhine	Rockenau	Neckar	12,680	895	545	350	0.4
Upper Rhine	Raunheim	Main	27,100	765	535	230	0.3
Middle Rhine	Cochem	Mosel	27,090	915	525	390	0.4
Lower Rhine	Schermbeck	Lippe	4,780	810	555	255	0.3

Table 3: Mean annual values of water balance components for river basins at gauges in the River Rhine basin for the time period 1961/90 Mittlere Jahressummen der Wasserhaushaltskomponenten ausgewählter Pegeleinzugsgebiete für die Zeitreihe 1961/90

* Surface area

River Rhine stretch	Gauge	River	MNO $\left[\mathrm{m}^3/\mathrm{s}\right]$	MQ $\left[\mathrm{m}^3/\mathrm{s}\right]$	MHQ $\left[\mathrm{m}^3/\mathrm{s}\right]$	Mq $\left[1/s \cdot m^2\right]$	MHQ/MNQ \Box
Alpine Rhine	Diepoldsau	Rhine	76	234	894	38	12
Hochrhein	Basel	Rhine	490	1,070	2,660	30	5
Upper Rhine	Maxau	Rhine	610	1,290	3,130	26	5
Upper Rhine	Worms	Rhine	677	1,440	3,430	21	5
Middle Rhine	Kaub	Rhine	790	1,720	4,250	17	5
Middle Rhine	Andernach	Rhine	930	2,120	6,110	15	
Middle/Lower Rhine	Cologne	Rhine	970	2,200	6,320	15	
Lower Rhine	Rees	Rhine	1,090	2,380	6,470	15	6
Hochrhein	Untersiggenthal	Aare	230	565	1,390	32	6
Upper Rhine	Rockenau	Neckar	35	138	1,010	11	29
Upper Rhine	Raunheim	Main	61	201	926		15
Middle Rhine	Cochem	Mosel	57	335	2,030	12	36
Lower Rhine	Schermbeck	Lippe	14	43	232	9	17

Table 4: Main data of gauges in the River Rhine basin for the time period 1961/90

Gewässerkundliche Hauptwerte ausgewählter Pegel im Rheineinzugsgebiet für die Zeitreihe 1961/90

per unit area (Mq) usually decreases in the direction of the flow (Tab. 3, Fig. 4), corresponding to the decrease of the run-off generation with increasing catchment area due to meteorological and catchment related characteristics as well (Tab. 4). This is also true for the main tributaries of the Rhine (Fig. 4). The spatial patterns of the evaporation show not such a clear picture. This is due to the fact that a general increase of evaporation

from the north to the south is counteracted by the increase in ground level elevation. Furthermore, the evapotranspiration values are modulated by land use characteristics, which are specific for the lowland, upland and alpine areas of the Rhine basin.

The discharge increases abruptly downstream wherever high-volume tributaries flow into the receiving waters. Such situations are especially downstream of the

Fig. 3: Longitudinal section of the River Rhine downstream of Reckingen up to the German-Netherland border Abflusslängsschnitt des Rheins von Reckingen bis zur deutsch-niederländischen Grenze

inflow of the large tributaries of the Rhine, i.e. the rivers Aare, Neckar, Main and the Mosel into the Rhine. At Diepoldsau not far away from the inflow of the alpine Rhine into the Lake Constance the mean discharge is approximately 234 m³/s and the mean discharge per unit area constitutes $38 \frac{\text{1}}{\text{s} \cdot \text{km}^2}$. By the mouth of the River Aare, the mean discharge has reached 565 m³/s. The Rhine's mean discharge (MQ)

Fig. 4: Mean annual totals of water balance components precipitation (P) , evapotranspiration (E) and run-off (R) as well as annual discharge per unit area for the time period 1961/90 for selected gauges of the River Rhine and selected tributaries

Mittlere Jahressummen der Wasserhaushaltskomponenten Niederschlag (P), Evapotranspiration (E) und Abfluss (R) der Zeitreihe 1961/90 für ausgewählte Rheinpegel und Nebenflüsse

almost doubles due to the Aare joining it and reaches around 1000 m3 /s. There are no significant rises in the mean discharge in the Upper Rhine valley between the rivers Aare and Neckar. Over this approximately 325 km-long stretch the discharge increases to around 1,290 m3 /s and the mean discharge per unit area reaches $26 \frac{1}{s} \cdot km^2$ at the mouth of the River Neckar. Again, the discharge only increases slightly between the mouths of the rivers Neckar and Main. With its mean discharge of approximately 206 m3 /s, the Main raises the Rhine's mean discharge to around $1,670 \text{ m}^3\text{/s}.$

Whereas the mean discharge grows at the mouth of the Mosel in relation to the size of the Mosel catchment area, the mean highest discharge increases disproportionately from around $4,250 \text{ m}^3/\text{s}$ to $6,110 \text{ m}^3/\text{s}$. This value indicates the high flood-risk potential, which the Mosel catchment area poses for the lower course of the Rhine. The Mosel's susceptibility to flooding is chiefly due to the pronounced relief and the low permeability of the bedrock in the upland section of its catchment area. Downstream from the mouth of the Mosel, the discharge only increases slightly. At Rees, near the German-Netherlands border, the Rhine's catchment area takes in $159,300 \text{ km}^2$ and the mean discharge is approximately 2,380 m³/s, corresponding to a mean specific discharge of around $15 \frac{\text{J}}{\text{s} \cdot \text{km}^2}$.

While the discharge of the River Rhine itself becomes more and more quite balanced downstream, in the upper courses of the smaller tributaries, however, the flow variability is high, as shown by quotient MHQ/MNQ. The variability is particularly high in those rivers where the upper reaches are contained in the uplands, e.g. the Rheinisches Schiefergebirge and the Black Forest. This corresponds to the general tendency for the discharge variability to drop as the catchment area increases because the larger the catchment area, the more local conditions are compensated.

The registered values of flow variability (Tab. 3) show further specific regional features in Rhine's hydrological structure. The discharge variabilities differ considerably between rivers, even they save comparable river basin areas. The rivers in the upland ranges (Neckar and Mosel) have significantly higher discharge variabilities (29 and 36) than the lowland rivers, which are mainly controlled by groundwater input. On the other hand the flow variability of the upland River Main is with a variability index of 15 comparable to the lowland River Lippe which takes a value of 17. This can be attributed to specific catchment characteristics of the River Main basin.

The flow variability within the alpine part of the Rhine basin shows a complex picture as well. While the variability index of the alpine Rhine up to Diepoldsau amounts to 12 times that of the River Aare is reduced to 6 and downstream at Basel only a value of 5 is found. This value persists along the Rhine up to the Kaub gauge located at the beginning of the Middle Rhine. The low variability index can be attributed to the influence of the lakes and reservoirs located in the alpine and Hochrhein basins, while further downstream the superposing of the different run-off regimes of the tributaries is an explanation for the low index values mentioned. Up to the Rees gauge the variability index increase to a value of 8.

It has to be noted, that the annual means of water balance components show a high year to year variability. The mean temporal fluctuation range of the annual precipitation totals during the 30-year reference period is, with regional differences, around \pm 20%. However, some annual values can differ considerably from the mean values of the 30-year period observed, which shows data from selected stations. These differences between the precipitation totals registered for individual years and the mean value clearly demonstrate that a 30 year averaging period is not necessarily representative of the mean precipitation totals at any one station or basin. It is perfectly possible for one extremely high or low annual value to have a decisive influence on the mean value.

Since precipitation varies considerably more than evapotranspiration, the average run-off over a number of years varies geographically in approximately the same way as precipitation does. Within individual years variations in precipitation and run-off also match each other fairly closely. The total variation in run-off from one year to next is often very large, mainly as a result of large variations in precipitation from year to year. Along the River Rhine this variability can be estimated at \pm 30%. In the tributaries this can be increase to \pm 60%.

The relationship between run-off in one year and in the next is weak. On the other hand there is a certain tendency for both dry and wet years to cluster. These clusters may be seen as natural coincidences, typical of the random variations in precipitation and hence runoff as well.

1.4 Hydrological regimes

In general "regime" is used in a hydrological sense to refer to the relative or absolute variations of one element of the water cycle within a particular time period (LHG/BWG 2002). "Discharge regime" is often used to designate the general hydrological behaviour of a river. The long-term average seasonal variations of discharge will be referred to as "regime" in accordance with the

classical use of the term. These regimes can be described in terms of the dimensionless Pardé coefficients (PK_i), defined as the ratios of monthly and yearly runoff or by long-term average monthly values. There is a long tradition of research dealing with characterisation of rivers using run-off regimes. PARDÉ (1933) in France, KELLER (1968) in Germany, GRIMM (1968), ASCH-WANDEN and WEINGARTNER (1983) in Switzerland, or MADER et al. (1996) in Austria studied the flow characteristics of rivers.

The run-off regime is a product of the temporal variation of the water balance in a catchment area and is, therefore, influenced by all the factors that control run-off.

Run-off regimes take into account the periodical discharge behaviour during the year, maximum and minimum flow periods, extreme flows over an extended observation period, and the frequency distribution of characteristic hydrological discharge values. For example, the knowledge of periodical occurrences of high or low-flows, or the reliability of a specific discharge for a given time or season, might be of special interest in water resources management (power stations, dilution of discharges etc.). The given run-off regime is moulded by the natural boundary conditions and can be modified by anthropogenic influences in the river basin (e.g. weirs, diversions).

Year diagrames composed of the twelve monthly values (Fig. 5 to 8) show characteristic curves that can conventionally be classified by the influence of, e.g., dry periods and/or number of maxima. According to KELLER (1961), *nival* regimes are dominated by snow storage and snow melt, in *nivo-pluvial* regimes the snow melt peak is higher than the peak resulting from rainfalls, in *pluvio-nival* regimes rainfall peaks exceed the snow melt peak, and *pluvial* regimes are only influenced by rainfall. Glacial regimes are dominated by storage of water in glaciers and run-off of glaciers. In glacial regimes the discharges depend on the seasonal temperature variations with a minimum in winter and maximum in summer. The daily variations in summer are dominated by the daily temperature regime in this regime type.

A detailed classification and a regionalisation of discharge regimes can be found in LHG/BWG (2002) and BMU (2003). The catchments under study there are between 10 km2 to 500 km2 for the Swiss part (LHG/BWG 2002, map 5.3) and from 200 km^2 to 800 km^2 for the German part of the Rhine (BMU 2003, map 3.11). An initial classification of regimes in Switzerland reveals distinctive alpine and midland-Jurassic, which differ from one another in their respective number of maxima. For example, regimes with a single maximum are

Mittlere Monatssummen der Wasserhaushaltskomponenten Niederschlag (P), Evapotranspiration (E) und Abfluss (R) der Zeitreihe 1961/90 für Einzugsgebiete ausgewählter Rheinpegel

found on the north side of the Alps above an average of catchment altitude of 1,550 m, whereas below this altitude regimes with several maxima occur. The natural flow conditions are depicted, but it is important to note that many rivers have been changed by human influences, especially in the Alps. Detailed information about this topic can be found in LHG/BWG (2002, map 5.3).

Generally, the flow regime in River Rhine is dominated by melt water and precipitation run-off from the Alps in summer months and by precipitation run-off from the uplands in winter. Therefore, the dominating regimes which can be found upstream of Basel are nival and nivo-pluvial regimes. There is a slightly decrease in the summer maximum which is caused by a reservoir storage of 1.9×10^9 m³, taken in summer and consumed in winter for power production. This volume corresponds to a mean run-off of about 50 mm in Rhine basin upstream of Basel. Also the retention in the alpine border lakes should be considered: this causes smoothing of the discharge trends.

Further downstream the influence of the uplands grows more and more, and over the year the discharge even becomes compensated. The pluvial regime with a

Fig. 6: Mean monthly totals of water balance components precipitaion (P), evapotranspiration (E) and run-off (R) for the time period 1961/90 for selected tributaries of the River Rhine

Mittlere Monatssummen der Wasserhaushaltskomponenten Niederschlag (P), Evapotranspiration (E) und Abfluss (R) der Zeitreihe 1961/90 für ausgewählte Nebenflüsse des Rheins

charge components from the high mountains and those from the hilly country complement each other nearly ideally. Pluvio-nival regimes are restricted to the higher parts of the tributaries mentioned. At the Mosel con-

Fig. 7: Mean monthly lowest (MoMNQ), highest (MoMHQ) and monthly arithmetic mean values (MoMQ) of discharge of selected gauges of the River Rhine for the time period 1961/90

Mittlere monatliche niedrigste (MoMNQ) und höchste (MoMHQ) sowie monatliche Mittelwerte des Durchflusses (MoMQ) ausgewählter Rheinpegel der Zeitreihe 1961/90

fluence the discharge maximum moves to the winter season, maintaining however a considerable discharge in summer thanks to the water supply from the alpine regions. On the one hand the winter maximum can be characterised by evapotranspiration during the growing season in summer exceeding the contribution of the precipitation to the run-off, in spite of the precipitation maximum in this period. On the other hand, winterprecipitation falls in the lower parts of the basin predominately as rain, while casual snowfall melts quickly. Going downstream the declining contribution of the tributary basins to the mean yearly run-off is mainly caused by regression of precipitation in the lower parts of the basin.

2 Overview of the impacts of climate change on run-off on the catchment scale

2.1 Global climate change

The global climate change, which is expected due to the anthropogenic-caused emissions of the so-called greenhouse gases, as well as an assessment of its possible effects are described in detail in the Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC 2001). In the $20th$ century the global average temperature rose around approx. 0.6°C and precipitation over land in middle and high latitudes of the northern hemisphere clearly increased. The

Fig. 8: Mean monthly lowest (MoMNQ), highest (MoMHQ) and monthly arithmetic mean values (MoMQ) of discharge of selected tributaries of the River Rhine for the time period 1961/90

Mittlere monatliche niedrigste (MoMNQ) und höchste (MoMHQ) sowie monatliche Mittelwerte des Durchflusses (MoMQ) ausgewählter Nebenflüsse des Rheins für die Zeitreihe 1961/90

largest part of the global warming over last 50 years can be probably attributed to the activities of humans. For 21st century the global warming is expected to continue at an accelerated rate and that will clearly change precipitation region specifically. Depending upon the accepted emission scenarios, climate models predict a rise in the mean global near-surface temperature of around 1.4°C to 5.8°C (ProCliM 2002). In the IPCC "Special Report on Emission Scenarios" (NAKICEN-OVIC et al. 2000) emission scenarios – the so-called SRES scenarios – were published. From these the B2 scenario was selected for the study within the Rhine basin. B2 is a "dynamics-as-usual" scenario, where differences in the economic growth across regions are gradually reduced and concerns for environmental and social sustainability at the local and regional level rise gradually along the time horizon up to the year 2100.

It is expected that the probability and the spatial distribution of extreme events will gradually shift with the climatic change. The extent and the character of the changes will be different depending upon the place and the kind of extreme events. Recently, throughout the world an accumulation of natural disasters has been registered, from which those in Central Europe, for example the flood events in the River Elbe and River Danube area in August 2002, cannot be exempted. This accumulation could be coincidental, caused by natural long-term climatic variations or as a consequence of the anthropogenic influences on climate. For reasons of principle it is difficult or even impossible to prove or exclude statistically a trend in the frequency from rare extreme events. It is conceivable that longterm changes of extreme events can only be proved when they have reached a considerable magnitude and caused great damage (OCCC 2003).

The aim of regional climate impact research is to transfer future prospects forecasts on a global scale to a regional scale and identify sensitive regions (SCHÄR 2000). Furthermore, in terms of sustainable development and according to the principle of precaution, the need for action and action strategies should be devised to minimise possible harmful events.

In order to study the impact of climate change on hydrology and to develop strategies for the protection and adjustment of water resources, it is necessary to consider in terms of river catchment areas. In the following selected statements about changes in the past as well as prospects for the future for the catchment area of the Rhine up to the German-Netherlands border ($AEo = 159,500$ km²) have been made. Whereby emphasis is on estimations of the Rhine itself. Studies at sub-basin level are at present being carried out in the project Climate Change and Consequences for Water Management (KLIWA), a joint project of the states Baden-Württemberg and Bavaria as well as the German Weather Service (BARTELS et al. 2004b).

2.2 Observed trends of hydrometeorological and hydrological variables in the Rhine basin

On the basis of the analysis of long time series of air temperature, station and areal mean precipitation as well as discharge, the long-period fluctuation behaviour can be studied. Different statistical characteristic values, such as, for example, the average values of the hydrological half-years of winter (November to April) as well as summer (May to October), are considered. A large portion of this fluctuation behaviour is related to the decade variability, i.e. for periods of approx. ten years duration weather periods of a certain kind frequently occur. This fluctuation shows a trend behaviour that, however particularly for precipitation and for discharge, is region-specifically strong pronounced. During the interpretation of trend analyses the dependence of the selected time period has to be considered. For an example in figures 9–11 time series from 1891 to 2002 of air temperature, areal mean precipitation and discharge for the Cologne gauge are depicted for the hydrological winter (and/or concerning the temperature representatively for the area of Central Europe, supplement after BAUR 1975). In the temperature series of Central Europe the positive trend, as determined for the global air temperature, clearly appears. High winter temperatures arise since 1990 in a more frequent manner. The trend of the winter precipitation likewise exhibits an increase. The analyses of precipitation changes show stronger positive trend since around 1970 (break-point analysis). These general tendencies are also supported by station related statistical investigations. KRÜGER (2002) determined for stations from Nordrhine-Westphalia in the summer a decrease of the precipitation depth and in the winter an increase. This trend is significant in summer at 26% and in winter at 32% of the stations. Also the trends of precipitation found by BARDOSSY and CASPARY (1990), SCHÖNWIESE et al. (1997), WIDMANN and SCHÄR (1997) as well as KLIWA (2003a) confirm this tendency as far as possible. Highly-correlated with the long-term fluctuations of precipitation is the discharge of the winter half-year. Since around 1980 an increase of high winter discharges can be registered. This trend is strongly pronounced in a regionally-specific way even in smaller river catchments (KLIWA 2002, 2003b; PFISTER et al. 2000). Generally, an accumulation of discharge-rich winters can be stated, in particular in the higher altitudes of the low mountain ranges aligned to the west.

Fig. 9: Decadal variability and linear trend of air temperature (LT) in Central Europe for the hydrological winter halfyear

Dekadische Variabilität und linearer Trend der Lufttemperatur (LT) in Mitteleuropa für das hydrologische Winterhalbjahr

Dekadische Variabilität und linearer Trend der Gebietsniederschlagshöhe (MGNh) für das Rheingebiet bis zum Pegel Köln für das hydrologische Winterhalbjahr

Fig. 11: Decadal variability and linear trend of discharge (MQ) at the Cologne gauge for hydrological winter halfyear

Dekadische Variabilität und linearer Trend des Abflusses (MQ) am Pegel Köln für das hydrologische Winterhalbjahr

As a cause for the observed trend behaviour of the hydrometeorological and hydrological time series a changed occurrence in the frequency and in the maximal duration of westerly atmospheric circulation patterns is considered (CASPARY 2004). Thus the positive winter precipitation trend is confirmed by an increase of zonal weather conditions for Central Europe (BARDOSSY a. CASPARY 1990; CASPARY 2004; GÜNTHER 2004; PFISTER et al. 2004). WIDMANN and SCHÄR (1997) do not attribute the trend for Switzerland to a significant change of frequency of weather conditions, but still see it as part of the natural variability with normal frequency of the weather conditions.

In table 5 characteristics of air temperature, areal mean precipitation and discharge at the Cologne gauge specified for the hydrological year and the hydrological half-years are listed. For the characterisation of the decadal variability the smallest and the largest deviation of the 10-annual average-value from the average value of the time series 1990/99 is used.

2.3 Estimation of the effect of climate change on the discharge regime of the River Rhine

The effects of climate changes on hydrology and implications for water resources in general have been investigated in the Rhine basin by applying various climate scenarios and hydrological models (KWADIJK a. ROTMANS 1995; MIDDELKOOP et al. 2001; MENZEL et al. 2002; KLEINN 2002). Results obtained by these scenario simulations mostly suggest higher winter discharges, as a consequence of an increase in winter rainfall and a slightly decrease in summer run-off, due to an increase of evaporation. But it has to be noted that ZEHE et al. (2004) have found a general decrease of precipitation and discharge in their $2xCO_2$ -scenario exper-

Fig. 12: Methodology of coupling results of global and regional climate models in hydrological impact analysis of climate change

Methodik zur Kopplung der Ergebnisse von globalen und regionalen Klimamodellen in der hydrologischen Klimafolgenforschung

iment in the Rhine basin. This indicates that the scenario techniques in use so far are accompanied with large uncertainties.

In order to be able to create a basis for the definition of water management action strategies, it is necessary, to assess the changes of the hydrometeorological variables in the Rhine area for the next decades with the help of suitable regional climatic scenarios and to convert these results to discharge scenarios, using water balance models. Figure 12 shows schematically this procedure in principle (changed after ANDRÉASSON et al. 2004).

All regional climate models and statistical procedures of today exhibit for different reasons uncertainties and process-determined pros and cons. The selection of a suitable model or procedure depends in the long run on the application purpose and is therefore to be evaluated in each case of concrete application. In the KLIWA project different regionalization procedures were used therefore, in order to get a bandwidth of possible results (BARTELS et al. 2004a). The respective results were made comparable by defining appropriate defaults in advance (see below) in order to be able to relate them to past knowledge levels of the analysis of the long-term behaviour of the hydrometeorological variables. Changes of precipitation, especially in the hydrological winter half-year, are of particularly interest. The results of the climate scenarios are used as input for water regime computations, covering the following variables precipitation, air temperature, relative humidity, air pressure, global radiation or duration of sunshine, and wind velocity.

The substantial steps of the conversion of the regional climate scenarios to the hydrological models are shown in figure 12. Statements for changes of the hydrometeorological variables which can be expected in the future (e.g. precipitation and air temperature) can be made best by the comparison of future scenario results with the simulated actual condition (control run), because existing biased errors of the climatic model are at least partly eliminated thereby. The resulting assessments of hydrological changes form the basis for an estimation of the effects on the water management.

The comparability of the regional climate scenarios in the KLIWA project was reached by the following defaults:

– All regional models use results of the global climatic model ECHAM4 of the Max-Planck-Institute for Meteorology in Hamburg (MPI) for the emission scenario B2.

– The quality of regional simulations is examined by comparison along and adjustment at measuring and observation data from 1971 to 2000. Thus, changed conditions of the recent past are considered. In the

Table 5: Results of trend analyses of air temperature of Central Europe areal precipitation depths, and discharge at Cologne gauge of hydrological half-years and years of time period 1891/2002

Ergebnisse der Trendanalysen der Temperaturreihe Mitteleuropas und der Gebietsniederschlagshöhen sowie des Abflusses				
für den Pegel Köln für hydrologische Halbjahre und das hydrologische Jahr der Zeitreihe 1891/2002				

* Trend/noise-ratio = (11a-average at the end of time series – 11a-average at the begin of the time series/standard deviation of time period 1961/90

** Time series 1891–1989

control run, which has to be accomplished in parallel, the influence of the global climatic model (ECHAM4) for the same time series becomes visible. With help of the control run the differences from the intended scenario period have to be determined, whereby biased errors of the ECHAM4 will be partially balanced.

– For the period 1951 to 2000 the complete and homogenized data records examined are made available of approximately 75 climate stations.

– For verification and validating runs statistically characteristic numbers are fixed for middle, extreme and persistence behaviour of the hydro-meteorological variables, specified above.

– For comparison of the regional models a uniform, in the nearer future lying time horizon is specified from 2021 to 2050.

– The results of model calculations are to be made available as daily values. Exception is the modelling of the MPI, which can supply hourly values.

The point results (station values) of the two statistical procedures (GERSTENGARBE et al. 2002; ENKE 2003) to determine climate scenarios for 2021–2050 were not yet used for modelling the Rhine, since station density in the foreign catchment area portions does not permit a scenario production. It is, however, intended to use these scenarios for selected tributaries of the Rhine in order to arrive at an estimation of the uncertainties. The results of the regional dynamic model REMO (JACOB a. PODZUN 1997) are available as time series of hourly values in the form of raster value files (1/6° x 1/6°, about 18 km x 18 km, JACOB et al. 2003).

The meteorological variables precipitation, air temperature, humidity, wind velocity, and radiation simulated with REMO serve as input for the water balance models LARSIM and HBV-SMHI. Comparative simulations for present climate and the climate scenario permit the quantification of possible hydrological effects.

For the Rhine basin the calibrated and well established LARSIM water balance model (BREMICKER 2000; EBEL et al. 2000) and the HBV-SMHI precipitation-run-off model (BERGSTRÖM 1996; EBERLE et al. 2001) are used.

The LARSIM (Large Area Runoff Simulation Model) computes on a raster of 18 km x 18 km the processes interception, actual evapotranspiration, snow accumulation, -setting and -melting, soil water and groundwater storage, lateral water transportation to water bodies (run-off concentration) as well as translation and retention in water bodies. Anthropogenic measures (e.g. water conduits as well as discharge regulations by retention basins and dams) can be modelled, too. The raster is co-ordinated with the regional climatic model REMO. The model was calibrated on the basis of measured hydrological and meteorological data for the period 1992/97 and verified for the period 1987/92.

The HBV (Hydrologiska Byråns Vattenbalansavdelning) model is a development of the Swedish Meteorological and Hydrological Institute (SMHI). The hydrological computation unit is the sub-basin, within which height zones are defined in order to improve simulation of snow processes. Each height zone is further subdivided into forested and non-forested areas to take into account the different hydrological behaviour of these land use units. Originally the model has been developed as a long-term simulation model working on a basis of daily values. For the modelling in the Rhine area sub-basins are used, which usually exhibit a surface size between 500 km^2 and $2,000 \text{ km}^2$.

Fig. 13: Mean half-yearly and yearly areal precipitation depths of the Rhine basin up to the Cologne gauge (observed data, validating run (VL), REMO control (CR) and scenario run (SC))

Mittlere Halbjahres- und Jahressummen des Gebietsniederschlages für das Rheingebiet bis zum Pegel Köln (Messwerte, Validierungslauf (VL), REMO-Kontroll- (CR) und Szenarienlauf (SC))

Fig. 14: Mean half-yearly and annual averages of areal air temperature of the Rhine basin up to the Cologne gauge (measured values, validating run (VL), REMO control (CR) and scenario run (SC))

Mittlere Halbjahres- und Jahresmittel des Gebietsmittels der Lufttemperatur für das Rheingebiet bis zum Pegel Köln (Messwerte, Validierungslauf (VL), REMO-Kontroll- (CR) und Szenarienlauf (SC))

Fig. 15: Discharge changes of hydrological winter half-year for selected gauges of the River Rhine and its tributaries by direct use of results of the regional climatic model REMO as averages for time periods 2020/29, 2030/39, and 2040/49

Änderungen des Abflusses im hydrologischen Winterhalbjahr für ausgewählte Rhein- und Nebenflusspegel bei direkter Verwendung der Ergebnisse des regionalen Klimamodells REMO als Mittelwerte der Zeitreihen 2020/29, 2030/39 und 2040/49

Fig. 16: Discharge changes of hydrologic summer half-year for selected gauges of the River Rhine and its tributaries by direct use of results of the regional climatic model REMO as averages for time periods 2020/29, 2030/39, and 2040/49

Änderungen des Abflusses im hydrologischen Sommerhalbjahr für ausgewählte Rhein- und Nebenflusspegel bei direkter Verwendung der Ergebnisse des regionalen Klimamodells REMO als Mittelwerte der Zeitreihen 2020/29, 2030/39 und 2040/49

Continuous simulations of time series of e.g. 30 years can be accomplished so far. The daily time step can be reduced if necessary to 1 hour, e.g. for special applications of floods. In this case, an adjustment of the hydrological model is necessary.

As an example for discharge scenarios for the Rhine area, the results of the LARSIM model, driven by the REMO control and scenario data, are presented. For the interpretation of the model results it has to be noted that the model climates (control and scenario run) differ still clearly from the observed climate. Observed climate is delineated from observed data as well as of data generated by REMO by the so-called validation run. In the validation run REMO is driven by data set of observed atmospheric global reanalysis data. Thus for example the deviation between the REMO control and validation run in the hydrological summer half-year is 14% and in the winter half-year 35% (Fig. 13 and 14). As deviation between control and scenario run a uniform increase results in both half-years of approximately 5%. The strongest increases are found to be the months January and November.

For the discharge changes represented in the figure 15 and 16 exemplarily for four important gauges the depicted results relate to the hydrologic half-years when directly using these scenarios. Also the scenario calculations exhibit a clear variability between the decades examined. Perhaps, with exception of the Cochem gauge, there is a strong and constant increase of the discharge in the winter half-year.

The precipitation increase simulated with REMO in the winter results in a substantially stronger discharge increase. This occupies the sensitivity of hydrological systems in relation to changes in the precipitation. Precipitation can be predicted most with difficulty in numerical weather forecast and climate models but it is the most important variable for the hydrological water resources related climate change impact estimation.

2.4 Climatic changes and hydrologic extreme values

Climate is defined as average weather conditions at a place or in an area. This is described statistically with average values and variability masses of meteorological variables. Extreme events are episodes, in which the weather deviates strongly from its long-temporal means and the fluctuations typical for a certain place and a certain season. They belong to the climate of a region and influence landscape and living conditions. Extreme events can lead, however, to devastating damage to cultures and social mechanisms. Knowledge of their frequency and intensity is therefore important for our society. They are considered in today's tasks of water resources planning and preventive measures.

In the knowledge around the rise of the global temperature the question about the correlation between extreme events and climate change is asked again and again. Did extreme events become more frequent as a consequence of the climatic change (OCCC 2003)?

Fig. 17: Schematic presentation of the effect on extreme temperatures when (a) the mean temperature increases, (b) the variance increases, and (c) when both the mean and variance increase for a normal distribution of temperature (IPCC 2001)

Schematische Darstellung der Auswirkungen auf das Auftreten extremer Lufttemperaturen, wenn (a) der Mittelwert ansteigt, (b) die Varianz zunimmt und (c) wenn Mittelwert und Varianz ansteigen bei Annahme normalverteilter Temperaturwerte (IPCC 2001)

Present knowledge is that the global climate change will also affect the frequency and intensity of extreme. events. There are indications that the frequency of extreme events could react particularly sensitively to a climate change. Responsible for this are on the one hand physical feedback mechanisms. On the other hand there are also statistical effects, by which the climate change in the frequency of extremes could manifest itself even more strongly than in "normal" weather events. In figure 17 this statistical sensitivity is illustrated for temperature extremes as an example. With a rise of probability of occurrence and an increase of the variability, more frequent and higher extreme values have to be expected.

In this sense a classification of the dry year 2003 was made by SCHÄR et al. (2004). Using historical data as well as applications of a regional climate model the group of researchers comes to the conclusion that the European summer climate reacts on climate change with an increase of the year-to-year variability and that thereby the unusual summer heat wave of 2003 can be explained. An amassment of the event "summer dryness" and consequently arising droughts and low water events cannot be excluded further on, therefore.

2.5 Evaluation of results

The results of the hydrologic climate impact research obtained so far suggest that the water resources management should argue with the system-dependent fluctuations and change potentials described in a more extensive way, despite the strengthening of large methodical uncertainties that still exist. The existing water resources action goals should be examined and new concepts for the consideration of the existing uncertainties be compiled. This refers both to measures of flood protection management and to the safety device of the water availability.

The water resources management should give increased attention to the recommendations of the Advisory Committee for Questions of the Climate Change in Switzerland (OCCC). The most important recommendations are in part:

– The possibility of a high hydrological sensitivity (means and extreme values) together with the sensitivity of the modern civilization requires a scientificallybased estimation of possible future developments of extreme events, an evaluation of its meaning for humans and environment and realizations of improved protection and adaptation strategies.

– In the last decade the hydrological extreme events pointed out that action is still given without climate

change to the protection from extreme events due to the increasing value concentration, damage vulnerability and the rising protection need. In the consciousness of the climate change the endangerment pictures, protection goals, and the residual risks accepted should be periodically adapted to the changing conditions and solutions with as large a flexibility as possible should be aimed at. In the medium-term it is to be foreseen that new calculation and planning methods, which are able to quantify the endangerments in a changing climate, must be developed.

– Already today a sufficient knowledge basis is present in order to seize measures against climate change and to the protection from extreme events. The research will still continue to increase in addition to the knowledge conditions in the future to reduce the uncertainties, and to be used itself as a more direct planning instrument.

The modelling of the water balance components actual evaporation, groundwater recharge, soil moisture, water equivalent of snow and finally the discharge have attained in the last years a greater importance in the operational hydrology and water resources management. For the estimation of design values and the enterprise of water-resource plants the appropriate hydrological models were usually provided for small (< 500 km2 , lower mesoscale) to medium-sized catchment areas $\approx 5,000 \text{ km}^2$, upper meso-scale), so far. Meanwhile investigations step to the consequences of the wide changes of our landscape and in addition to the effects of climate change. Thus also the demand on hydrological modelling of large rivers and basins $(> 10,000 \text{ km}^2, \text{macro scale})$ grows stronger.

Integrated river basin management is called the challenge today. It aims at the safety device of the water availability, at the improvement of the flood protection and the flood precaution, in addition, especially in low water periods. Besides this the maintenance of the various uses of waters, like e.g. water supply and power supply, navigation as well as the guarantee of ecological minimum requirements, are important tasks of water resources management.

3 Biogeochemistry of the River Rhine basin

"Volger hat festgestellt, daß der Rhein bei Basel jährlich etwa 27,5 km3 Wasser führt, das in etwa 10 000 Teilen nicht einmal 2 Teile gelöster Stoffe, größtenteils Kalk, enthält. Daraus läßt sich berechnen, daß der genannte Strom seinem schweizerischen resp. dem daran grenzenden Areale Kalkmassen von 3500 Mio kg … entzieht. Die Gesamtmasse aufgelöster Fester Stoffe aber, welche im Verlaufe eines Jahres an Basel vorrübergleiten, entspricht nach *dem erwähnten Forscher … einem Felswürfel von 387 Fuß Höhe, Breite und Dicke."*

HIPPOLYT HAAS (1892): Aus der Sturm und Drangperiode der Erde. Berlin, 243. Cited after O. VOLGER (1857): Erde und Ewigkeit. Frankfurt. This citation is possibly the oldest dealing with transport of matter in the Rhine. Otto Volger was reader in geology and mineralogy at the Senckenbergischen Naturforschenden Gesellschaft in Frankfurt and one of the first to calculate continental erosion and an oceanic salt age. He became famous for founding the Freie Deutsche Hochstift in 1859 and for the purchasing and restoration of Goethe's Birth House in Frankfurt in 1863.

3.1 Introduction

From 1980 to 1990 a research group of the Geological-Paleontological Institute of the University of Hamburg coordinated a worldwide effort to measure and understand carbon fluxes in large rivers. The project, under the auspices of the Scientific Committee on Problems of the Environment (SCOPE) and funded by the United Nations Environmental Program (UNEP) and the German Ministry of Research and Technology (BMFT), invited scientists from Africa, Asia, America and Europe to collect river samples, analyse as many parameters in the field and in their labs as possible and to submit sample for analysis of total dissolved and particulate organic carbon and their amino acid and carbohydrate composition at Hamburg. In addition, scientists were invited to review the data available on riverine carbon transport in their respective countries (DEGENS et al. 1991).

In this context the first attempt was made to look at the long-term River Rhine data under the aspect of its carbon biogeochemistry (KEMPE 1982, 1984, 1988; KEMPE et al. 1991). This study took advantage of raw data measured and published in annual reports by the International Commission for the Protection of the River Rhine starting in 1963 through 1978 (s. Fig. 1). A total of 1,100 full chemical analyses where used in the study covering nine long-term stations on the Rhine and Mosel with a frequency of eight samples per year and seven stations covering one or two years with a sample frequency of 24 per year. In this way it was possible to evaluate the seasonal behaviour of the Rhine as well as its downstream changes and long-term trends. Total transport of dissolved and suspended solids has been calculated, also using the database of the International Hydrological Decade Yearbooks (KEMPE et al. 1981). Additionally a first factor analysis of the available data was done (KEMPE a. LAMMERZ 1983). Later VAN DER WEIJDEN and MIDDELBURG (1989) ran a more complete factor analysis of Rhine data based on 240 water samples from the years 1975–1984 taken at the Lobith Station. They also addressed the question of heavy metal transport, both in the dissolved phase as well as in sediments. In 1988 and 1989 Jan VEIZER and his group at Bochum conducted a sampling campaign involving water and shell (*Dreissena polymorpha*) samples to look at the carbon, oxygen and strontium isotopes of the Rhine and its principal tributaries (BUHL et al. 1991). Since the finalization of the manuscript several other studies have dealt with various aspects of the Rhine and its tributaries. HIRSCHFELD (2003) has analysed the stable isotope, main ions and aspects of carbon dynamic of the Rhine for the years 1999–2001 based on samples taken at Cologne, in the Mosel and at several places in the Lake Constance system. Data concerning nutrient dynamics or time-trends were not considered. But no study has – to our knowledge – addressed the biogeochemistry of the system in general. Hence, reviews on the entire Rhine catchment are not updated yet and are summarised here in the context of the RhineLUCIFS concept. The relationship with hydrological aspects given above is obvious. Investigations on sediment budgets occasionally lack consideration of solute transport – in the Rhine a much larger mass transport of weathering products than suspended sediment.

3.2 Discharge

The Rhine is $-$ by discharge $-$ the $40th$ largest river on earth, by its transport of nutrients though it ranks among the top ten, illustrating the profound anthropogenic impact this river has suffered (KEMPE 1982). Table 7 gives some of the basic information about the Rhine in comparison with the Seine and

Table 6: Characteristics of available hydrological models in the River Rhine basin Kenndaten der verfügbaren hydrologischen Modelle für das Rheingebiet

Name	Spatial resolution	Number of land use classes	Equation for calculation of evapotranspiration	Study area
LARSIM	18 km x 18 km	14	Penman-Monteith THOMPSON et al. (1981)	River Rhine basin up to German-Netherland border
HBV-SMHI	\sim 1,000 km ²		FAO-Grass-Reference-Evaporation WENDLING (1995)	River Rhine basin up to German-Netherland border

Table 7: Comparison between three major Central European river basins influenced by North Atlantic weather conditions. For source of data see KEMPE et al. (1991)

Vergleich der drei wesentlichen zentraleuropäischen Einzugsgebiete, die durch die Wetterverhältnisse im Nordatlantik gesteuert werden. Nach verschiedenen Quellen aus KEMPE et al. (1991)

* This erosion rate does not take into account re-deposition within the system, it represents only the lowering of the landscape attributed to the exported material.

+ Without free CO₂-C which amounts to 0.19 10⁶ t/a

Elbe, three rivers of similar latitude and industrialization in Central Europe. In comparing these rivers with each other, some characteristics of the Rhine come out much clearer than if looked at individually.

It follows that the Rhine has an almost three times higher discharge yield than the other two rivers. This is due to the fact that it alone taps alpine precipitation. The long-term hydrograph of the Rhine (Fig. 18), shows maximal discharges in February when the lowlands receive rain and provide up to 70% of the Rhine water. In May the snowmelt in the Alps begins, leading to a secondary maximum, during which the alpine Rhine provides between 50 and 70% of the discharge. During low discharges (September–October) both sources deliver water and towards winter the lowland tributaries, especially the Mosel, become gradually of greater importance (VAN DER WEIJDEN a. MIDDELBURG 1989). All in all the hydrograph appears – due to the steady addition of snow and glacial melt water in summer – to be rather buffered with regard to discharge peaks. Also, the great alpine lakes serve as buffers against extreme discharge events.

Figure 19 gives an overview of the isotopical development of the Rhine according to the measurements of BUHL et al. (1991). The δ ¹⁸O value becomes steadily heavier as lowland tributaries, which are fed by isotopically heavier rain than the high peaks of the Alps, are added. The 87Sr/86Sr ratio is principally reflecting the geological period of the sedimentary rock, which is being weathered. The water mostly is derived from Tertiary and Mesozoic terrains with low ratios and only in

Fig. 18: Long-term hydrograph (1936–1968) of the River Rhine at Rees Station

Hydrograph des Rheins an der Station Rees (1936–1968)

the Rhenish uplands do solutions from older rocks with higher ratios enter. However, the amount of strontium in these tributaries is low so that the impact on the River Rhine ratio is low. The most important upward step in the curve is found where the Alsatian salt mines discharge their wastewaters, which contain high concentrations of strontium with an 87Sr/86Sr ratio of 0.70947. In a sense the Sr ratio is a reflection of the salt input to the Rhine; it correlates highly with the Na and Cl concentrations in the River Rhine.

3.3 Processes governing biogeochemistry

This background information about the hydrography and the general provenance of the weathering solutions is the context under which the biogeochemistry of the River Rhine has to be viewed. Biogeochemistry tries to assess the chemical interactions between biological and geological processes. It is of interest because these processes govern input, output and in-river transformation of the major (O, C, N, P, Si, S) and minor (Ca, Fe, Mo ….) "biogenic" elements and it determines the origin and fate of the riverine organic matter. Specifically, the carbon budget is of central importance since is offers a bulk measure of both the overall weathering rate in the basin and of the biological activity both in the basin and in the river. The following processes are those, which influence the carbon and nutrient budgets most prominently:

– Photosynthesis and respiration (governed by nutrients inputs and labile C, plus light and temperature);

gas exchange of e.g. O_2 , CO_2 , CH_4 , H_2S , NO_x (governed by photosynthesis and respiration, temperature, turbulence);

– precipitation and dissolution of carbonates (governed by the concentrations of Ca, HCO_3 , CO_3 , SO_4 and $pCO₂$ and T);

– erosion, flocculation and sedimentation (governed by mucopolysaccarides);

– landscape lowering and TDS and TSS transport (governed by vegetation cover, seasonality, climate and bed rock petrography).

Almost all of the biogeochemical processes are severely influenced by man, and it is important to understand the kind and magnitude of this interference. Most of these interferences have a long historic perspective such as:

– Deforestation (Neolithic and Roman land clearing, Alemanic take-over, Franconian Empire, mediaeval deterioration, advance of modern farming);

– civil engineering (cut-off of river meanders, channel deepening, dredging, diking, reservoir construction, weirs);

diffuse runoff, aerosol deposition, acid rain, industrial

accidents); – water withdrawal and addition (sewage plant outlets, ground water enrichment, bank filtration, channels, mine discharges).

3.4 Carbon Budget and pCO₂

A sensitive indicator of the riverine biogeochemical processes is the partial pressure of the carbon dioxide $(pCO₂)$ of the river water. It can be calculated through aqueous numeric models using pH, temperature and the concentrations of the main ions as input parameters (s. e.g. KEMPE 1982). The results of the recalculation of the 1,100 samples used in the study in 1982, show that the River Rhine has a very low $pCO₂$ (and high pH) when it issues from Lake Constance. In summer months it can drop even below atmospheric pressure of 360 ppmv. This is due to the fact that photosynthesis in the lake, fuelled by nutrients, consumes free $CO₂$. Much of the organic substance thus produced is settled in the lake, removing carbon and nutrients. Additionally, by increasing the pH, bicarbonate is transferred to carbonate, which in turn aids the summer precipitation of calcite in the lake's epilimnion. Additionally the excreted mucus of the phytoplankton causes the fine-grained lithoclastics to settle by gluing it together. Therefore, when leaving Lake Constance, the Rhine carries a limnic biogeochemical signature: i.e. its water is essentially devoid of inorganic suspended matter and of dissolved nutrients, it has a high pO_2 , as well as pH and a low pCO_2 , which peaks in winter (Fig. 20).

Downstream of Basel, however, the water changes its internal characteristic quickly because the non-limnic tributaries add labile C, nutrients and suspended matter. Therefore photosynthesis is prevented and respiration takes over. The river quickly acquires a low pO_2 and pH and high $pCO₂$, which peaks in summer when

Fig. 19: Isotopic development of the River Rhine according to the measurements of BUHL et al. (1991) for autumn 1989 for the profile and of autumn 1988 for the tributaries. Locations are simply ordered by number from Lake Constance to the Netherlands border. Only a few tributaries are given (floating points of similar colour as the continuous profiles) Entwicklung des Isotopenspektrums des Rheins nach Untersuchungen von BUHL et al. (1991) im Herbst 1989 für das Längsprofil und Herbst 1988 für die Zuflüsse. Die Messorte sind entlang des Rheins vom Bodensee zur niederländischen Grenze angeordnet. Für die Zuflüsse sind nur Einzelwerte angegeben, die farblich den Parametern des Längsprofils entsprechen

Fig. 20: General scheme of the $pCO₂$ downstream change of the River Rhine between limnic and riverine conditions (KEMPE 1982)

Schema der Veränderung von $pCO₂$ des Rheins zwischen limnischen und fluviatilen Verhältnissen (KEMPE 1982)

temperature driven respiration is highest. This pattern prevails for the rest of the downstream course of the Rhine.

Figure 21 shows the long-term means of the $pCO₂$ of all the Rhine stations involved. The steady downstream increase of the average $pCO₂$ is clearly seen. Annual long-term averages peak at the Braubach Station with over 6.000 ppmv, i.e. ca. 20 times atmospheric $pCO₂$. It is interesting to note that the three stations in the delta distributary arms of the Rhine show a similar longterm mean. This illustrates that the riverine $pCO₂$ is not a local characteristic but a signal created by upstream input of organic C. The same conclusion was drawn by BUHL et al. (1991) in their study of the carbon isotopes of dissolved inorganic carbon (DIC). In autumn 1989 the δ ¹³C decreased from -4.4 at the outflow of Lake Constance to -10.7 below the mouth of the Main (Fig. 19). All the tributaries come in with lower $\delta^{13}C$ values than the Rhine itself, illustrating their large organic loads, already partly respired. It is interesting to note that the δ ¹³C is not further decreasing downstream in spite of these light C inputs. It may be speculated that this is due to ongoing carbonate dissolution caused by the increased $pCO₂$, which would add heavier carbon.

Figures 22 and 23 show the detailed $pCO₂$ records of some of the investigated stations. One can clearly see

Fig. 21: Longitudinal pCO_2 profile of the River Rhine from Lake Constance (right) to the three delta arms of the River Rhine (left). The solid line refers to annual long-term means, the broken line to the years 1978 and 1978 (KEMPE 1982) *p*CO2-Längsprofil des Rheins vom Bodensee (rechts) zu den drei Deltaarmen (links). Die durchgezogene Linie markiert jährliche Mittelwerte, die gestrichelte Linie die Jahre 1978 und 1978 (KEMPE 1982)

that the Stein Station, just below Lake Constance, has the lowest $pCO₂$ of all stations with values lowest in summer. At Kembs, this pattern is already modified with a slightly increased $pCO₂$ and a minimum shifted towards autumn and at the Seltz Station the seasonality of the limnic $pCO₂$ is clearly lost. The graph also shows the supersaturation of the two carbonate minerals calcite and dolomite: At Stein the Rhine is much supersaturated with regard to both minerals. This supersaturation is largely lost at the Seltz Station and at the Braubach Station; supersaturation has become a rare event. This shows that in fact calcite dissolution could indeed smooth the δ^{13} C signal in spite of the fact, that all of the tributaries bring in low δ ¹³C DIC which should otherwise bring down the δ ¹³C signal in the Rhine gradually.

Even with this understanding of the source of $pCO₂$, its magnitude is somewhat of an enigma. This is because the $CO₂$ should be produced by oxygen consumption. If one plots the concentration of oxygen versus temperature and the equivalent $pCO₂$ arising from the total consumption of this oxygen in respiration (Fig. 24) then the $pCO₂$ of water would fall in the range of 6,000 to 9,000 ppmv between 0 and 35°C. Thus the Lower Rhine should be almost oxygen free. This is, however, not the case. At the Braubach Station the long-term means of the O_2 concentration amounts to 5.6 mg/l, with a temperature mean of 12.8°C and a $pCO₂$ mean of 6,300 ppmv. Furthermore, one can recalculate the oxygen deficiency (i.e., the difference between the measured oxygen concentration and its saturation at the temperature of measurement) and use this value to calculate the free $CO₂$ concentration and its respective $pCO₂$ the oxygen consumption could have produced. When plotting all of the oxygen-deficit generated pCO_2 values versus the actual pCO_2 , then one should expect that the regression of the two values should originate at zero and have a slope of one, i.e. if all the free $CO₂$ is due to oxygen consumption in the water. Figure 25 gives this plot for the values of the Braubach and Lobith Stations, which shows that the regressions neither pass through zero nor do they have a slope of one. In fact, the measured pCO_2 is always

*Fig. 22: p*CO₂ records of the Stein, Kembs and Seltz Stations for the year 1974–1977, illustrating the downstream increase of the $pCO₂$ (here plotted as its negative logarithm, i.e. the peaks represent low values and the troughs high values of $pCO₂$), the change in the seasonality and the decreasing supersaturation of the minerals calcite and dolomite. The scale of the saturation is the same as the $pCO₂$, i.e. the saturation index is used which is defined as the log of the ratio between the ion activity product and K_{calcite} at the temperature of measurement. Note that the larger the grey (for calcite $=$ Cc) or dark-grey areas (for dolomite $=$ dol), the larger the supersaturation (KEMPE 1982)

*p*CO2 Werte der Stationen Stein, Kembs und Seltz für die Jahre 1974–1977, die flussabwärtige Zunahme des $pCO₂$ (hier dargestellt als negativer Logarithmus, d.h. die Höhen zeigen niedrige, die Senken hohe Werte des $pCO₂$), die Änderungen im Jahresgang und die abnehmende Übersättigung der Minerale Kalzit und Dolomit. Die Skalierung der Sättigung ist identisch mit der des $pCO₂$, d.h. der Sättigungsindex ist dargestellt, der als Logarithmus das Verhältnis des Ionenaktivitätsproduktes und von K_{Kals} für die Messtemperatur beschreibt. Man beachte, dass die Zunahme der hellgrauen Fläche (für Kalzit = Cc) und der dunkelgrauen Fläche (für Dolomit = dol) die zunehmende Übersättigung beschreibt (KEMPE 1982)

much larger than the $pCO₂$ explained by the oxygen deficiency. The oxygen-deficit generated $CO₂$ pressure amounts to 3,240 ppmv for the record of Lobith on average and to 3,210 ppmv for Braubach, compared to the actual long-term averages of pCO_2 of 6,320 and 4,990 ppmv, respectively.

Thus one must postulate that remineralization in the river is fuelled by another oxygen source. This could be nitrate. In figure 26 the correlation matrixes for the parameters used in the calculations are given. At the Braubach Station we find a highly significant (99%) negative correlation between the $pCO₂$ and the nitrate concentration and a highly positive correlation between nitrate and oxygen. For the Lobith Station the correlation between the pCO_2 and nitrate is still negative, but not significant (<90%) but nitrate and oxygen are still highly correlated. Also $pCO₂$ values are highly correlated with chemical oxygen demand (COD) and biological oxygen demand (BOD) values, hinting towards a $CO₂$ source by respiration of labile carbon compounds as well. All in all, one could sarcastically state, that the Rhine would have been anaerobic, were it not for its large pollution with nitrate! Nitrate respiration supposedly begins only at or below oxygen levels of ca. 3 mg/l. These levels are, however, not quite reached in the waters of the Rhine. One can therefore only speculate that the nitrate consumption occurs in anaerobic macroflocs or in the sediment of the river. In this way, nitrate could be reduced locally, slowly imprinting the observed CO_2 -patterns to the Rhine water by the formation and disintegration of countless generations of macroflocs in the water.

*Fig. 23: pCO*₂ records of the Braubach, Lobith, Kampen, Vreeswijk and Gorinchem Stations for the years 1963–1978, illustrating the high $pCO₂$ (here plotted as its negative logarithm, i.e. the peaks represent low values and the troughs high values of $pCO₂$) of the downstream section of the River Rhine and its largely undersaturated state with regard to the minerals calcite and dolomite. Note that at Braubach calcite saturation has rarely been encountered, i.e. normally the River Rhine here shows a large undersaturation, making dissolution of particulate calcite feasible (KEMPE 1982)

*p*CO2 Werte der Stationen Braubach, Lobith, Kampen, Vreeswijk und Gorinchem für die Jahre 1963–1978. Dargestellt sind die hohen *p*CO₂-Werte (hier dargestellt als negativer Logarithmus, d.h. die Höhen zeigen niedrige, die Senken hohe Werte des *p*CO2) im Unterlauf des Rheins und die stark untersättigten Verhältnisse bezüglich der Minerale Kalzit und Dolomit. Man beachte, dass an der Station Braubach die Kalzitsättigung nur sehr selten eintritt, d. h., dass normalerweise der Rhein hier eine deutliche Untersättigung aufweist, die zur Lösung partikulären Kalkes führt (KEMPE 1982)

Fig. 24: Relation of oxygen concentration at saturation versus temperature and pCO_2 generated by the total consumption of oxygen at saturation (KEMPE 1982)

Verhältnis der Sauerstoffkonzentration bei Sättigung im Verhältnis zu Temperatur und $pCO₂$ bei vollständigem Sauerstoffverbrauch bei Sättigung (KEMPE 1982)

The correlation of the various parameters with discharge is also interesting to note. In figure 26 it is illustrated that $pCO₂$ is negatively correlated with discharge, but oxygen and pH are positively correlated, showing that the source of the labile carbon is diluted at high waters. Total organic carbon **(**TOC) is consequently also negatively correlated with discharge, but not as highly significant. Similarly $PO₄$ is also diluted at high discharge while $NO₃$ does not show any correlation with discharge at all, i.e. it does not follow a dilution model. The Q-mode varimax factor analysis of the two stations yielded six factors explaining more than 90% of the variance in the data (Tab. 8) (KEMPE a. LAMMERZ 1983):

The first three factors are identical in both stations, being factors that are associated with the $pCO₂$, temperature and discharge. The others are clearly associated with organic and nutrient pollution. VAN DER WEIJDEN and MIDDELBURG (1989) used a much larger data set of the Lobith Station, including the years from 1975 to 1984. In the dissolved fraction three main factors were extracted, factor 1 encompassing the dissolved heavy metals and phosphate, factor 2 containing the discharge and the main ions plus phosphate, and factor 3 contains ammonia, nitrate, and silica. Also BUHL et al. (1991) run a factor analysis of their data, finding that factor 1 (a dilution factor) (45.8% of variance) contains conductivity, most major ions, phosphate and the three isotopes, while factor 2 (18.7% variance) contains $Ca, Mg, PO₄, Fe, Mn and Zn, and factor$ 3 (11,3% of variance) is determined by temperature and aluminium and factor 4 (7.5% variance) refers to pH only. Since all three data sets tested contain different parameters they cannot be compared directly. Nevertheless it is quite clear that higher discharge dilutes the main ions, heavy metals and phosphate but that the other nutrients are more related to seasonality, i.e. temperature and that the pCO_2 (and hence pH) is related to the load with organic carbon.

Biogeochemical parameters are not only linked statistically, but also by geochemical and biochemical reactions. We already discussed calcite precipitation and dissolution and respiration and photosynthesis described by:

1 mol CO₂ + 1 mol H₂O + 1mol CaCO₃ ⇔ $2 \text{ mol } HCO_3^- + 1 \text{ mol } Ca^{2+}$ l mol CO₂ + 1 mol H₂O ⇔ 1 mol CH₂O + 1 mol O₂

Fig. 25: Plot of all pCO_2 values from the Braubach and Lobith Stations versus the pCO_2 , which can be explained by the measured oxygen deficit in the water (KEMPE 1982)

Darstellung aller pCO_2 -Werte der Stationen Braubach und Lobith im Verhältnis zum pCO_2 , der durch das gemessene Sauerstoffdefizit im Wasser erklärt werden kann (KEMPE 1982)

Table 8: Q-mode varimax factor analysis of River Rhine data (pCO2, Q [discharge], O2, PO4, NO3, BOD [biological oxygen demand], COD [chemical oxygen demand], T [temperature], pH, alkalinity [only for Braubach Station]). For more information on the parameters see KEMPE (1982), and for the full statistical explanation see KEMPE and LAMMERZ, (1983). Only factor loadings of >|0.5| are given (except where in brackets). Q-Modus Faktorenanalyse von Rheindaten (β CO₂, Q [Abfluss], O₂, PO₄, NO₃, BOD [biologischer Sauerstoffbedarf], COD [Chemischer Sauerstoffbedarf], T [Ttemperatur], pH, Alkalinität [nur für Station Braubach]). Weitere Informationen zu den Parametern finden sich bei KEMPE (1982), eine vollständige statistische Analyse bieten KEMPE und LAMMERZ (1983). Nur Faktoren >|0.5| sind dargestellt (mit Ausnahme der Werte in Klammern)

Station	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Cumulative % of variance
Lobith $(1963 - 78)$	$-\rho CO_2 \text{pH}$	-T, O_2	$Q, -PQ4$	$\rm COD$	(PO ₄ , NO ₃)	O_2 , BOD	
$%$ variance	34.0	19.7	13.6	10.8	8.8	3.9	94.2%
Braubach $(1963 - 78)$	$-\rho CO_2$ pH	-T, O_2 , NO_3	$-Q$, $-O_2$, PO_4	BOD	Alkalinity	$\rm COD$	
% Variance	30.6	21.8	16.2	9.7	7.0	5.8	91.1%

Correlation Matrix of Rhine at Lobith 1963-78

Correlation Matrix of Rhine at Braubach 1963-78

Fig. 26: Correlation matrix of biogeochemical parameters of the Lobith and Braubach Stations (data 1963–1978) Korrelationsmatrix der biogeochemischen Parameter der Stationen Lobith und Braubach (Daten 1963–1978)

3.5 Nutrients Ratios and Transport

Organic substance, here represented by $CH₂O$, is however not only composed of C, H and O, but also of N and P. In marine plankton the C:N:P ratio is 106:15:1. This ratio is called the Redfield Ratio and it allows estimating how much organic carbon could, for example, be sequestered by a certain stock of nutrients.

For the Lobith Station the average elemental ratios amount to $(C, N, P \text{ in bold numbers})$:

348:31:79:27:1:51 for HCO₃-C:CO₂-C:TOC:NO₃- $N:PO₄-P:O₂-O$

And for the Braubach Station to:

338:37:70:15:1:46 for HCO₃-C:CO₂-C:TOC:NO₃- $N:PO₄-P:O₂-O$

For comparison the ratios of the Mississippi and the Amazon are given:

Mississippi: **1200**:134:**11:1** (HCO₃-C:TOC:NO₃-N: $PO₄-P$

Amazon: **74**:39:24:2.3:**1.5**:1.8:2.9:**1** (DIC:DOC:FPOC: CPOC:NO₃-N:DON:PON:PP)

Fig. 27: Concentrations of nitrate versus phosphate in some of the world rivers. Note that the regression through the data is close to the 15:1 line, the Redfield ratio with which marine plankton incorporates N and P into their organic matter (KEMPE 1984)

Konzentrationen von Nitrat und Phosphate in ausgewählten Flussläufen. Man beachte, dass die Regressionslinie dicht bei der 15:1 Linie verläuft, die als Redfield-Ratio die Aufnahme marinen Planktons von N und P beschreibt (KEMPE 1984)

(Abbreviations: $TOC = total organic carbon, DIC =$ dissolved inorganic carbon, DOC = dissolved organic carbon, CPOC = coarse particulate organic carbon, $FPOC = fine$ particulate organic carbon, $DON = dis$ solved organic nitrogen, PON = particulate organic nitrogen, PP = particulate phosphorous.)

These ratios show how much organic carbon can eventually be formed from these riverine nutrient sources. For example in the case of the Rhine enough N and P is transported in solution to sequester as much as one third of the total inorganic carbon load of the river, ca. 700,000 t of C/a (comp. Tab. 7). This proportion is much less for the Mississippi, even though it also is charged with high loads of nitrate and phosphate. In the case of the Amazon, enough particulate phosphate (PP) is transported in order theoretically to sequester the entire inorganic carbon load of that river. It is, however, questionable if all of this phosphate is available to quick bacterial turnover and if it is not quickly settled once it is mixed into coastal waters. Also the nitrate load and its ratio to PP is low, owing to the fact that much of the nitrate produced in the river system is already either taken up by plants and plankton or

Fig. 28: 16 year record of PO₄ and NO₃ concentrations at the River Rhine stations of Lobith and Braubach (KEMPE 1982) 16-jährige Messreihe von PO4- und NO3-Konzentrationen an den Stationen Lobith und Braubach (KEMPE 1982)

is respired in the anaerobic flood plain waters, i.e. in the vast Amazonian varzeas.

These numbers illustrate that the river inputs to the oceans and specifically those rivers with an increased anthropogenic nutrient load are an integrated part of the global carbon cycle. Figure 27 plots some of the average nutrient concentrations published in the SCOPE/UNEP project and other databases (KEMPE 1982, 1988). Anthropogenic river-born nutrients could account for an additional carbon sink in the size of ca. 0.1 Gt/C per year (KEMPE 1984). Data bases of river transports are, however, still quite incomplete and it often takes years before overview publications become available.

Also river loads change significantly interannually, due both to climatically induced discharge fluctuations and due to increases in nutrient inputs from fertilization and community sewage. Long-term trends are also evident in the Rhine. Figure 28 plots the phosphate and nitrate concentrations over time. At the Lobith Station the NO_3 -N transport changed between 1963 and 1978 from 180,000 to 250,000 t/a and the PO_4 -P transport changed from $8,000$ to $25,000$ t/a in the same time interval.

3.6 Outlook

This short review of some of the knowledge available on the biogeochemistry of the River Rhine illustrates the importance of understanding sources and processes of the biogeochemical important parameters in the Rhine system. The next step would be to use the current data of the International Commission for the Protection of the River Rhine and extract a much more complete picture of the interdependencies of the various parameters and then construct a routing model. Such a model, which tries to describe the element flux from one station to the next, is used to gain an understanding of the quantitative side of the various biogeochemical processes in the river, its tributaries and the influence of other aspects of global change affecting the basin. This aim is just now (2005) being followed in our research group by Dr. Jens Hartmann, who obtained the entire data set from the Bundesanstalt für Gewässerkunde in Koblenz in electronic form.

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