Process based regional modeling of water and solute fluxes in Pleistocene aquifer systems - Implications for water management strategies under pressure of global change

Habilitation

submitted by
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Preface

The thesis includes 5 manuscripts of scientific papers, which have been printed or accepted by peer-reviewed journals. One manuscript was printed in a peer-reviewed journal of the American Institute of Hydrology (AIH) “Hydrological Science and Technology”. The references are listed in the following:


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1. Introduction

The expected climate change is intensifying the pressure on water resources in North-Central Europe, strengthened by historical impacts, land use development and complex hydrological boundary conditions in the young glacial landscape. Meanwhile, the hydrological cycle has become more and more problematic (MLUR 2002). Decreasing groundwater levels and landscape runoff have been recognized in many regions of Brandenburg since several years (Suckow et al. 2002, Dreger and Michels 2002). Due to the expected predictions of changing rainfall intensity, duration and spatio-temporal distribution in connection with increasing temperatures, this status will be worsen in the next decades (Gerstengarbe 2003, Claußnitzer et al. 2008). It is a challenge to manage the ever-scarcer water resources, their uses/services, and their after-use disposal based on process knowledge without creating environmental and economic damage.

The expected change in the water budget has a strong impact on land use practices as well as on soil and water cycle properties and functioning. The prediction of the resources development requires an area wide assessment of the impact effects on water and substance cycle. However, the less effective description of substance migration processes reproduced by actual regional model instruments will remain as unsolved problem (Kunkel et al. 1999, Behrendt et al. 1999, Böhlke et al. 2002, Behrendt and Dannowski 2005). Although the basic processes in the substance cycle especially for nutrients and trace metals have long been understood, their behavior in complex natural systems including different scales is still topical. There is a substantial uncertainty in the magnitudes and rates of the cycling at the watershed and river basin scale (McLay et al. 2001, Tomer and Burkart 2003, Onsoy et al. 2005).

The development of risk assessment tools is actually lacking in validation methods which include regional hydraulic and geochemical process knowledge. The implementation of relevant subsurface substance transformation and transport processes is therefore essential for improving the prediction efficiency of the model tools. Better parameterization is needed to enhance the quality of the models that are actually used (Schlesinger et al. 2006).

The results of this thesis allowed the identification and quantification of the main geochemical processes at the different interfaces in the landscape. The aim was the development of a set of parameters and indicators that function as proxies for characterizing the substance dynamics in the Pleistocene aquifer systems under consideration of the geochemical environment. The proxies were used to parameterize a conceptual regional
groundwater model, which was developed to mirror redox based substance transformation via the entire groundwater flow path at large-scale. This model approach would enhance future planning reliability and can be used for scenario analysis and the validation of new, adapted water management strategies.

Complex deterministic hydraulic und hydrochemical models like MODFLOW (McDonald and Harbaugh 1988), FEFLOW (Diersch 1996) or PHREEQC2 (Parkhurst and Appelo 2000), can be used to describe the different processes at the field scale or in small-scale basins. However, it is still a great challenge to transform this local-scale process knowledge into the mesoscale. The large number of spatially distributed hydraulic and geochemical parameters that must be considered in order to obtain a detailed description of the complex conditions at mesoscale suggests that field investigations and direct-measurement methods are too expensive and time-consuming for this regional assessment. Hence, an alternative approach would be the implementation of GIS processing which can provide a conceptual replication of complex geologic, hydraulic and geochemical conditions to serve as a basis the for mathematical modeling of the hydraulic and hydrochemical processes occurring in the landscape.

In Pleistocene landscapes most of the water pollution results from agricultural sources, often in combination with inappropriate water management operations. The corresponding technical land- and water management measures and their effects on local nutrient budgets have been known since decades (Dabbert and Frede 1998, Kersebaum et al. 2005). However, in order to improve the management concepts, their function and influence on the regional substance flow via the entire soil – groundwater – surface water path must be considered. The presented model concept is able to meet this requirement.

The approach resulted in 3 different scopes and steps, which are represented by the discussed publications:

1. Large-scale modeling of the groundwater flow as a basis for solute transport modeling
2. Process studies for the identification of geochemical parameters and indicators to provide for large-scale transport modeling
   a. Identification of regional geochemical patterns in aquifer systems
   b. Process studies at the interface between groundwater and surface water combined with regional balance calculations
3. Parameterization of large-scale models in the landscape using deduced geochemical indicators exemplarily for the quantification of denitrification processes.
In the unconsolidated rock region of North-Central Europe, groundwater flow and discharge of groundwater into rivers and channels is the main component of the regional water cycle. Surface water runoff, with less than 5% of the total runoff, plays only a minor role. Therefore, the discharge of groundwater from Quaternary deposits is one of the main components needed for identifying and quantifying the solute flux throughout the whole region. The geological structure of the landscape is very complex with a high variance in the hydraulic and hydrochemical parameter distributions. The different groundwater systems of Brandenburg relate to glacial structures like glacial valleys, till highlands and end moraines. These aquifers are characterized by specific geochemical and hydraulic conditions. Typical glacial aquifer types are:

1. anaerobe, confined/unconfined aquifers in discharge regions, dominated by glacial valleys and floodplains (e.g. Oderbruch)
2. unconfined oxic aquifers in recharge regions, dominated by till plateaus and end moraines (e.g. Fläming, Barnim/Lebus)
3. anaerobe, confined aquifers in complex moraine and till dominated transit regions (e.g. Uckermark).

Water resources in the Pleistocene landscape are influenced mainly by two hydrological compartments: the recharge areas and the discharge areas. To react to the expected impacts of climate change it is necessary to develop management strategies particular for these regions, for they act as dominating regions that influence the water and solute flux over time and space. While recharge regions are strongly influenced by decreasing water availability, the substance budget of floodplains responds very sensitively to management measures. Where nutrient leaching from diffuse sources is concerned, floodplains operate as regions with a high substance accumulation potential in the landscape. Under specific conditions of land use, climate, biology and hydrology, floodplains can exist over a long time with high accumulation of organic and inorganic compounds (Richardson et al. 2001). Therefore, detailed process studies of geochemical and hydraulic interactions were realized exemplarily at the Oderbruch region. This region was chosen for the intensive geochemical and hydrological investigations because the Oderbruch is the greatest poldered floodplain in Germany with well-known hydraulic boundary conditions based on a well-grounded data base.

The investigations in the Oderbruch region discussed in this thesis started in 1994 with a project funded by the German Research Foundation (DFG): “Die hydrochemischen
Verhältnisse im oberflächennahen pleistozänen Grundwasserleiter des Oderbruch”. This project was a cooperation between the FU Berlin Institute for Geological Science, Division for Geochemistry, Hydrogeology and Mineralogy (Prof. A. Pekdeger) and the ZALF Institute of Hydrology (Prof. J. Quast and Dr. C. Merz). The Project ended in 1998 with a PhD thesis published by Torsten Liedholz (2001). The comprehensive investigations represent the first geochemical process studies carried out in the Oderbruch polder. Based on these investigations, the Oderbruch became a nationwide test field for anaerobic groundwater processes within the DFG priority program 546 “Geochemical processes with long-term effects in anthropogenically affected seepage- and groundwater”. From 1997 to 2003, more than 6 scientific groups concentrated their investigations in this region (Schulz and Hadeler 2003). For 6 years, the author at ZALF coordinated their activities.

Two further projects started within the priority program 546. The first was entitled “Migrationsverhalten umweltrelevanter Spurenstoffe unter wechselnden Milieubedingungen im oberflächennahen Grundwasserleiter des Oderbruchs”. This project was managed by the FU Berlin, Institute for Geological Science, Division for Geochemistry, Hydrogeology and Mineralogy (Dr. A. Winkler) and the ZALF Institute of Hydrology (Dr. C. Merz). The validity period was from 1997 until 2003. This project was completed with a PhD thesis published by Peter Schuhmacher (2003). Publications D and E are based upon the results of this project.

The second DFG-project was titled “Quantifizierung der Stoffumsätze unter raum/zeitlich variablen Infiltrationsbedingungen im SPP Testgebiet Oderbruch”. This project was a cooperation among the Division for Geology, Geophysics and Geoinformatic of the FU-Berlin (Prof. A. Pekdeger), the ZALF Institute of Hydrology (Dr. C. Merz, Prof. J. Quast) and the Institute of Geography and Geology, Ernst Moritz Arndt University Greifswald (Prof. M.-T. Schafmeister). The validity period was from 1989 until 2003. This project was also completed with a PhD thesis published by G. Massmann (2002). The publications B and C were based upon the results of this project.

The scopes 1 and 3 are not directly connected to these DFG-projects. The relevant publications A and F were based upon investigations performed between 1998 and 2008 at the Institute of Landscape Hydrology (former Institute of Hydrology) under projects titled “Water availability and water quality” and “Substance transport and transformation in river basin scale” financed by the ZALF budget. The external scientific board of ZALF evaluated this project.
2 Synthesis of the papers

2.1 Large-scale modeling of the groundwater flow: A tool for impact assessment of global change on water resources

The prediction of landscape development under changing environmental and climatic conditions requires the assessment of land and water management impacts. Under the specific hydrogeological conditions of the glacially formed landscapes, knowledge on groundwater-borne transport is essential for the comprehensive understanding of the water and substance cycle. The geological structure of the landscape is very complex with a high variety in the hydraulic parameter distributions. Various processes emerge from this complexity marked by interdependencies between the hydrological and geochemical system behaviors.

Several models have been established to calculate the water and substance budget in small basins. Some of them were dynamic and spatially aggregated like CREAMS (Knisel 1980) and OPUS (Smith 1992); others were event-driven, spatially detailed like AGNPS (Young et al. 1989). Different models had been developed and applied. They were mainly site-related but were also suitable for regional approaches (CANDY Franko et al. 1995, HERMES Kersebaum 1994, SOCRATES Mirschel et al. 2002). Dannowski et al. (1994) modeled diffuse nitrogen inputs into surface waters only by the use of statistical data. This model approach was then extended by Behrendt et al. (1999). Their MONERIS model covered the main input pathways for nutrients (N, P) into the surface waters while considering the entire catchment area. This immission-oriented source apportionment approach, however, was based on budget calculations from the position of the receiving water body and could therefore not handle reduction measures for individual sites in the basin. The minimum area of the contributing catchments was more a data-related restriction, which must not be smaller than some tens of square kilometers. Kunkel et al. (1999) developed a GIS based grid-oriented model for the analysis of diffuse nitrate inputs into surface waters, which focused on the main runoff components (direct runoff and base flow) as input pathways for nitrogen from non-point sources.

However, comparisons between the modeled nitrogen inputs into surface waters and measured actual nitrogen concentrations in rivers and channels still showed significant discrepancies (Böhlke et al. 2002, Schlesinger et al. 2006). On the global scale, based on the world’s total N production of 100 TgN yr\(^{-1}\) as fertilizers together with further anthropogenic supplies of reactive nitrogen (58 TgN yr\(^{-1}\)), the rivers actually removed only a relatively small portion (\(~20\) TgN yr\(^{-1}\)) of this ingress from the landmass (Green et al. 2004). The major
contingent remained or was depleted in the system plant/soil and in seepage- and groundwater (Galloway et al. 2004). Without considering the effective geochemical processes at the regional scale, reasonable predictions concerning the impact of new land use systems on water quality would not be feasible (Onsoy et al. 2005, Schlesinger et al. 2006). The development of the large-scale groundwater flow model discussed in paper A started with the use of available hydrological models like MIKE SHE (Abbott et al. 1986) to prove a conceptual parameterization particularly adapted for Pleistocene catchments (Steidl et al. 1997, 1999). The aim was the development of a tool for risk assessments under changing climate conditions (land use change and changing water dynamics) to minimize negative impacts according to the guidelines of the European water framework directive. Further development of this approach included the construction and implementation of physical based, large-scale hydrogeological aquifer models in GIS environments. The resultant conceptual hydrogeological data models were sufficiently accurate in describing the heterogeneity of the aquifer structure without the demand for additional data from boreholes and profiles.

Complex deterministic hydraulic models like MIKE SHE, MODFLOW or FEFLOW could be used to describe hydraulic processes prevailing at scales of < 150 km². At larger scales, simplified models could be advantageous, e.g. based on Darcy’s law / Piston flow approach (Abbott and Refsgaard 1996, Wendland and Kunkel 1997). However, even a simple deterministic model concept needed pre-processed data. In using the classical deterministic approach, a large amount of data was required for obtaining the necessary detailed description of the complex hydrogeological situation. The large number of distributed parameters that must be considered in regions with > 200 km² proved field investigations and direct-measurement methods to be too expensive and time-consuming for this assessment (Cushman 1986). Therefore, an alternative to field measurements was the adoption and implementation of thematic maps and available (mostly classified) hydrological data. Using this information, the GIS based model could provide a conceptual replication of a complex geological and hydrogeological structure by systematically reducing scale-dependent parameters as shown in paper A.

Short summary of paper A:

Sufficient knowledge of the hydrogeologic situation is the basis for modeling the regional substance flow. However, at larger scales, field investigations and direct-
measurement methods are too expensive and time-consuming for providing the required hydrogeological data. Therefore, a method was developed to produce a comprehensive conceptual data model to parameterize Pleistocene aquifer systems. The application of GIS technologies enabled the development of a methodical approach for describing the hydrogeological conditions of aquifer systems in mesoscale watersheds using available thematic hydrogeological data and digital elevation models. The development of a hydrogeological data model was therefore a prerequisite for modeling the groundwater component and substance flux. The approach was developed in a watershed with an area of 220 km² (Stoebber catchment) and applied to the Uecker basin (2400 km²), located in the north of the State of Brandenburg.

The following classified data from the hydrogeologic map developed by the Central Geological Survey of the GDR (HYKA 50, scale 1:50,000, Voigt 1987 a, b) could be used to provide an area-wide data model of the different aquifers in mesoscale regions:

- Distribution, thickness, and hydraulic conductivity of the mapped aquifers
- Stratigraphic structure of the aquifers and barrier layers (aquitards)
- Thickness of the unsaturated zone
- Potentiometric surface
- Identification of unconfined and confined aquifers
- Hydraulic connections between different aquifers.

The conceptual approach implied the implementation and description of the general hydrogeological and hydrological structures. However, the parameterization was only based on classified data sets. This approach enabled the consideration of the decisive flow functions in the aquifer and in the landscape, e.g. for an effect analysis of land use changes on ground- and surface water quality. It does not enable for the exact downscaling of results to a single point in the landscape like a point measurement in a river, channel or in the groundwater.

The methodical approach is explained briefly in the following points. The spatial distribution of the aquifer properties was determined through estimating the depth of the units’ bases of the hydrogeologic units for each respective grid point. This was achieved with digital topographic information and the classified thickness of the unsaturated and saturated zones. The depth was verified by the calculated
groundwater head, the water and pressure conditions in the aquifer, as well as by known drilling profiles which could be used additionally. Hydraulic parameters were assigned to each layer of this geometric model, e.g. the classified hydraulic conductivity from maps and additional deterministic information like measurements from field sites. All digitized information was converted from vector to grid format. The grid format represented a compromise between the requirements for resolving and the amount of information needed by the calculations. The main steps of further processing were:

- Classification of the geologic and hydraulic parameters and assignment to all grid points in the data model.
- Reducing the spatial heterogeneity and aggregation of the parameters through a systematic schematization of the structure with GIS data model processing.
- Deriving the regional data model from the aggregated and spatial connected parameter records and verification of the hydrogeologic plausibilities with GIS visualisation functions.

The information from the maps was not sufficient to assign all the parameters needed in the model. Some parameters, such as thickness and spatial distribution of aquitards like the moraines of the different glacial phases were not available from the HYKA 50 and were supplemented by data from drilling profiles and expert knowledge. As a second source for this information the lithologic map (scale 1:50 000, Cepek 1999) was used, which is available for the region of the former GDR. This map could be used to identify the distribution and thickness of the aquitards. The processing is nontrivial and reveals a lot of experience and knowledge of the regional geology. Unknown hydraulic parameters like the effective porosity, which is an essential transport parameter for each grid element, were calculated from the saturated hydraulic conductivity based on functions and algorithms reported by Busch et al. (1993) and Abbott and Refsgaard (1996).

The groundwater model approach introduced in paper A served as a basis for an upgrade for considering geochemical transformation processes and a spatio-temporal differentiation of the solute transport behavior. As discussed in paper F, the model was enhanced by detailed geochemical process knowledge in order to enhance the modeling quality via the path ‘soil – groundwater – surface water’ at regional scales. When the hydrogeologic GIS data model was used, the hydraulic interpretation of different catchment compartments in connection
with the derived geochemical conditions provided a comprehensive hydraulic-chemical characterization of the aquifer systems.

2.2. Process studies to determine and parameterize solute fluxes at large scales

2.2.1 Identification of effective regional geochemical patterns in aquifer systems

In order to predict the solute flux in the landscape it is important to consider the controlling processes along the entire subsurface flow path. It is obvious that only regional effective geochemical groundwater conditions can be used as general indicators for a process based modeling approach. The distribution of such regional geochemical patterns in the Pleistocene landscape was primarily identified and described in the Oderbruch region by Kofod et al. (1997) and Liedholz (2001). Therefore, this floodplain was selected for further investigation, and a basic hydrological and geochemical characterization of the Oderbruch region will be presented in the next two sections.

Hydraulic situation of the Oderbruch region

The Oderbruch is a poldered floodplain which belongs to the Oder river basin that covers an area of about 800 km$^2$. The surface of the polder is lower than the base of the Oder River showing a low gradient slope ($< 0.25 \%$). The hydrological situation is characterized by permanent bank filtration of river water into the aquifer and groundwater movement towards the slightly inclined polder area. In contrast, near the surrounding highlands, recharge of groundwater from the western and eastern plateaus dominates. From the Barnim/Lebuser highlands in the West, the average recharge amounts to 1.8 m$^3$ s$^{-1}$ (Quast 1972). The recharge from the Oder amounts to 1.5 to 3.5 m$^3$ s$^{-1}$ at MWL (mean water levels). There is no information regarding the amount of recharge from the Polish side available. Groundwater recharge by seepage is not easy to quantify. It strongly depends on the spatial distribution and thickness of the alluvial loam which covers the aquifer. Up to now, no exact results exist. Quast (1994) expected a maximum of 50 to 70 mm recharge based on climatic water balance calculations.

The Oderbruch belongs to a climatic zone with relatively low precipitation and high evapotranspiration. It is one of the regions in Germany with the least rainfall (long lasting average of 472 mm a$^{-1}$) and a potential evapotranspiration of 620 mm a$^{-1}$. Therefore, the Oderbruch belongs to a semiarid climatic zone (Veit et al. 1987). During the winter season, the climate balance is positive, whereas in the summer period between April and September
the balance is negative (~ - 250 mm). During the dry period, soil cracks with preferential flow appear in the alluvial soil, which partly influence the water and substance flux to the groundwater (Müller et al. 1992).

Figure 1: Hydraulic regions in the Oderbruch (after Kofod et al. 1997)

The aquifer, consisting of sandy and gravel sediments, reaches a thickness of 30 m in the western part and 15 to 20 m in the eastern part near the Oder River. The aquifer is covered by an alluvial loam with a thickness of 1 to ~ 4 m. Considering an average aquifer thickness of 20 m and an effective porosity between 0.15 and 0.25 the effective water storage in the aquifer reaches 2.4 to 4 billion m$^3$. Based on the spatial distribution of regional groundwater levels and flow gradients, Kofod et al. (1997) defined 4 different regions characterized by specific hydraulic gradients and flow velocities (Figure 1):

Region 1 is located parallel to the edge to the western plateau with an area of 158 km$^2$. It is characterized by relatively high hydraulic gradients ($I < 0.005$). The calculated amount of recharge from the highlands reaches ~ 125 Mio m$^3$ yr$^{-1}$ (Kofod et al. 1997). An equipotential
surface causing a watershed divide that separates the groundwater, which is influenced by the Oder from the groundwater that is influenced by the plateau.

Region 3 is located in the southern part of the Oderbruch and represents the largest part of the polder area. The groundwater surface shows a constant gradient, approximately $I = 0.0005$ towards NW. The amount of discharge is relatively constant with $4.7 \text{ Mio m}^3 \text{ yr}^{-1}$ (Kofod et al. 1997). This region is influenced by the direct infiltration of river water with hydraulic gradients directed to the polder centre. Nieschen, one of the main investigations sites for groundwater - surface water interaction is located in this region.

Region 4 is located in the northern part of the polder. Due to low surface elevation and relatively high groundwater levels, this area is called “Nasser Polder”. The hydraulic gradient is small ($i = < 0.0002$) with a discharge of less than $1 \text{ Mio m}^3 \text{ yr}^{-1}$. The groundwater velocity is low and therefore the residence time of the groundwater is high. Kofod et al. (1997) estimated residence times of several hundred years which could be verified by $^3\text{H}/^4\text{He}$ measurements in the groundwater (Sültenfuß and Massmann 2004).

Region 2 parallel to the dike is characterized by bank infiltration of Oder water into the aquifer. The potentiometric surface shows steep gradients $I = 0.01$ directed to the polder centre (W). During the first 500 m distance, the gradient decreases rapidly due to the pressure release from drainage. The groundwater shows high upward gradients in the direction towards the drainage channel. More than 80% of the infiltrating water is discharging into the main channel that is positioned directly behind the dike.

**Geochemistry**

Redox processes determine the geochemical conditions of groundwater systems and control the behavior of various dissolved constituents, such as organic and inorganic contaminants (Appelo and Postma 1996). In the Oderbruch region nothing was known about the redox environment in the deeper groundwater during the regional infiltration process. Therefore, the understanding of geochemical processes that affected the groundwater during the bank filtration and the interaction between shallow groundwater and the alluvial loam was considered to be of particular importance to understand the basic geochemical processes in floodplains.

The hydrochemical situation in the groundwater of the Oderbruch is characterized by anaerobic redox conditions with redox values of $< 150 \text{ mV}$, the absence of free oxygen and relatively high concentrations of redox-sensitive trace metals like iron and manganese (Kofod
et al. 1997, Quast et al. 2000). The transition of oxic river water to anaerobic groundwater proceeds very quickly during the bank filtration process. After a short travel and reaction time O$_2$ and NO$_3$ are consumed within the first few meters of the infiltration path. The spatial distribution of the redox potential and the Fe concentrations correlate very well with the different hydraulic regions classified by Kofod et al. (1997). The lowest redox values (0-50 mV) were detectable in the northern part of the Oderbruch (Region 4), which is characterized by slow groundwater velocities and long residence times (Fig. 2). Anaerobic environmental conditions with Fe and minor SO$_4$ reduction are coherent with these hydraulic conditions. To determine a regional distribution of the saturation index (SI) for ferrihydrite more than 150 groundwater samples were modeled with PHREEQC (Merz et al. 2001a). The distribution of the SI showed unsaturated conditions in the northern and middle part of the polder region. In this region, the Fe$^{2+}$ concentration is controlled by the dissolution of hydroxides in the sediments which is limited kinetically.

In region 3 (southern part of the polder), the redox potential showed values, which were 100 mV higher on average. A good correlation exists with the higher flow velocities and lower residence times of the groundwater. Free oxygen could not be proven in the whole aquifer, which is influenced by the bank filtration process. The SI values for ferrihydrite indicated a balance between ferrous and ferric iron.

Region 1, which is influenced by recharge water from the Lebus/Barnim plateau, showed different geochemical conditions. Free oxygen, redox potential > 240 mV and trace elements concentrations below the detection limits are distinct indicators for stable aerobic conditions. Clearly positive SI values for ferrihydrite were calculated. The Ca and Mg concentrations were above saturation which can be explained by the contact with till and calcareous sands common at the plateau. Groundwater analyses from the Lebus plateau showed data comparable to those taken in region 1 of the polder (Merz et al. 2000, Liedholz 2001).

The regional geochemical distribution patterns showed a high temporal and spatial stability. Considering the years 1994 to 2000 no change could be demonstrated by multiple geostatistical analyses carried out by Schafmeister and Liedholz (1998) and Schafmeister (1999). Even after the outstanding flood event in the summer of 1997, no regional change in the distribution pattern could be proven (see paper E).

The regional distribution of geochemical parameters was fitted using a geostatistical model GEO-EAS (Englund and Sparks 1991). Variograms were calculated to specify the regional coherence of the redoxpotential and Fe concentrations. The results confirmed a spatial correlation of both parameters for a distance of 6-8 km (Quast et al. 2000, Merz et al. 2001a).
The relatively high nugget effect indicated by the variogram was an interesting aspect. This result was important because it indicated two processes that are controlling the substance dynamic in this region. One is the regional distribution of redox zones, which are controlled by the long-term infiltration of river water into the aquifer. This aspect, discussed by Kofod et al. 1997 and Quast et al. 2000, was named “lateral flow hypothesis”. The hypothesis is based on the assumption that main geochemical patterns in the Pleistocene aquifer systems are controlled by specific redox processes along regional groundwater flow paths. Water management measures like lowering of the groundwater table locally modify these regional patterns. The presented risk assessment approach includes this context as a basic component.

The second process, hidden in the nugget effect, shows the direct influence of the seepage water following small-scale heterogeneities of the alluvial loam (local distribution, lithology and thickness) and specific local anthropogenic influences like e.g. drainage channels.

Figure 2: Spatial distribution of the redox values [mV] in the Oderbruch aquifer (left) and the calculated variogram (right) (after Merz et al. 2001a)

Investigations in the northern part of the Oderbruch started in the region 2 at Bahnbrücke site, where the infiltration of river water into the aquifer controls the hydraulic and geochemical conditions of the polder (Fig. 1). This region was chosen to identify and specify the complex geochemical and hydraulic processes affecting the geochemical environment in the aquifer. The amount of aquifer recharge and the main flow gradient had already been calculated by Quast (1972) and Quast and Müller (1973). However, the exact flow characteristics in the
polder, the discharge behavior in the direct environment of the channels and water budget
calculations were still topical. The hydraulic contact between river and groundwater is more
or less unhindered and the steep hydraulic gradient between the water level of the river Oder
and the groundwater table results in permanent lateral infiltration of river water into the
aquifer.

**Short summary of paper B**

Aquatic systems are often characterized by redox reactions that control the availability
of redox-sensitive species such as O₂, NO₃, Mn²⁺, Fe²⁺, SO₄, H₂S or CH₄. Redox
sequences, driven by the consumption of dissolved or sedimentary bound organic
matter and characterized by the reduction of electron acceptors, can be observed in a
number of hydrochemical systems. The reactions generally proceed from the highest
energy yield downwards (Froehlich et al. 1978, Berner 1981 a,b). The reasons for the
specific order of a typical redox sequence, starting with the consumption of O₂ and
proceeding downwards to the zone of methanogenesis, are of both thermodynamic
and kinetic/microbial nature (Appelo and Postma 1996). The resulting redox zones,
characterized by either the presence or absence of a redox species as suggested by
Champ et al. (1979) and Berner (1981 a,b), do not necessarily have sharp boundaries.
Simultaneous use of several oxidants has been observed in some cases (Postma and
Jakobsen, 1996).

The study results identified 5 zones of different redox processes in the deeper
groundwater (Fig. 3). While conservative tracers like Cl⁻ can show transient behavior,
the performance of all redox components is stationary. The system seems to be well
buffered, since input variations of redox sensitive species and hydraulic differences
show no effect at all. Conditions within the river water are oxidizing. During
infiltration (zone I) at the river base O₂ and NO₃ are consumed within the first few
meters or even decimeters of underground passage. The reduction probably happens
within the riverbed. The most significant changes in processes related to microbial
degradation of organic matter during bank filtration are often reported to occur within
the first meter of infiltration (Jacobs et al. 1988, Bourg and Bertin 1993, Doussan et
al. 1997).

Fe(hydr)oxide reduction dominates the hydrochemistry of zone II. The Mn²⁺ content
of the water increases up to a distance of 150 m from the Oder (below the main
drainage ditch) where Mn(hydr)oxide reduction rises to a distinct maximum. The Fe$^{2+}$
concentration of the groundwater increases just after Mn$^{2+}$ does and continues to rise
within the entire studied area. Since the Fe and Mn-(hydr)oxide reduction processes
consume acidity and produce inorganic carbonate, pH and HCO$_3^-$ also increase in flow
direction. After reaching peak concentrations of almost 0.1 mmol l$^{-1}$ at 150-175 m of
river distance, the Mn$^{2+}$ concentrations decrease to below 0.01 mmol l$^{-1}$ at a distance
of 600-700 m from the Oder, in the zone III. Possibilities for a Mn$^{2+}$- sink could be
the precipitation of rhodochrosite, which has long been described by several authors
for marine sedimentary environments (Li et al. 1969, Suess 1978, Thompson et al.
dimensional transport and reaction model approach has successfully reproduced the
processes near the river with a redox model supplemented by a kinetic
precipitation/dissolution approach (Holzbecher et al. 2002).

Figure 3: Redox sequences during bank filtration in the northern Oderbruch

At 3 km river distance the zone IV starts. SO$_4^{2-}$ concentration decreases below 0.3
mmol l$^{-1}$. The SO$_4^{2-}$ decrease is accompanied by increasing HS$^-$ concentrations. The
sulfidic zone is comparatively small due to changing hydraulic conditions in zone V.
The dissolution process of Fe$^{2+}$ from the hydroxides at the sediments can be described
by a linear fit through a Fe$^{2+}$ versus travel time graph. This correlation indicates a
zero$^{th}$ order process. It results in a dissolution rate of 0.0033 mmol l$^{-1}$ a$^{-1}$. The
exponential fit of SO$_4^{2-}$ versus travel time indicates that the reduction is controlled by a
first order decay process typical for many microbiologically mediated processes like the denitrification. The corresponding constant rate is 0.0169 a\(^{-1}\) equivalent to a half-life of 41 years.

Zone V represents the polder centre with a river distance of 5 km. It is characterized by low pH and high Fe, Mn, Ca, DOC and SO\(_4\) concentrations. High Fe\(^{2+}\) concentrations were expected from the continuously progressing redox reactions. However, from observations made in zone I-IV, one would expect DOC and SO\(_4\) concentration particularly to decrease with increasing infiltration distance, as they do near the river. In the present reducing environment, the SO\(_4\) concentration can only be equal or less than the river input concentration. Instead, SO\(_4\) concentrations increase sharply to > 4 mmol l\(^{-1}\) in the central polder, although HS\(^-\) concentrations continue to increase. DOC seemed to be the major reductant for the redox processes described above and should therefore continue to decrease as well. However, towards the polder centre, DOC concentrations in the groundwater approximately double.

As discussed in paper B, the Oderbruch polder shows a distinct interrelation between the hydraulic properties and the groundwater chemistry. The investigation results confirm the lateral flow hypothesis and enable the regional consideration of redox sequences at larger scales. However, a clear geochemical anomaly is noticeable in region 4 (“Nasser Polder”). The expected field of proceeding SO\(_4\) reduction is disturbed. High sulfate concentrations in the groundwater and in the seepage concentration profiles of the alluvial loam indicate an exceptionally high substance flux in this region. The NO\(_3\) concentrations measured in the soil profiles exceed more than 600 mg l\(^{-1}\) and more than 1200 mg l\(^{-1}\) SO\(_4\) (Kofod et al. 1997).

Therefore, intensive geochemical studies were performed along a transect to identify the relevant processes. These results are discussed in paper C. The paper clarifies, based on stable isotope data, the basic question of whether the sulfate reduction latently proceeds in the expected aquifer compartment and why the expected redox sequence is disturbed. The aim was to determine sources and sinks of SO\(_4\) in the groundwater and to prove whether an additional source of local FeS\(_2\) oxidation within the alluvial loam exists that explain the extraordinary concentration pattern of SO\(_4\) in the aquifer. To that end, stable isotope data from wells located in a 5 km transect along the flow direction from the Oder River to the polder centre were used.
Summary of paper C

Stable isotope analysis of $^{34}$S and $^{18}$O has been used for decades to identify and quantify bacterial reduction and oxidation of sulfur species in the field. Bacteria of the genus *Desulfovibrio* and others catalyze the reduction of SO$_4$ (e.g. Jorgensen 1982), producing dissolved sulfide and mineralized carbon. This reaction is isotopically competitive due to the preferential consumption of the lighter isotopes ($^{32}$S and $^{18}$O). It leads to the formation of H$_2$S and HCO$_3$ depleted in $^{34}$S and $^{18}$O relative to the original SO$_4$. Consequently, the residual SO$_4$ fraction will become heavier, i.e. enriched in $^{34}$S and $^{18}$O (e.g. Harrison and Thode 1958, Kaplan and Rittenberg 1964, Nakai and Jensen 1964, Lloyd 1968, Rees 1973). Pyrite oxidation is microbially catalyzed and proceeds in several intermediate steps to produce Fe, H$^+$ and SO$_4$. Fractionation effects are represented as $^{34}$S of the sulfate minus $^{34}$S of sulfide. In most cases, the sulfur isotopic composition of SO$_4$ resembled the one of the sulfidic sulfur source.

The main potential sulfate sink in the Oderbruch aquifer is sulfate reduction. The SO$_4$ content of the groundwater at the field-site Bahnbrücke lies within the range observed in the river water (about 1 mmol$^{-1}$ of SO$_4$). In contrast, a sudden drop in Eh, O$_2$ and NO$_3$ content plus a gradual increase of Mn$^{2+}$ and a little later Fe$^{2+}$ in solution indicate anoxic, reducing groundwater conditions (compare publication B). Even though the groundwater does not show any sign of SO$_4$ depletion at Bahnbrücke, traces of sulfide were detected and a faint odor of H$_2$S was occasionally noted during sampling. Despite the fact that the error associated with the S$^-$ measurement is relatively large at these low concentrations, the sulfide content clearly increases along individual flow-paths. Both the $^{18}$O and $^{34}$S signature of the groundwater-SO$_4$ reflect a shift towards heavier residual SO$_4$ with travel distance. The presence of sulfide in the groundwater as well as its isotopic signature of SO$_4$ clarify that biogenic SO$_4$ reduction does take place at the field-site Bahnbrücke, even though the SO$_4$ content of the groundwater is not obviously affected.

Further inland the increasing sulfate contents are caused by an additional SO$_4$ input from the unsaturated zone that have a clear division between confined and unconfined hydraulic conditions, as was already observed by Kofod et al. (1997). Where the groundwater is unconfined, the formerly hydrous alluvial loam became strongly drained and the resulting morphological texture changes, such as shrinking fissures,
enabled a preferential and increased downward flow, at least where the loam has a limited thickness. In addition, lateral flow velocities are much lower in the central polder as compared to closer to the river. The groundwater shows a layering in terms of SO$_4$ content, although there is no dividing impermeable layer in between the filter screens. The shallow wells contain about 1/3 more SO$_4$ than the deeper wells. The values were very stable over the time span of sampling. This indicates that the additional SO$_4$ source is located in the upper sediment layers. The input of SO$_4$ besides other water constituents, therefore largely depends on the hydraulic situation. In the zone with increased sulfate concentrations, $^{34}$S values of groundwater sulfate decrease with lower $^{34}$S-SO$_4$ values in the shallow wells, demonstrating that 'lighter' SO$_4$ is added from above. The $^{34}$S-SO$_4$ value of the reduced precursor within the loam should be lower than 5 ‰, because no or only little isotopic fractionation occurs during sulfide oxidation (Field 1966, Steiner and Rafter 1966, Taylor et al. 1984). Since the groundwater contained hardly any SO$_4$ in the previous zone, the major part of the SO$_4$ originates from oxidative dissolution of Fe(II)-sulfide (mainly pyrite) within the fine-grained, organic rich alluvial loam by either oxygen and/or nitrate. Nitrate is likely to be an important electron acceptor, since more than 90 % of the polder area are used for agricultural purposes. Since redox processes are microbially catalyzed, availability and consumability of organic carbon controls the reduction rates. In the case of the Oderbruch aquifer, the reaction rate of SO$_4$ reduction varies strongly with depth. Combining hydraulic and hydrogeological considerations, the wells sampled for isotopic analysis can be subdivided into three zones with very different SO$_4$ reduction rates. The approximate age was derived from the hydraulic model. A semi-log graph of age versus SO$_4$ reveals linear decay curves for each well group, indicating that the reduction is a first order decay process typical for many biologically mediated processes. On such a plot, the slope of each fit represents the half-life of the reduction process. Half-life in the shallow wells near the river is 423 days and for the confined glacio-fluvial aquifer (shallow and deeper wells) 18,550 days (50 years). The number of data points for each group (4, 3 and 11 points, including river) is sufficient for giving statistically significant results ($r = 0.89$) only in the latter case. The reason for the reductions differing over several orders of magnitude, lies within the different organic carbon contents of the sediments. The glacio-fluvial aquifer contains little C$_{org}$ (<0.1 wt.% C$_{org}$, mean value of 78 samples throughout the entire observation area), while the
shallow wells near the river were placed in or near a local microenvironment with a much higher sedimentary bound \( C_{\text{org}} \) content.

The rate of the aquifer \( \text{SO}_4 \) \( (t_{1/2} = 50 \text{ years}) \) lies between those reported for Canada (Robertson and Schiff 1994) with \( t_{1/2} = 3 \) years and Germany (Strebel et al. 1990) with \( t_{1/2} = 75-100 \text{ years} \). At Sturgeon Falls (Robertson and Schiff 1994), the sediment properties of the homogeneous silty fine sands (\( C_{\text{org}} = 0.03 \text{ wt.}\% \)) were different and \( \text{SO}_4 \) concentrations were much lower (<0.3 mmol l\(^{-1}\)). The Fuhrberger Feld aquifer (Strebel et al. 1990) like the Oderbruch aquifer, was formed during the Pleistocene ice ages and the sands and gravel (0.1-1 wt.\% \( C_{\text{org}} \)) resemble those investigated in the present study. It seems that the similar origin and consequently the similar composition of the \( C_{\text{org}} \) content, rather than the total amount, determines the rate of reduction in different aquifer systems. In some areas where \( \text{SO}_4 \) concentrations remained constant, \( \text{SO}_4 \) reduction could only be identified by isotopic evaluation.

The investigations proved that the \( \text{SO}_4 \) originated from river water infiltration and from oxidative dissolution of \( \text{FeS}_2 \) within the alluvial loam covering the aquifer sands in the centre of the polder. This leaching process resulted from the change of confined hydraulic conditions near the river to unconfined conditions in the central polder as described in paper C. However, this change is not of natural origin. In the northern part intensive groundwater lowering has been occurring for the last decades. The lowering of the groundwater table below the base of the alluvial soils by non-adapted water management results in a significant increase in hydraulic gradients and percolation rates. Percolation rate increase provides oxidation in soils and in the unsaturated zone through the transportation of oxygen and nitrate into greater depth. These aerated zones are potential sources for nutrients (N and P) and trace metals indicated by exceptionally high sulfate concentration.

### 2.2.2 Process analysis and regional balancing of management controlled water and substance exchange between groundwater and surface water

The Pleistocene landscape is widely used for agricultural purposes. However, due to its glacial genesis the landscape is rich with small surface waters like ponds, potholes and small lakes with waterlogged areas spread over the till plateaus. In the discharge areas where wetlands originally dominated, drained floodplains dominate now characterized by shallow groundwater surfaces, upwardly flow gradients and even arthesic conditions. For centuries, it
was normal practice to drain nearly all regions to cultivate the landscape (recharge and
 discharge) and to enable an effective discharge of water out of the landscape. Today, more
 than 80% of the whole water network in Brandenburg is of artificial origin (MLUR 2003). It
 will be a big challenge to handle this vast drainage system in the future under the pressure of
 climate change. However, a good solution is not a question of cutting all drainages or filling
ditches and channels. The aim must be a sustainable management of drainage systems for
ongoing agricultural land use without excessive losses of water and solutes.
The handling of local drainage of waterlogged sites is still a large problem in Germany
(Lübbe 2008). The tile drainage systems are a precondition for agricultural land use but high
nutrient fluxes directly from the topsoils are observed. Nitrate and phosphate delivered by
drainage have a strong eutrophying impact on downstream water bodies in all parts of the
world (Kahle 2005, Skaggs et al. 2008). The drainage water has the character of fast interflow
and shows minor retention potential. Due to the mostly unknown spatial distribution of the
tile drain systems and lack in concentration measurements, it is hardly possible to balance
this substance flow. The actual way to handle this problem is to locally install purification
ponds that can be used for the accumulation of biomass and to induce biogeochemical
transformation processes (Steidl et al. 2008).
Where another type of drainage is concerned, substance losses through open ditches and
channels are critical, especially in discharge regions. These channels are in direct contact
with groundwater and show intensive exchange rates of water and contaminants. For the
adaption of management strategies, it is essential to identify geochemical and hydraulic
processes that control degradation or fixation of pollutants in the streambed sediments. For
prospective mitigation strategies, management measures should be adjusted to enable the
stabilization of geochemical retention zones that act as natural barriers between aquifer and
drainage channels.
The investigations for this approach were exemplarily performed in the Oderbruch. The
polder area is lower than the water level of the main river. Hence, groundwater drains to a
drainage network, which stretches over the entire region. Such a network disturbs the natural
sink function of the floodplain. However, due to the anaerobic conditions in the alluvial loam
and in the aquifer, groundwater is actually not affected by nitrate contamination. Relevant
nitrate concentrations could neither be proven in the deeper aquifer nor in the drainage
channels. Nevertheless, increased SO$_4$ and NH$_4$ concentrations indicate latent nitrate leaching
from the soils and the alluvial loam based on processes already discussed in paper B and C.
The glacial aquifer sediment contains geogenic trace metals from weathered Scandinavian base material. Redox sensitive trace metals such as Fe, Mn, As, Cu, Cd, and Zn are mobilized from aquifer sediments under anaerobe conditions and discharge into the surface waters as described by Brown et al. (2000), Groffman and Crossley (1999) and McArthur et al. (2001). In the Oderbruch, Fe and Mn were found with concentrations above the threshold of drinking water. Merz et al. (2001b) observed that under specific hydraulic and geochemical conditions, trace elements can accumulate in the channel sediments during the discharge process. The fixation is controlled by the precipitation of hydroxides and oxides, by adsorption to Fe/Mn-hydroxide coatings or by carbonate precipitations in redox transition zones, as discussed by Appelo et al. (2002) and Selim et al. (2001).

The accompanying studies are summarized in the papers D and E. The objectives were the identification and regional quantification of the geochemical exchange processes under the predominant hydraulic conditions. The aim was to identify the function and stability of geochemical barriers through detailed characterization of trace metal migration behavior. The selected trace metals react very sensitively due to the redox processes in geochemical and hydraulic transition zones and can be used as an indicator for redox-dependent solute flux from channel drainage systems. For this reason, dissolution and precipitation processes were examined to allow the exemplary analysis of oxidation, reduction and mixing processes. Results indicated that the interaction of groundwater and surface water was, as it turned out, a basic component in the assessing and balancing of flow and substance transport processes in this typical pleistocene discharge region.

**Short summary of papers D and E**

The drainage system of the Oderbruch region consists of three main hydraulic ditch types. The first two types (sites Zollbrücke and Bahnbrücke), show permanent discharging conditions in combination with low and high hydraulic gradients, the third type (Nieschen) shows discharging, but seasonally dry conditions (Fig. 4). The latter is strongly influenced by changing groundwater levels, which result in an intensive periodical change of the hydrochemical environmental situation. During the exfiltration phase at Nieschen, the deep, anoxic groundwater rises and mixes with shallow groundwater that has higher oxygen content. During the discharge phase, oxidation dominates in the upper part of the profile. Discharging metal ions from the aquifer oxidize and precipitate as or together with amorphous Fe(OH)₃ in the channel bottom sediments. When the water levels are low, the channel runs dry with
cumulative oxidation in the streambed sediments. The resulting oxidation zone has a thickness of 70 to 80 cm and is positioned in between the fluctuating water levels. The total Fe concentration in the sediment varies between 1-2 g kg\(^{-1}\) in the anaerobic aquifer (background concentrations) and nearly 45 g kg\(^{-1}\) in the oxidation zone under the ditch floor. The increasing Fe content in the oxidation zone belongs mainly to the oxalate fraction indicating a high amount of fresh, amorphous Fe hydroxides. Under these environmental conditions, Fe is present mainly as ferrihydrite (Cornell and Schwertmann 1996).

Figure 4: Map of the Oderbruch region, including the drainage ditch system and locations of the investigation sites

The accumulation rate of trace metal in the oxidation zone was determined by local balance calculations. In the streambed sediments of Nieschen channel an effective chemical barrier with high Fe accumulation can be observed. This Fe dominated oxic horizon controls the accumulation of Mn > Cu > As > Zn > Cd, which are mainly associated with fresh, amorphous Fe oxyhydroxides. The accumulation varies between nearly 100 % for Fe, 80 % for Cu, 60 % for As and less than 10 % for Mn, Zn and Cd. These calculations are based on the dissolved trace metal ion
concentration in the shallow groundwater and modeled discharge rates for the respective channel transects.

Investigations under permanent discharging conditions were performed in the northern part of the Oderbruch region at Zollbrücke. Sequential extraction of channel sediments of Zollbrücke shows a significant accumulation of different trace elements in the first 30 cm of the profile. The results indicate mass accumulation in the following order: Fe > Mn > As > Cu > Zn > Cd. In terms of the distribution of metal enrichment, except for Mn, clearly lower accumulation rates than those for Nieschen were observed. In relation to the dissolved trace metal ion concentration in the shallow groundwater, the accumulation varied with 20 % for As, 15 % for Fe, 13 % for Mn, 10 % for Cu and less than 6 % for Zn. The accumulation was mainly controlled by oxidation and degassing of CO$_2$. During the discharge process, the degassing of 1 mmol l$^{-1}$ CO$_2$ was calculated. This change in the carbonate balance led to the oversaturation of calcite and rhodochrosite in the upper part of the profile, which explained the higher accumulation rates for Mn.

The potential risk of trace metal discharge increases when the hydraulic system changes to constantly high hydraulic gradients. Where the ditch type Bahnbrücke is concerned, high water and high solute flux into the drainage system could be observed. Water budget calculations showed that 80 % of the bank filtrate discharged into this drainage ditch. Under the hydraulic conditions of permanent discharge at high rates, the chemical gradient between the aquifer and the ditch is not steep. Only low oxidation impact could be detected in the bottom floor sediments. Oxidation was restricted. The measured data, fitted with PHREEQC in the geochemical model, indicated only a minor dissolution of atmospheric oxygen and oxic iron precipitation. Therefore, the enrichment of trace metals was very low in comparison to Nieschen and Zollbrücke. Only marginal Fe and Mn accumulation was reported. No significant enrichment of Cd, Zn, As, and Cu could be detected. The Fe content increased from background values (1.5 to 2 g kg$^{-1}$) to a maximum of 3.2 g kg$^{-1}$ sediment. The enrichment was restricted to a thin horizon directly under the ditch bottom. The thickness of this horizon did not exceed 10 cm. The oxic accumulation horizon was marked out to the reduction zone, with a change in the environmental conditions within a few centimeters. The fixation of Mn, while parallel to Fe, was very low. Less than 1 % of Mn was fixed in the sediments.
The regional matter balance calculations showed that during mean high water levels in the Oder River 90,000 m$^3$ d$^{-1}$ discharge into the active channels. During exfiltration more than 130 kg d$^{-1}$ of iron and 150 kg d$^{-1}$ of manganese were removed from the aquifer sediments and transported into the channels. However, because of the ditch type, defined by the hydraulic situation, the amount of the trace metal fixed in the sediments under the ditch floor, showed a high variability. In ditches that dry up periodically, only marginal negative impact on the surface water could be observed. This was because of the intensive retardation of iron in the chemical barrier built up in the oxidation zone directly under the channel bottom.

However, considering the effective enrichment factors determined exemplarily in Nieschen and Bahnbrücke, ~55 kg d$^{-1}$ of iron and < 2 kg d$^{-1}$ of manganese were fixed in the drainage ditch sediments whereas the surplus migrated into the surface waters of the drainage ditches. It was obvious that the main discharge of trace metals occurred in the permanent exfiltration ditch type. More than 90% of the amount of iron that migrated into the surface water was associated with the Bahnbrücke type. The manganese that migrated into the surface water mainly belonged also to the permanent discharging ditch type located in the north of the Oderbruch region. Although the length of the Bahnbrücke ditch type only reached 35% of the total length, more than 95% of the total manganese and iron discharged into these ditches.

2.3  **Regional assessment of agricultural impact using redox potential as proxy for the denitrification potential**

Risk assessment for agricultural land use systems at the river basin scale should be consistent with the expected impacts on soil, water and sediments. It should also be defined in terms of valuable and practicable indicators, which are in line with the targets defined by the European Water Framework Directive (WFD). However, risk assessment at the river basin scale actually lacks the consistent link between the various effective processes and selected indicators following the EU-DPSIR approach of Smeets and Weterings (1999) at different scales. Therefore, a clear correlation between processes and indicators is needed in model approaches to assist the mitigation of agricultural impacts through adapted management.

To achieve the targets of the EU Water Framework Directive (WFD), good ecological status of all surface waters and good quantity and quality standards in groundwater should be reached by 2015. In practice this implies the reduction of N-loads to below the concentration
level of 25 mg l\(^{-1}\) nitrate in the groundwater. To reach this aim, management practice should reduce nitrate fertilization in sensitive regions in combination with area wide application of “good agricultural practice”. The main problem will be the identification of sensitive regions with low retention potential for nitrate and the target-oriented application of adapted management strategies. This approach requires the identification of:

- spatial and temporal distribution of the nitrate leaching from soils
- solute transport along the groundwater flow path
- effective regional geochemical patterns in the aquifers
- indicators that allow the quantification of regional denitrification potential
- socio-economic circumstances.

Up to now there has been a good understanding of the main leaching processes of nitrate from soils at the field scale (Ernstesen et al. 1998, Cannavo et al. 2004, Kersebaum et al. 2005). But an integrated soil-water-sediment risk assessment approach, which allows impact balancing by diffuse N-pollution at different scales is still needed, in which basin management decisions are taken into consideration. The discussed approach includes the identification of geochemical indicators and the definition of variables and boundary conditions for the spatial quantification of regional denitrification rates.

Impacts of land use and climate controlled environmental threats on the sediment-water-river system can be monitored through indicators that play a key role in the subsurface environment. Indicators should be easy to measure or to quantify but, still sensitive enough to mirror environmental changes in space and time. Furthermore, they should comply with the complexity of the environmental processes. Their identification requires a good understanding of the geochemical and hydraulic processes in the landscape and should be related sufficiently to contaminant transport and accumulation processes. The parameterization of the GIS based regional groundwater flow model with process related indicators creates a platform that describes the geochemical and hydrological interactions based on groundwater redox milieu and residence time.

Redox-dominated microbial degradation processes mainly cause the limitation of nitrate pollution from agricultural land use systems (Dick et al. 2000, Böhlke 2002). Denitrification can reduce significant amounts of nitrate in the vadose and saturated zones through microbial activity (Buchau et al. 2000). Organic carbon is an important electron donator during this degradation process in the sediment-water system. The organic material is decomposed by microorganisms which sequentially use the stock of available electron acceptors (Dassonville
et al. 2004). Typical redox sequences in nature start with the consumption of $\text{O}_2$ and proceed downwards to the zone of methanogenesis (Froehlich et al. 1978, Appelo and Postma 1996). The denitrification process is positioned at the beginning of the redox sequence and limited mainly by the availability of free oxygen. With the beginning Mn-Fe reduction defined by redox values of less than 150 mV, the denitrification process would already be completed (Holzbecher et al. 2002). For this assumption to be valid, the predominance of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple buffering the redox system is a prerequisite. This could be proven for the major anaerobic aquifer systems in the Pleistocene study region. Therefore, the ferrous/ferric redox state was used as proxy to describe the redox conditions in the groundwater.

Although the landscape is very complex and heterogeneous, with regard to almost all parameters, landscapes are highly structured and at larger scales, geochemical processes are influenced by these structures. The grade of aquifer coverage for example shows high correlations with the environmental redox conditions in the groundwater. The hydraulic interpretation of different structure units, considered in terms of groundwater flow direction and residence time in connection with the redox state, allows the allocation of spatially distributed chemical reaction pools along the calculated regional groundwater flow path.

As long as surface and groundwater are in close hydraulic contact (in the sense of effective recipients of nitrate), the total residence time of groundwater can be calculated along its flow path from recharge into the aquifer to discharge into the surface water. With the implementation of the geochemical proxy-indicators in the model algorithms, it is possible to define redox-dependent half-life times and denitrification potential for the groundwater-borne nitrate flow in regional aquifer systems. The overall result is the spatially distributed nitrate retention factor usable for regional adaptation and validation of management strategies.

**Summary of publication F**

The characterization of the predominant geochemical processes was undertaken in different regions of Brandenburg to represent the main aquifer types in the glacial landscape: The Oderbruch region as an example of anaerobic, confined/unconfined aquifers in floodplains, two field sites at the Barnim/Lebus Plateau (Worin, Reichenow) exemplary for unconfined oxic aquifers in recharge areas (Kersebaum 2000, Merz et al. 2000), the Quillow catchment (Uckermark) and parts of the Fläming Highlands as examples for the deeper, anaerobic and confined aquifers (Merz et al.
The Fläming Highlands themselves are an important recharge area, but the deeper aquifer systems have a transit character, comparable to the Uckermark. To quantify the denitrification rate, a first order decay process typical for biologically mediated processes was used. The required parameters such as the rate constant were based on field measurements and experimental results with similar or comparable sediments. The denitrification rate of nitrate along a flow path between entry into groundwater and arrival at any point considered in the grid model was described by a time-dependent function where the half-life of nitrate degradation was introduced. In this approach, the existing GIS based hydraulic algorithm was enhanced for the consideration of the nitrate degradation potential, based on first order rate constants. The corresponding half-life for each grid cell was calculated using Equation 1:

\[
\frac{dc_{NO_3}}{dt} = k_{NO_3} \cdot c_{NO_3,0}, \quad t_{1/2} = \frac{\ln(2)}{k_{NO_3}}
\]

with

- \(c_{NO_3,0}\) initial concentration of nitrate, \(mg l^{-1}\)
- \(k_{NO_3}\) reaction rate constant, \(yr^{-1}\)
- \(t_{1/2}\) half-life, \(yr\)

The more anaerobic conditions produced a very short half-life especially in covered and deeper groundwater systems. The half-life of less than a year could be assumed where degradable carbon compounds or reduced sulfur ferric compounds were present in the aquifer sediments (Böttcher et al. 1990). In the case of uncovered aquifers, which are very common in Brandenburg, aerobic redox conditions dominated. In these regions a low denitrification potential was determined resulting in a definitely longer half-life.

Groundwater quality is mainly influenced by intensive reactions and processes controlled by the local geological/stratigraphic conditions (Hannappel and Voigt 1997). Therefore, regionalization was performed through the allocation of geochemically based reaction rates to classified regional geologic structures. The needed information was drawn from a hydrogeological map which describes the spatially distributed potential sensitivity towards groundwater pollution. The original map, published by Hannappel (1996), contained classified data on the stratigraphic composition of the covering layers and the distance to the water table, and defined
different hydrogeomorphic units. The spatial correlation of redox-controlled denitrification rates was based on these hydrogeomorphic units adopted from the hydrogeological map. Over all, seven different aquifer units with respective denitrification half-life times were defined.

In the final step, the denitrification rate for each grid cell along a complete groundwater flow path was modeled. From this procedure, a groundwater flow based retention potential for nitrate at the regional scale was calculated using Equation 2:

\[
R = 1 - \prod_{i=1}^{n} e^{-\ln(2) \frac{t(r_{0})}{t_{1/2,i}}} \tag{2}
\]

with \( t(r_{0}) \) residence time in grid cell i along the groundwater flow path, \( r_{0} \)

\( t_{1/2,i} \) half-life of denitrification in grid cell i

Typical questions like regionalization, identification and quantification of the linked hydro-geochemical processes together with the prediction of the system behavior under changing boundary conditions can be answered with this approach. The results reflected the wide range of denitrification rates in the aquifer systems. In connection with the high variety of groundwater residence times they provided a substantial overview of the sensitive and less sensitive regions (due to diffuse nitrate contamination) in the landscape.

The validation of the bottom-up conceptual modeling approaches with point measurements was very critical. Therefore, the improvement required distinct cause-effect analyses in selected validation areas. The western part of the Oderbruch aquifer was exclusively supplied by discharging groundwater from the Plateaus of Barnim and Lebus and characterized as recharge areas in the overall model. Therefore, the model results for this region should be mirrored by the nitrate distribution of the Oderbruch aquifer. The measured nitrate distribution data showed a convincing congruence with the model results. Only the low nitrate concentration in the Stoebber river delta seemed inconsistent with the low retention potential modeled for this region. However, this situation was clearly the result of low nitrate inputs as the Stoebber valley belongs to a nature protection area connected with a high percentage of forest, restricted fertilization and extensive green land farming.
3. Conclusions

With progressive climate change occurring, the protection of hydrological resources in the younger Pleistocene glacial landscapes creates the need for innovative water management strategies and risk assessments for the future. Impacts on water resources are intensified due to changing water balances and changing land use systems in the water basins. Groundwater recharge is expected to decrease. Pressure on groundwater quality is expected to increase due to increasing fertilizer, pesticide application and irrigation to sustain the yield of energy crops. Furthermore, changing groundwater flow patterns can threaten groundwater and surface water quality due to changing hydrological boundary conditions in the landscape.

Water management should begin with a geospatial analysis of the inputs and the losses of nutrients and other substances (Richardson et al. 2001). It is important to identify the effective hydraulic flow paths, fluxes, stores and the residence times to quantify the redox-dependent degradation processes of pollutants.

Based on this knowledge, the cause/effect chain of climate and technological changes and their impacts on water quality can be assessed explicitly. The approach followed here based on three different steps:

1. The application of deterministic models for the identification and quantification of geochemical and hydraulic parameter sets.
2. The use of a more empirical conceptual model approach to provide parameterization of hydraulic and geochemical conditions in large aquifer systems. Typical questions like prediction of the system behavior under changing boundary conditions can be answered in principle with this modeling approach.
3. In the third step, adapted agricultural land use and water management strategies can be validated by calculating realistic scenarios of water and solute fluxes under different boundary conditions. In the case of nitrate leaching, recharge and nitrate concentrations patterns of potential land use schemes can be externally modeled by specific models (e.g. HERMES, Kersebaum 1994) that take water and nutrient balances, soil cover and tillage characteristics, pesticide application frequencies and potential irrigation arrangements into consideration. It would be advantageous to apply specific water management models like WBaMo for the approval of water management approaches in floodplains (Dietrich et al. 2007).

The results represent the basic information for the evaluation of management strategies. They include the system knowledge, which is a prerequisite for adapting the management to the
different hydrogeological regions of the landscape. The regions show specific hydraulic and geochemical characteristics that control the water and solute fluxes. Therefore, effective mitigation of pollution should be based on management strategies specifically adapted for regions of high sensitivity (Fig. 5). Recharge areas e.g. are dominated by uncovered, unconfined aquifers and therefore vulnerable to groundwater contamination, especially from nitrate. The geochemical environment in the seepage and groundwater is characterized by high oxygen contents with low DOC concentrations. Under oxic conditions the denitrification process is strongly restricted indicating high risk for nitrate contamination of the aquifer systems. In addition, floodplains and lowlands play an essential role in the water and substance cycle of the landscape and react very sensitively because of water management measures.

Figure 5: Modeling approach for the evaluation of management strategies under pressure of global change

Furthermore, adapted land use approaches should be linked to the enhancement of groundwater recharge and regional water balance. Due to the climate change, water availability will be clearly limited. However, innovative water management can stabilize or even improve the water budget in the landscape. Artificial enrichment of groundwater in
areas of scant natural recharge and storage of surface water (i.e. ponds and lakes during periods of water surplus e.g. during winter time) certainly should play an important role in the future. Usually recharge ponds are located along the course of streams in the discharge regions (Blomquist et al. 2004). An artificial recharge is used to improve a short cycle drinking water supply but is an inappropriate strategy for stabilizing the hydrological cycle. In contrast, water infiltration from ponds and lakes in recharge areas far away from big streams can be a feasible method of recharging underlying regional aquifers (Itzbicki et al. 2008). However, it is still a problem to buffer the surplus of surface water over a longer period because high evaporation rates in the semi-arid climate of NE Germany will reduce potential water stocks rapidly. The implementation of these innovative strategies into concrete management approaches for Brandenburg is a research topic of the INKA-BB project which is part of the BMBF-Joint Research Project KLIMZUG.

Taking a step forward, local storage of surface water or even treated waste water directly in aquifer systems can protect the water pool against evaporation and overexploitation. This water can be used for irrigation and stabilization of the regional water balance. Nevertheless, there still are many open questions regarding the influence of the regional groundwater flow regime, quality maintenance, technical problems and energy balances. The use of wastewater can have a positive impact on agricultural production and water budget. However, little research has been done to understand what long-term effects there are, specifically in terms of irreversible damage to soils, groundwater resources and environment. This measure requires intensive coordination between different participants like federal policies, local authorities and stakeholders. But under the assumption of minimized negative impacts and an adapted regional waste water management such innovative strategies should be considered in the future for handling the progress of decreasing groundwater recharge and to improve groundwater quality through optimized agricultural land use.

Beside recharge areas, floodplains and lowlands play an important role in the water and solute cycle of the Pleistocene landscape. Nutrient storage, denitrification and carbon fixation are the characteristic processes in these regions. No management strategies are reasonable without detailed knowledge about processes and gradients which control the water and solute fluxes. Only proper land and water management through biogeochemistry can improve the preservation of these sensitive natural ecosystems. In flatlands and floodplains most of the water pollution results from agricultural pollution in combination with inappropriate water management operations (Böhlke et al. 2002, Twarakavi and Kaluarachchi 2005). For example, excessive lowering of the groundwater and false drainage management, which is
still a common practice, destroy the soil properties and derange the sink function of the whole system (Fig. 6). Still farmers place high pressure on local water resources authorities to intensify drainage measures in the regions especially in springtime and autumn, the seasons with the high rainfall. But as shown in the Oderbruch, intensive drainage shows no positive effects regarding the drainage effect on loamy alluvial soils. It only causes high costs because there is no hydraulic connection between the groundwater and the surface water standing in the fields (Merz et al. 2004).

Figure 6: Hydraulic and geochemical interactions during lowering of the groundwater table in floodplains (after Quast et al. 2000, changed)

The critical influence of water management measures can be emphasized by looking at the regional balance of trace metals. Nearly 90% of the groundwater-originated trace metals in drainage channels are associated with only one specific drainage type. This type is characterized by a constant groundwater discharge under steep hydraulic gradients. In the streambed sediments of these channels, redox transition zones are not developed which potentially can react as effective geochemical barriers. Therefore, water management practices should strengthen and adjust the redox transition zones deep in the sediment below the channel floor.

Regarding the aspects mentioned above, it is reasonable to initiate additional charge of fresh, oxidized surface water from the accompanying river systems into the channels by drainage sluices. Certainly, these measures should be done based on proper water balance calculations and in close collaboration with the stakeholders to balance competition between different water and land use demands. In terms of the processes, long lasting mean to high water levels
in the pre-flood river are most critical for the solute fluxes. During these periods, which will cumulate in the future due to the climate scenarios, enough surface water would be available and could be used to stabilize the redox barriers deep in sediments. Additionally, the total amount of groundwater discharge should be reduced by lowered pumping rates and locally adjusted channel water levels.

The implementation of process-based indicators into a conceptual regional transport model approach can sharpen an instrument that can prevent or, at least, reduce prospective negative impacts on regional water resources. However, it should be clear that the introduced regional model approach is a conceptual approach, which does not imply a “top down” description of the realistic solute concentration patterns. Besides, it does not consider the bypass transport paths, like tube drainage and interflow, as well as specific hydraulic and geochemical interactions that occur at the interface between groundwater and surface water. The implementation of these locally controlled processes will be a challenge for the next years.

The described model approach can be used for the evaluation of protection measures adjusted to the spatially distributed hydrological processes and geochemical water-sediment interactions in the landscape. Modeling results combined with distinct local management recommendations should provide the complex knowledge for the evaluation and adaptation of land and water management valid for the glacial landscapes in the northern hemisphere under the pressure of global change.

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