

Aus dem Institut für Natur- und Ressourcenschutz
der Christian-Albrechts-Universität zu Kiel

**INTEGRATED MONITORING, ASSESSMENT AND MODELING OF
NITROGEN AND PHOSPHORUS POLLUTION IN A LOWLAND
CATCHMENT IN GERMANY**

A long-term study on water quality

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SUMMARY

Water pollution caused by nitrogen (N) and phosphorus (P) is originated by diffuse and point sources. The point pollution is linked to wastewater from domestic and industrial sewage, whereas diffuse pollution is mainly from rural areas with agriculture and livestock. The monitoring, assessment and modeling of N and P in a lowland catchment were carried out to verify the development of N and P pollution over the last 20 years, and to develop mitigation alternatives to reduce N and P concentrations into rivers. In this study, 462 km² of the upper part of the Stör catchment, a typical rural lowland catchment located in Northern Germany was investigated. The data sets of water quality used in this study were: (i) a monthly water quality monitoring campaign from August 2009 until July 2011 in 21 sampling points, (ii) a daily monitoring campaign using an automatic water sampler located at the outlet of the study area from August 2009 until August 2011, (iii) a monthly water quality campaign from the wastewater treatment plants (WWTPs) from December 2009 until August 2010 (Honsel, 2011; Redeker, 2011), and (iv) a historical monthly water quality campaign from March 1991 until March 1995 in 21 sampling points (Ripl et al., 1996). The main water quality parameters analyzed were: total phosphorus (TP), soluble orthophosphate-phosphorus (PO₄-P), particulate phosphorus (PP), total nitrogen (TN), nitrate-nitrogen (NO₃-N), ammonium-nitrogen (NH₄-N) and total suspended sediment (TSS). TP, PO₄-P, TN, NO₃-N and NH₄-N concentrations were ranked according to the German LAWA classification to compare the data with the Water Framework Directive (WFD) targets. The ecohydrological model Soil and Water Assessment Tool (SWAT, Arnold et al., 1998) was used to simulate water balance, sediment load and nutrient load (NO₃-N and TN). Also, a historical scenario of 1990s and future alternative scenarios were simulated. The results show an improvement in water quality for TP, TN and NO₃-N from 1991-1995 compared to 2009-2011. Nevertheless, TP, TN, NO₃-N and NH₄-N concentrations did not reach the standards set by the WFD. Only PO₄-P

concentration is ranked as moderately polluted agreeing with the WFD targets. The monthly and daily data set showed a typical seasonal variability of water quality with higher N and P concentration in winter. Currently, PP represents the major part of TP pollution and is highly dependent on TSS. 92% of TP load originates from diffuse sources. $\text{NO}_3\text{-N}$ represents the major part of N pollution, 94% from $\text{NO}_3\text{-N}$ load is from diffuse sources. The major part of $\text{NH}_4\text{-N}$ load comes from WWTPs (61%). The results of modeling with the SWAT model showed a good performance for calibration and validation of daily discharge at three gauging stations of the upper Stör catchment. The calibration and validation of sediment and nutrient ($\text{NO}_3\text{-N}$ and TP) load were successful simulated with the SWAT model. In order to use the SWAT model to explain the improvement of TP and $\text{NO}_3\text{-N}$ load over the last 20 years, a historical scenario representing the decade of 1990 was simulated. The TP and $\text{NO}_3\text{-N}$ load of the historical scenario were simulated satisfactorily. The quantity of fertilizer and application calendar of management practices were the main necessary changes to achieve a satisfactory model performance of the historical scenario. Based on the development of the actual land use and of the historical scenario, best management practices (BMPs) scenarios were proposed to reduce N and P pollution in the upper Stör catchment. The most effective practices to minimize the $\text{NO}_3\text{-N}$ and TP load were the reduction of N and P fertilizer application and the increasing of conservation areas, such as field filter strips. Hydrological processes that affect the N and P transport processes are complex and the ecohydrological SWAT model can help to explain N and P changes which occur in the watershed. Also, the SWAT model can help catchment managers to identify suitable BMPs, and thus improve the water quality in surface aquatic systems in the future.

**INTEGRIERTE MESSUNG, MODELLIERUNG UND BEWERTUNG DER
STICKSTOFF- UND PHOSPHORBELASTUNG IN EINEM
TIEFLANDEINZUGSGEBIET IN DEUTSCHLAND: Eine Langzeitstudie zur
Wasserqualität**

ZUSAMMENFASSUNG

Stickstoff- (N) und Phosphorbelastungen (P) in Gewässern stammen aus diffusen und punktuellen Quellen. Die Punktquellen resultieren aus hauptsächlich Haushaltsabwässern und industriellen Abwässern, während der diffuse Austrag hauptsächlich aus landwirtschaftlicher Nutzung stammt. Die Überwachung, die Bewertung und die Modellierung von N und P in einem Tieflandeinzugsgebiet wurden durchgeführt, um die Entwicklung von N- und P-Belastung in den letzten 20 Jahren zu überprüfen, und Maßnahmen zur Reduzierung von N- und P-Konzentrationen in Fließgewässern zu entwickeln. In dieser Studie wurden 462 km² des oberen Stör-Einzugsgebietes, einem typischen Tieflandeinzugsgebiet im Norden Deutschlands, betrachtet. Die in dieser Studie verwendeten Wasserqualitätsdaten stammen aus: (i) monatlichen Kampagnen zur Überwachung der Wasserqualität von August 2009 bis Juli 2011 an 21 Messstellen, (ii) einer Kampagne mit täglicher Auflösung mit einem automatischen Wasserprobenehmer am Auslass des Untersuchungsgebietes von August 2009 bis August 2011, (iii) einer monatliche Wasserqualitätskampagne aus den Kläranlagen von Dezember 2009 bis August 2010 (Honsel, 2011; Redeker, 2011), und (iv) einer historischen monatlichen Wasserqualitätskampagne von März 1991 bis März 1995 an 21 Messstellen (Ripl et al., 1996). Die wichtigsten analysierten Wasserqualitätsparameter waren: Gesamt-Phosphor (TP), lösliches Orthophosphat-Phosphor (PO₄-P), partikulärer Phosphor (PP), Gesamt-Stickstoff (TN), Nitrat-Stickstoff (NO₃-N), Ammonium-Stickstoff (NH₄-N) und das suspendierte Sediment (TSS). TP, PO₄-P, TN, NO₃-N und NH₄-N Konzentrationen wurden im Rahmen der Vorgaben der Länderarbeitsgemeinschaft Wasser (LAWA) eingeordnet, um sie mit Zielvorgabe der Wasserrahmenrichtlinie (WFD) zu vergleichen. Das ökohydrologische Modell SWAT wurde verwendet, um den Wasserhaushalt, die Sedimentfracht und die Nährstoffbelastung (NO₃-N und TN) zu simulieren. Auch ein historisches Szenario der 1990er Jahre und alternative Szenarien wurden simuliert. Die Ergebnisse zeigen eine Verbesserung der Wasserqualität für TP, TN und NO₃-N von 1991-1995 im Vergleich zu 2009-2011. TP, TN,

NO₃-N und NH₄-N-Konzentrationen erreichten nicht die Standards der WFD. Lediglich die PO₄-P Konzentration kann nach LAWA als mäßig belastet eingestuft werden und erfüllt damit die Anforderungen der WFD. Die Monats- und Tageswerte zeigten eine typische saisonale Variabilität der Wasserqualität mit höheren N- und P-Konzentrationen im Winter. Derzeit stellt PP den Hauptteil der TP-Belastung und ist stark von TSS abhängig. 92% der TP-Belastung kommt aus diffusen Quellen. NO₃-N stellt den größten Teil der N-Belastung, 94% der NO₃-N-Belastung kommt aus diffusen Quellen. Der größte Teil der NH₄-N-Belastung kommt aus Kläranlagen (61%). Die Ergebnisse der SWAT-Modellierung zeigten eine gute Kalibrierungs- und Validierungsgüte des täglichen Abflusses an den drei Messstationen des oberen Stör-Einzugsgebietes. Monatliche Sedimentfracht, NO₃-N- und TP-Belastung wurden für den Kalibrierungs- und Validierungszeitraum mit dem SWAT Modell erfolgreich simuliert. Die Simulation des historischen Szenarien repräsentiert das 1990er Jahren und wurde simuliert, indem nur die Landnutzungskarte und die Managementpraktiken verändert wurden, um die Verbesserung von TP und NO₃-N in den letzten 20 Jahren mit dem SWAT-Modell zu erklären. Die TP- und NO₃-N-Belastung des historischen Szenarien wurden zufriedenstellend simuliert. Die Düngermenge und die Zeitpunkte der Managementmaßnahmen waren die wichtigsten notwendigen Änderungen, um eine zufriedenstellende Modellgüte des historischen Szenario zu erreichen. Basierend auf der Entwicklung der aktuellen und historischen Szenarien wurden neue Szenarien zu den bestmöglichen Managementmaßnahmen (BMPs) vorgeschlagen, um die N- und P-Belastung im oberen Stör-Einzugsgebiet zu reduzieren. Die effektivste Maßnahmen, um die NO₃-N- und TP-Belastung zu minimieren, waren durch die Reduktion der N- und P-Düngung und die Einrichtung bzw. der Ausweitung von Schutzstreifen, wie z. B. Ackerrandstreifen, zu erzielen. Hydrologische Prozesse, die die N- und P-Prozesse beeinflussen, sind komplex, und das ökohydrologische SWAT-Modell kann helfen, die N- und P-Änderung in dem Einzugsgebiet zu erklären. Die Modellierung mit SWAT kann Einzugsgebietsmanager bei der Auswahl geeigneter BMPs unterstützen, um die Wasserqualität des Oberflächengewässersystems in der Zukunft zu verbessern.

MONITORAMENTO, AVALIAÇÃO E MODELAGEM INTEGRADA DA POLUIÇÃO POR NITROGÊNIO E FÓSFORO EM UMA BACIA HIDROGRÁFICA DE PLANÍCIE NA ALEMANHA: Um estudo de longa duração sobre qualidade da água

RESUMO

A poluição hídrica causada por nitrogênio (N) e fósforo (P) é originada por fontes difusas e pontuais. A poluição pontual está relacionada com efluentes de esgoto doméstico e industrial, enquanto a poluição difusa é originária principalmente de áreas rurais com agricultura e pecuária. O monitoramento, a avaliação e a modelagem de N e P em uma bacia hidrográfica de planície foi executado para verificar o desenvolvimento da poluição por N e P ao longo dos últimos 20 anos, e para obter alternativas de mitigação para reduzir as concentrações de N e P que chegam aos rios. Nesse estudo, 462 km² da parte superior da bacia do rio Stör, uma típica bacia hidrográfica rural de planície no norte da Alemanha foi considerada. Os bancos de dados de qualidade da água utilizados nesse estudo foram: (i) campanha de monitoramento mensal de qualidade de água de agosto de 2009 até julho de 2011 em 21 pontos de amostragem, (ii) campanha de monitoramento diária usando um coletor automático de amostras de água na saída da área no período de agosto de 2009 até agosto de 2011, (iii) campanha mensal de qualidade de água proveniente das estações de tratamento de esgoto (WWTPs) de dezembro de 2009 a agosto de 2010 (Honsel, 2011; Redeker, 2011), e (iv) campanha histórica de monitoramento mensal de qualidade de água de março de 1991 até março de 1995 em 21 pontos de amostragem (Ripl et al., 1996). Os principais parâmetros de qualidade de água analisados foram: fósforo total (TP), ortofosfato solúvel-fósforo (PO₄-P), fósforo particulado (PP), nitrogênio total (TN), nitrato-nitrogênio (NO₃-N), amônio-nitrogênio (NH₄-N) e sedimento total em suspensão (TSS). Concentrações de TP, PO₄-P, TN, NO₃-N e NH₄-N foram classificadas de acordo com a classificação alemã de LAWA para comparar os dados com as metas da Diretrizes do Quadro das Águas (WFD). O modelo ecohidrológico SWAT foi usado para simular balanço hídrico, carga de sedimento e carga de nutrientes (NO₃-N e TN). Também, um cenário histórico da década de 1990 e novos cenários alternativos foram simulados. Os resultados mostram melhoria na qualidade da água para TP, TN e NO₃-N de 1991-1995 comparada com 2009-2011. Concentrações de TP, TN, NO₃-N e NH₄-N não alcançaram os padrões da WFD. Somente a concentração de PO₄-P foi classificada como

moderadamente poluída, atingindo a meta da WFD. O banco de dados mensal e diário mostrou uma típica variabilidade sazonal da qualidade da água, com maiores concentrações de N e P no inverno. Atualmente, PP representa a maior parte da poluição de TP e é altamente dependente de TSS. 92% da carga de TP vem de fontes difusas. $\text{NO}_3\text{-N}$ constituiu a maior parte da poluição de N e 94% da carga de $\text{NO}_3\text{-N}$ vem das fontes difusas. A maior parte da carga de $\text{NH}_4\text{-N}$ vem das WWTPs (61%). Os resultados de modelagem com o modelo SWAT mostram uma boa performance da calibração e validação da vazão diária em três estações de medição da parte superior da bacia hidrográfica do rio Stör. A calibração e a validação da carga mensal de sedimento, $\text{NO}_3\text{-N}$ e TP com o modelo SWAT foi simulado com sucesso. O cenário histórico, representando a década de 1990, foi simulado, no qual somente o mapa de uso e as práticas de manejo foram modificadas, visando usar o modelo SWAT para explicar a melhoria de TP e $\text{NO}_3\text{-N}$ ao longo dos últimos 20 anos. A carga de TP e $\text{NO}_3\text{-N}$ no cenário histórico foi satisfatoriamente simulado. Quantidade de fertilizante e calendário de aplicações das práticas de manejo foram as principais mudanças necessária para alcançar um satisfatório desempenho do cenário histórico. Baseado no desenvolvimento do atual e do cenário histórico, novos cenários com boas práticas de manejo (BMPs) foram propostas visando reduzir a poluição por N e P na parte superior da bacia hidrográfica do rio Stör. As práticas mais efetivas para minimizar as carga de $\text{NO}_3\text{-N}$ e TP foram relacionadas com a redução da aplicação de fertilizantes e o aumento das áreas de preservação, tal como as faixas filtro de campo. Processos hidrológicos que influenciam os processos de N e P são complexos e o modelo ecohidrológico SWAT pode ajudar a explicar mudanças que ocorrem em uma bacia hidrográfica. Também, o modelo SWAT pode ajudar gestores de bacias hidrográficas na identificação de BMPs, e assim melhorar a qualidade de água em sistemas aquáticos de superfície no futuro.

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LIST OF ABBREVIATIONS

AC	Autocorrelation
acf	Autocorrelation function in the R program
ADJ_PKR	Peak rate adjustment factor for sediment routing in the subbasin
ALPHA_BF	Base flow alpha factor
ANION_EXCL	Fraction of porosity from which anions are excluded
BMPs	Best management practices
BSN	Basin input file of SWAT
CDN	Denitrification exponential rate coefficient
CH_COV_1	Channel erodibility factor
CH_COV_2	Channel cover factor
CH_K2	Effective hydraulic conductivity in main channel alluvium
CH_N2	Manning's "n" value for the main channel
CMB1	Combination of the scenarios DMA20, DFA20, CSC and WFS30
CMB2	Combination of the scenarios DMA50, DFA20, CSC and WFS10
CMN	Rate factor for humus mineralization of active organic nutrients
CN2	Initial SCS runoff curve number for moisture condition II
CSC	Cultivation system in contour considering USLE_P=0.5 for agriculture in areas with more than 2% of slope.
DDRAIN	Depth to subsurface drain
DEM	Digital elevation model
Dep-Imp	Depth to impervious layer in soil profile
DFA20	Decrease of mineral fertilizer application in 20%
DIN	Dissolved inorganic N
DIP	Dissolved inorganic P
DMA20	Decrease of organic manure application in 20%
DMA50	Decrease of organic manure application in 50%
DO	Dissolved oxygen (mg/l)

DWD	German Weather Service
E_a	Amount of evapotranspiration
EPCO	Plant uptake compensation factor
ERORGP	Phosphorus enrichment ratio for loading with sediment
ESCO	Soil evaporation compensation factor
GDRAIN	Drain tile lag time
GIS	Geographic Information System
GW	Groundwater input file of SWAT
GW_DELAY	Groundwater delay time
GW_REVAP	Groundwater REVAP coefficient
GWQMN	Threshold depth of water in the shallow aquifer required to occur the return flow
GWSOLP	Concentration of soluble phosphorus in groundwater contribution to streamflow from subbasin
HLIFE_NGW	Half-life of nitrate in the shallow aquifer
HRU	Hydrologic response units
HYDGRP	Soil hydrologic group
LAWA	German State Working Group of Water (Länderarbeitsgemeinschaft Wasser)
LKN	Schleswig-Holstein's Government-Owned Company for Coastal Protection, National Parks and Ocean Protection (Landesbetrieb für Küstenschutz, Nationalpark und Meeresschutz, LKN-Schleswig-Holstein)
LLUR	State Agency for Agriculture, Environment and Rural Areas (Landesamt für Landwirtschaft, Umwelt und ländliche Räume)
MGT	Management input file of SWAT
MLUR-SH	Ministry of Agriculture, Environment and Rural areas of Land Schleswig-Holstein. (Ministerium für Landwirtschaft, Umwelt und ländliche Räume des Landes Schleswig-Holstein)
n	Number of values
N	Nitrogen
N_UPDIS	Nitrogen uptake distribution parameter
NH ₄ -N	Ammonium-nitrogen
NO ₃ -N	Nitrate-nitrogen
NO ₃ -N _{obs}	Measured NO ₃ -N
NO ₃ -N _{sim}	Simulated NO ₃ -N
NPERCO	Nitrate percolation coefficient
NSE	Nash-Sutcliffe efficiency

P	Phosphorus
P_UPDIS	Phosphorus uptake distribution parameter
PAD	Padenstedt
PBIAS	Percent bias
PHOSKD	Phosphorus soil partitioning coefficient
PO ₄ -P	Orthophosphate-phosphorus
PPERCO	Phosphorus percolation coefficient
PRF	Peak rate adjustment factor for sediment routing in the main channel
PSP	Phosphorus availability index
Q _{gw}	Amount of return flow
Q _{obs}	Measured discharge
Q _{sim}	Simulated discharge
R ²	Coefficient of determination
RCHRG_DP	Deep aquifer percolation fraction
RCN	Concentration of nitrogen in rainfall
R _{day}	Amount of precipitation on day i
REVAPMN	Threshold depth of water in the shallow aquifer for REVAP or percolation to the deep aquifer to occur
RMSE	Root mean square error
RSR	RMSE observations standard deviation ratio
RTE	Main channel input file of SWAT
SAR	Sarlsruhe
SCS	Soil Science Service
SDNCO	Denitrification threshold of water content
Sed _{obs}	Measured sediment
Sed _{sim}	Simulated sediment
SFTMP	Snowfall temperature
SMFMN	Melt factor for snow on December 21 st
SMFMX	Melt factor for snow on June 21 st
SMTMP	Snow melt base temperature
SOL	Soil input file of SWAT
SOL_AWC	Available water capacity of the soil layer
SOL_BD	Moist bulk density (g/cm ³)
SOL_CBN	Organic carbon content (% soil weight)
SOL_K	Saturated hydraulic conductivity (mm/h)

SOL_Z	Depth from soil surface to bottom of layer (mm)
SPCON	Linear parameter for calculating the maximum amount of sediment that can be reentrained during channel sediment routing
SPEXP	Exponent parameter for calculating sediment reentrained in the channel
STDEV	Standard deviation
SURLAG	Surface runoff lag coefficient
SW ₀	Initial soil water content
SWAT	Soil and Water assessment Tool
SW _t	Final soil water content
t	Time (days)
TBZ	Technical Operation Center (Technisches Betriebszentrum)
TDRAIN	Time to drain soil to field capacity
TIMP	Snow pack temperature lag factor
TN	Total nitrogen
TP	Total phosphorus
TP _{obs}	Measured TP
TP _{sim}	Simulated TP
USLE	Universal Soil Loss Equation
USLE_K	USLE equation soil erodibility factor
USLE_P	USLE equation support practice factor
WFD	Water Framework Directive
WFS10	Use of edge of field filter strip with width of 10 m
WFS30	Use of edge of field filter strip with width of 30 m
WIL	Willenscharen
W _{seep}	Amount of water entering the vadose zone from the soil profile
WT	Water temperature (°C)
WWTP	Urban Waste Water Treatment Plant
WWTP-L	WWTP Lagoons
WWTP-MB	WWTP with mechanic and biological treatment
WWTP-NP	WWTP with mechanic, biological and tertiary N and P elimination treatment
\bar{Y}	Arithmetical mean
Y ^{obs}	Measured value
Y ^{sim}	Simulated value

1 INTRODUCTION

The increase in human population, the need to expand food production and biomass production for bioenergy are some reasons of water pollution in the world in the last decades (Grizzetti et al., 2013). Water pollution is caused by point sources and non-point sources. Point pollution is linked to wastewater from domestic and industrial sewage, whereas the non-point, or diffuse pollution comes mainly from rural areas with agriculture. One of the major issues of water pollution are nitrogen (N) and phosphorus (P) loads in aquatic environmental systems, which are responsible for water eutrophication.

High levels of N and P concentration in European rivers have led the European Community to take various measures to prevent water pollution. In 1991, two directives, namely the Nitrate Directive (EEC, 1991a) and the Urban Waste Water Treatment Directive (EEC, 1991b) were launched in order to decrease the nitrate-nitrogen ($\text{NO}_3\text{-N}$), as well as to reduce the N and P loads from domestic wastewater. In 2000, the Water Framework Directive (WFD) was implemented, which has the objective to established good water quality and ecological status of all water bodies until 2015 in all European Union member states (EC, 2000).

The monitoring of N and P concentration in the river systems supplies essential information to catchment managers assessing water pollution levels and identify the main pollutant sources (Burt et al., 2010), in order to select mitigation alternative practices to reduce eutrophication risks (Drolc and Koncan, 2008; Withers and Sharpley, 2008). In the decade of 1990, Ripl et al. (1996) coordinated the project called "Stör project I and II" at the upper river Stör catchment in Germany. In this project, water quality was monthly monitored from March 1991 until March 1995. Thus, a consistent historical database of water quality is available to compare the development of water quality over the last two decades.

After the NO_3 -Directive (EEC, 1991a), the German law regulated the use and management of fertilizers in accordance with good fertilization practices (DÜV, 1996; DÜV, 2006; DÜNGG,

2009). Furthermore, in order to improve the water quality, after 1991 many projects of restoration of the river Stör and its tributaries were initiated, with emphasis on prevention of bank erosion (Dickhaut, 2005), reforestation of the riparian zone (Martini, 2000) and suitability of the sinuosity of the river (Jensen, 2009; Maaß, 2012). In addition, several measures are realized for the restoration of the rivers, e.g. stone ramps, gravel riffles, instream deflectors, removing of embankments, sand traps, and the introduction of large woody debris (Brunke and Lietz, 2011).

Based on the WFD (EC, 2000), several studies were carried out to verify the development of the N and P pollution status over time. Kronvang et al. (2008) reported a successful reduction on N pollution in Denmark. For these authors, the improvement on treatment of wastewater and the decrease of N fertilizer are responsible for the improvement on the water quality in Denmark. Iital et al. (2005) found a significant reduction on N pollution in Estonia from 1984 to 2001 due to (i) substantial reductions in the use of organic and inorganic fertilizers, (ii) reduction of cultivated and ploughed areas and increased proportions of grassland and abandoned land and (iii) improvements in farm management practices. Behrendt et al. (2000) stated reducing of P load in some watersheds in Germany due to decrease of P emissions caused by point sources and reduction of P emissions caused by erosion. Thus, a new monitoring program of water quality in the upper Stör catchment can help to understand the evolution of N and P pollution over time and can show the effects of recent environmental legislation on nutrient loads.

Beyond the monitoring and assessment of water quality, modeling of hydrology, sediment, nutrients and pesticides are an useful approach to predict hydrological processes and pollutants load. Models are increasingly used worldwide to predict water quantity and quality at the watershed scale (Bittelli et al. 2010). In this study, the SWAT model (Soil and Water Assessment Tool, Arnold et al., 1998) was used. The SWAT is an ecohydrological model developed to predict the impact of land management practices on water, sediment and agricultural chemical yields in large complex watersheds with varying soils, land use and management conditions over long periods of time (Arnold et al., 1998; Arnold and Fohrer, 2005; Neitsch et al., 2011). In addition, the SWAT model can help to understand the changes occurring in watersheds, as well as to predict new scenarios of land use aiming to reduce water pollution.

The focus of this dissertation is put on the development of N and P pollution over the last 20 years in a typical rural lowland catchment in northern Germany. Therefore, researches based on monitoring, assessment and modeling of water quality in the upper Stör catchment were carried out. The central research questions of this study are:

1. Did the N and P concentrations in the surface water bodies improve between the years 2009-2011 and 1991-1995?
2. What is the seasonal pattern of N and P pollution?
3. What are the main characteristics of N and P pollution in a typical rural lowland catchment?
4. What are the main sources of N and P pollution in the upper Stör catchment?
5. Is possible to predict N and P pollution through ecohydrological modeling?
6. Can the SWAT model help to explain the changes in water quality over the last 20 years?
7. What environmental measures can reduce N and P loads in rural lowland catchments?

2 LITERATURE REVIEW

2.1 Lowland areas

Lowland river systems and their catchments are typical ecosystems with small amplitude in altitude, low flow velocity, high groundwater table and a substantial share of typical organic soils (Hesse et al., 2008). Drainage systems like tile drainage and open ditches change the natural water balance and influence the instream water quality due to a faster nutrient transport (Schmalz et al., 2007; Schmalz et al., 2008a). McDowell et al. (2011) found significant nutrient loads via artificial drainage in agricultural areas.

In the past centuries, the landscape and the river network changed considerably, mainly due to river regulation to increase the agricultural area (Gessner et al., 2009). The natural catchment water balance is susceptible to substantial alteration by human activities, such as river regulation or drainage systems, and has indeed been altered in most areas (Schmalz and Fohrer, 2010).

The hydrological cycle of lowland areas is governed by the close interaction of surface water dynamics and the corresponding directly connected shallow groundwater aquifer. Runoff generation processes, as well as the extent and spatial distribution of the interaction between surface water and groundwater, are controlled by floodplain topography and by surface water dynamics (Krause and Bronstert, 2007). The regulation of the lowland systems led to a reduction of retention time of water and nutrients, which contributed to water quality problems in the river network and coupled lakes (Hesse et al., 2008).

2.2 Water pollution of surface water bodies

Water pollution problems have been encountered all over the world in the last decades. Many

substances are potential pollutants: nutrients used in agricultural systems, especially nitrogen (N) and phosphorus (P) (Pieterse et al., 2003; Pereira et al., 2009; Rothwell et al., 2010; Bouraoui and Grizzetti, 2011; Hennemann and Petrucio, 2011; Najjar and Khan, 2011; Lam et al., 2012), heavy metals (Chon et al., 2012; Martin, 2012) and pesticides (Reichenberger et al., 2007; Schriever et al., 2007; Laini et al., 2012; Ulrich et al., 2013). In surface water bodies, the input of N and P plays an important role in water quality because these nutrients are essential for phytoplankton (Wu et al., 2011, Norton et al., 2012) and macrophyte growth (Jarvie et al., 1998; Pozo et al., 2010) and for water eutrophication (Jickells, 2005; Drolc and Koncan, 2008; Cao et al., 2011a). Two of the most commonly recognized symptoms of eutrophication are harmful algal blooms and hypoxia (Liu et al., 2012). According Grabowska (2012), favorable conditions for phytoplankton growth consists if total N > 1.5 mg/l, total P > 0.1 mg/l, water temperature is between 18-25°C and pH is between 6 and 9. Among ecosystems with a high risk of water pollution, lowland catchments are frequently affected by N and P pollution due to the intense interaction between the aquatic and terrestrial systems (Krause et al., 2007). Krause et al. (2007) showed that the impact of nutrients is much higher in lowlands during low flow conditions in summer when the river runoff is originated by groundwater discharge (circa 30%). Schipper et al. (2011) verified that the impact of soil contamination from heavy metal in lowland areas could be larger than expected because the effects of flooding can increase the toxic effect.

Nutrients enter surface waters through point or diffuse sources (Pieterse et al., 2003; Withers and Sharpley, 2008; Withers and Jarvie, 2008; Merseburger et al., 2011). Point sources can enter at fixed locations, e.g. wastewater treatment plant outlets, industries, pig farms or aquaculture (Schaffner et al., 2009; Merseburger et al., 2011). While point sources cause abrupt hydrological and chemical discontinuities along the stream, diffuse sources are not as spatially discrete and cause more gradual changes (Merseburger et al., 2011). Wu and Chen (2013) verified that diffuse pollution was the dominant contribution for nutrient load (97% for total N and 94% for total P). Diffuse sources contribute through many different pathways and are highly dependent on land use and management (Pieterse et al., 2003; Kronvang et al., 2008; Tao et al., 2010). The application of N and P fertilizer in agriculture and pasture areas are the major sources of diffuse pollution (Sileika et al., 2006; Lassaletta et al., 2009; Lam et al., 2010, Jarvie et al., 2010). Fertilizer management is one way to reduce nutrient loads in surface water bodies (Pieterse et al., 2003). According to Kronvang et al. (2008), the measures

applied in the agricultural production system need to focus on improved utilization of animal manure, fertilizer and crop rotation plans, maximized utilization of feed-stuffs and limitations on total N application. Tao et al. (2010) verified that N concentration was positively and significantly correlated to population growth and N fertilizer use in the catchment. However, these authors could not find which factor played a more dominant role in impacting the N load in the Yellow River. Jarvie et al. (2010) found that the intensive livestock farming on heavy clay soils resulted in a much higher total P load in stream water compared with other arable farming systems. According Gao et al. (2012), the impact of agriculture on water quality clearly becomes more evident when agriculture is the dominant form of land use in the catchment.

While the export of nutrients to lakes from point sources, such as municipal and industrial outflows, is independent of climate, transfers from non-point or diffuse sources are highly sensitive to climatic factors (Jennings et al., 2009). Gao et al. (2012) verified that a large amounts of runoff during rainstorms act as major means of export for P at times of eutrophication risk in agricultural catchments.

2.3 Phosphorus

Phosphorus (P) is an essential element for all forms of life on earth. It is a primary constituent of deoxyribonucleic acid (DNA) and adenosine triphosphate (ATP), which are responsible for the encoding of genetic instructions and intracellular energy transfer within living cells (Suh and Yee, 2011). P is indispensable and not replaceable in crop cultivation and the survival of animals and humans is also strictly dependent on receiving adequate amounts of P in the diet (Linderholm et al. 2012). Most of the P in animals and humans is found in bones and teeth, but P is also a part of many enzymes, the energy carrier in cells, as ATP and is an important part of nucleic acid, the main structure of genes (Suh and Yee, 2011; Linderholm et al., 2012).

In the earth's crust, P is found in form of minerals including Apatites (fluoro-, chloro-, hydroxy-apatite) (Delgado and Scalenghe, 2008), Vivianite (Fagel et al., 2005), Wavellite (Nunes et al., 2012) and Phosphorites (Arning et al., 2009). In soils, the total P (TP) content is usually < 1 g/kg (Delgado and Scalenghe, 2008). The three major forms of P in soils are

organic P associated with humus, insoluble forms of mineral P, and plant-available P in soil solution. P enters the biosphere by weathering or mining (Bennett et al., 2001; Suh and Yee, 2011). Currently, P is mostly obtained from mined rock phosphate and is often combined in mineral fertilizers with sulfuric acid, nitrogen, and potassium (Cordell et al., 2009). The annual global mining flux (approx. 18 Tg/year) and weathering flux (approx. 20 Tg/year) are similar in magnitude (Bennett et al., 2001). Most plants contain P in concentrations varying between 0.1% and 0.4%, and its significance in stimulating root growth and accelerating plant ripening is proven (Ott and Rechberger, 2012).

2.3.1 P pollution of water bodies

In natural aquatic ecosystems the P concentration is low and is considered a limiting factor for macrophyte growth (Meybeck et al., 1989; Gao et al., 2009). In the classification of water trophic level from Meybeck et al. (1989), water bodies with TP concentrations > 0.10 mg/l are classified as hypertrophic. In the environment, the most important form of soluble P occur as oxidized phosphate (primarily H_2PO_4^- and HPO_4^{2-}) (Sharpley and Halvorson, 1994). Hanrahan et al. (2005) suggested a possibly significant role for reduced, inorganic forms of P in bacterial metabolism and as evolutionary precursors of biological phosphate compounds. Reduced inorganic forms of P include phosphorus acid (H_3PO_3), hypo phosphorus acid (H_3PO_2) and various forms of phosphides (Hanrahan et al., 2005). According to these authors, the reduced P has been detected in anaerobic sediments, sewage treatment facilities and in industrial and agricultural processes.

P loading to streams can occur by both surface runoff and subsurface transport, but subsurface P transport often is negligible (Mittelstet et al., 2011). P transport by runoff can occur as soluble ($\text{PO}_4\text{-P}$) and particulate form (PP) (Sharpley and Halvorson, 1994). PP is transported in catchment runoff during storm events in association with soil colloids, particles and aggregates (Withers et al., 2009). PP comprises all solid phases, like P adsorbed to soil particles and organic matter eroded during runoff. Generally, PP constitutes the major fraction of P transported from arable land (Sharpley and Halvorson, 1994). While $\text{PO}_4\text{-P}$ is, for the most part, immediately available for plant uptake, PP can provide a long-term source of P for aquatic plant growth (Sharpley and Halvorson, 1994; May et al., 2001). Gao et al. (2012)

described that soil particulate, derived from agricultural sources, primarily acts as an adsorption for P in water bodies, and large amounts of runoff during rainstorms act as major means of export for P at times of eutrophication risk in agricultural catchments. The quantity lost is a function of runoff and availability, which is affected by inputs and the ability of the soil to retain P (McDowell, 2012). Kim et al. (2011) verified a significant relationship ($R^2=0.87$) between the content of P in the soil and the concentration of P in runoff. In addition, Gao (2012) reported the effect of pH on the release of P from sediment. He verified that the sediment released significant amount of P under strong acid (pH 3) and alkaline conditions (pH 9).

Lehtoranta and Ekholm (2012) examined the effect of soil erosion on the inhibition of aquatic eutrophication. They concluded that the link between erosion and aquatic eutrophication is more complex than previously thought, and thus needs to be examined from a wider perspective than merely accounting for the loading and bio availability of soil-bound P. For Burgin et al. (2011), aquatic microbiology has shown that the cycling of P is closely linked to the availability of common electron acceptors, Fe oxides and SO_4 , through the anaerobic mineralization reactions taking place in sediments. After the soil particles have found their way to the bottom of a water body, they will eventually face an anoxic environment, occurring in these conditions a drastic impact on Fe cycling and thus also crucially affect the fate of P (Ekholm and Lehtoranta, 2012).

In mountainous catchments, losses of P by runoff are strongly related with sediment and slope (Sileika et al., 2005; Hu et al., 2013). According to McDowell (2012), losses are exacerbated if surface runoff or drainage occurs soon after P inputs (e.g. fertilizer and/or manure and dung). In lowland catchments in Northern Germany, tile drains are important pathways for sediment (Kiesel et al., 2009) and P transport (Tiemeyer et al. 2009). Coelho et al. (2012) verified significant proportion of PO_4 -P in tile drains in agricultural areas, while TP and sediment load losses in this areas were low. Thus, P can be transported below the root zone to the unsaturated zone and through an aquifer in agricultural settings (Domagalski and Johnson, 2011). Also, Mittelstet et al. (2011) verified that subsurface P contributions can be significant in riparian zone soils with spatial variability in hydraulic conductivity, preferential flow pathways, and limited sorption capacity.

In the US, Domagalski and Johnson (2011) studying PO_4 -P in groundwater verified that P

transport to a stream was demonstrated most clearly at the Nebraska location, although groundwater transport did contribute to the stream loads at other sites. A low concentration of iron oxides in the sand and silt of Nebraska soils resulted in low sorptive capacity. The median concentration of $\text{PO}_4\text{-P}$ at the groundwater/stream interface was 0.2 mg/l at the Nebraska location. In another case, agriculturally applied P will likely not be transported through the aquifer under current management practices. That was demonstrated most clearly at the Maryland location. Although oxides were close to saturation with respect to P in the unsaturated zone, the aquifer solids had high sorptive capacity because of the low groundwater pH (< 5) within the aquifer. Under that condition, $\text{PO}_4\text{-P}$ concentrations were low to undetectable in the aquifer and transport to the stream was not a concern. A similar situation occurred at Indiana although for different reasons. The apparent situation for P in Indiana was very low transport out of the root zone to the sub-surface. It was surmised that the clay and carbonate chemistry of the root zone effectively sequestered P, and as a result oxides in the subsurface sorbed what little available P which was present in groundwater (Domagalski and Johnson, 2011).

2.3.2 Strategies of P mitigation

Mineral P fertilizers processed from fossil reserves have enhanced food production over the past 50 years and, hence, the welfare of billions of people (Schröder et al., 2011). Humanity is facing an enormous challenge in managing water quality and quantity to secure adequate food production without undermining the ecological life support systems on which human society also depends. Water management in agriculture is a key component in solving some of the most pressing trade-offs between an increase in agricultural production that can contribute to food security and economic growth on one hand, and dealing with the losses of important ecosystem benefits that also sustain human well-being and livelihoods on the other. (Gordon et al., 2010). Fertilizer P, however, has not only been used to lift the fertility level of formerly poor soils, but also allowed people to neglect the reuse of P that humans ingest in the form of food and excrete again as faeces and urine and also in other organic wastes. Consequently, P mainly moves in a linear direction from mines to distant locations for crop production, where a large fraction eventually may become either agronomic inactive due to over-application, unsuitable for recycling due to fixation, contamination or dilution, and harmful as a polluting

agent of surface water (Schröder et al., 2011).

Global reserves of phosphate rock worth mining are limited (Linderholm et al. 2012). According to Cordell et al. (2009), the current global reserves may be depleted in 50 - 100 years. This means that not only the water pollution is a problem with P losses to water bodies, but also the low efficiency of P fertilizer use. Elser and Bennett (2011) point out that about half of the P applied to land (80% of the P mined) is lost to waterways via soil erosion and leaching. Poor interception of added P by roots also contributes to inefficient P fertilizer use efficiency (Dungait et al., 2012).

Ott and Rechberger (2012) calculated the P balance for the European Community. They estimated a per capita consumption of 4.7 kg P/year, of which only 1.2 kg P/year reach the consumer. According to the authors, the main losses are accumulation in agricultural soils (2.9 kg P/year), followed by losses to landfills (1.4 kg P/year) and to the hydrosphere (0.55 kg P/year).

Reducing losses in the food chain and increasing agricultural efficiency are also likely to contribute significantly to averting a future phosphate crisis (Cordell et al., 2009). According to Dungait et al. (2012), the best efficiency in the use of nutrients is the objective of the sustainable agriculture and can be achieved with the following strategies: more efficient use of mineral fertilizers, increased recovery and recycling of waste nutrients, and better exploitation of the substantial inorganic and organic reserves of nutrients in the soil. Organic fertilizer such as biowaste compost represents an adequate substitute for commercial inorganic P fertilizers (Krey et al., 2013). Linderholm et al. (2012) testing alternative sources of P concluded that sewage sludge used directly on farmland is an efficient option in terms of energy and emissions of greenhouse gases, but also added most cadmium to the soil.

According to Schröder et al. (2011), amounts of P applied in agriculture could be considerably reduced by optimizing land use, improvement of fertilizer recommendations and application techniques, modified livestock diets, and adjustment of livestock densities to available land. Such a concerted set of measures is expected to reduce the use of P in agriculture whilst maintaining crop yields and minimizing the environmental impact of P losses.

Strategies to mitigate P losses depend on the farming system (McDowell, 2012). The effectiveness of measures to reduce sediment losses from agricultural soils is dependent upon

a wide range of factors such as crop type, soil type, slope, drainage, vegetative cover, cultivation methods, timing of operations and proximity to water courses (Rickson, 2013). The first step is to maintain a farm P balance (inputs - outputs) close to zero and the agronomic optimum. The next step is to use mitigation strategies in areas that lose the most P, but occupy little of the farm or catchment's area. Focusing on these areas, termed critical source areas, is more cost-effective than farm or catchment-wide strategies (McDowell, 2012).

Experiences in various countries suggest improvement in tillage management to reduce P losses. In Brazil, Nunes et al. (2011) verified that no-tillage system was more efficient to use the P fertilizer than the conventional tillage. This effect occurs due to three facts: (i) increase of organic P, especially in the surface layers because of decreased mineralization of organic matter, (ii) decrease of adsorption with Fe and Al oxides (Tiecher et al., 2012) and (iii) limited biological mineralization of organic matter due to formation of stable complexes of organic P with aluminum and iron (Redel et al., 2008). This means that fertilizer management in no-tillage during several years leads to P accumulations, remaining this P on the soil after crop harvest, which may increase P availability for crops grown afterward (Pavinato et al., 2009). Also in Brazil, the organic management promoted an increase on the available-P forms by avoiding and/or decreasing the rate of transformation of the inorganic P in more stable P forms, enhancing the P cycling. Constant applications of organic compost in organic farming favored the increase of P content in the deepest soil layers (Xavier et al., 2009).

In Australia, Malik et al. (2012) concluded that organic P sources, particularly those with high P concentration can stimulate the formation of organic P forms in soils which may provide a long-term slow release of P source for plants and soil organisms. They also verified that the P added with organic amendments was less prone to sorption and precipitation than inorganic P, due to the lower concentration of water-soluble P and stimulation of microbial activity by the addition of carbon. In Canada, Coelho et al. (2012) investigated tillage systems on P and sediment losses. They found that minimum tillage system with swine manure compared to conventional tillage, reduced particulate P and sediment loss by overland runoff, but not soluble P loss. In Spain, over-fertilization, low efficiency of P fertilizer and irrigation management were reasons to water eutrophication (Skhiri and Dechmi, 2012). In Australia, Bartley et al. (2012) studying P losses by runoff from about 514 different geographical sites,

verified different TP concentration in different land uses. They found median of TP concentration from 5.8 mg/l for forestry, 1.4 mg/l for bananas, 0.9 mg/l for dryland cropping and 0.4 mg/l for pastures. In China, Huang et al. (2013) verified that livestock breeding was the main contributor to P losses by runoff, accounting for 35% of the TP load in 2003 and 43% in 2007. The authors suggest that livestock breeding should be controlled to reduce TP load.

A plan to minimize losses of diffuse source of P could be expected to be more effective when implemented at specific areas which have more P losses (Kim et al., 2011). Conceptually, control at source is more effective than remedial measures that simply interrupt sediment pathways to water receptors (Rickson, 2013). One example was the decrease of P on detergents in wastewater in many countries including Germany (Statham, 2012). Furthermore developments in biotechnology over the past 25 years have allowed scientists to engineer genetically modified animals for use in various areas of agriculture (Forabosco et al., 2013). The best example is the development of the Enviropig (Golovan et al, 2001), a genetically modified pig using the gene for bacterial phytase, an enzyme that breaks down the phosphorus-rich compounds called phytate, has been introduced into a line of Yorkshire pigs. These pigs produce phytase in their saliva, which allows them to make use of the otherwise indigestible phytate in feed grains. They are able to digest plant phytase P, which accounts for 50-80% of the P in cereal grains that is unavailable to conventional pigs. This capability eliminates the need to add either expensive supplemental P or phytase to the diet, reducing substantially P in the manure (Meidinger et al., 2008). Twelve years after the development, the technology is still working its way through federal approval processes in the United States and Canada (Elser and Bennett, 2011). This biotechnology has the highest potential for P reduction in the aquatic environment but legislation and ethics implications will prevent using transgenic animals in the short term (Kebreab et al., 2012).

Delivery of P to receiving waters can be reduced not only by reducing P inputs to soils but also by increasing P sinks in watersheds (Bennett et al., 2001). Biological resources such as submerged macrophyte biomass can be exploited under human control to avoid the degradation of aquatic ecosystems resulting from over-exploitation. The maintenance and restoration of the stable state of submerged macrophyte dominance should be one of the best choices for the management of eutrophic shallow lakes with reference to a better water

quality, because it is very difficult or even impossible to cut down the internal and external nutrient loading of shallow lakes (Gao et al., 2009). On other hand, for suppressing phytoplankton blooms, establishing riparian shading in headwater areas is a far more effective mitigation option than curtailing nutrient inputs (Hutchins, 2012). For Desmet et al. (2011) in upstream areas, dominated by small streams, the occurrence of high macrophyte biomass density may play a very important role in acting as a temporary sink for nutrients.

Managers of catchments where eutrophication pressures are regarded as high require accurate knowledge of the status of P, source of P and the interactions of P with the local environment in order to implement mitigation policy effectively (Greene et al. 2011). Moreover, the symptoms of eutrophication in both fresh and salt waters can lead to loss of aesthetic, ecological, and economic value of aquatic ecosystems (Bennett et al., 2001).

Kröger et al. (2013), based on the understanding of soil P dynamics, recommend the following strategies to enhance P retention in downstream agricultural landscape: a) use soil amendments (e.g., organic-rich substrates such as biochar or calcium-rich substrates such as gypsum) to increase P sorption capacity; b) oxygenate sediments to prevent phosphate desorption during Fe and SO₄ reduction and subsequent phosphate release; c) buffer pH, thereby preventing acidic conditions that dissolve aluminum compounds and release P; d) promoting organic matter production, increasing phosphate adsorption; e) preventing desiccation of sediments and soil to prevent microbial catalysis and P release; and f) increasing plant production and biomass P incorporation to reduce phosphate loads at times when aquatic P demand is highest in downstream waterbodies.

2.4 Nitrogen

Nitrogen (N) is the major plant nutrient and is applied in large amounts to agricultural land to maintain optimal yields (Ladha et al., 2005; Dawson and Hilton, 2011) and/or to increase grain quality (Divito et al., 2011), but also has an enormous relevance for the environment (Küstermann et al., 2010). After carbon, the main nutrient constraining biomass development in terrestrial and aquatic ecosystems (including agricultural systems) is the N. Considering that the organic N pool is just a form of stored N in ecosystems, the primary supply is

originated from the atmosphere, as biotic and non biotic fixation (Delgado and Scalenghe, 2008).

In the soil, most N is stored in organic form. Plants mostly use the inorganic forms nitrate (NO_3^-) and ammonium (NH_4^+). In aerated soils, NO_3^- is dominating because NH_4^+ is rapidly converted to NO_3^- by nitrifying microorganisms (Muchovej and Rechcigl, 1994). In soils, N application may affect soil processes and cycles. These could involve increases in crop residues return to soil, changes in soil organic matter dynamic, $\text{NO}_3\text{-N}$ content and pH decrease (Divito, et al., 2011). N transformations are strongly affected by soil water content (Rückauf et al., 2004). They showed that $\text{NO}_3\text{-N}$ transformation into organic compounds occur preferably under dry soil conditions. Plant growth and plant uptake of $\text{NO}_3\text{-N}$ added do not affect transformation into organic N compounds. Furthermore, the efficiency of plant uptake is best under wet soil conditions. Therefore, $\text{NO}_3\text{-N}$ is very susceptible to loss via leaching (Kurunc et al., 2011), has large potential to pollute groundwater (Darwish et al., 2011) and surface water bodies (Lassaletta et al., 2009), especially in lowland catchments where the groundwater is responsible for a significant part of the hydrological components (Lam et al., 2010). In aquatic environment systems, N exists in four main forms: organic N (proteins, amino acids and urea), ammonia (either as free ammonia [NH_3] or as ion NH_4^+), nitrite (NO_2^-) and NO_3^- (Binkley et al., 1999). NH_3 is highly toxic for aquatic organisms, even in very low concentrations (Randall and Tsui, 2002). NO_3^- and NH_4^+ together with phosphate contribute to water eutrophication (Jickells, 2005; Drolc and Koncan, 2008).

N retention is the difference between inputs and outputs of N to a given freshwater system (Saunders and Kalff, 2001). Three processes contribute to N retention: denitrification, sedimentation and uptake by aquatic plants. The denitrification, based on anaerobic respiration, which reduces NO_3^- to N_2O , is the most important sink (removal process) for reactive N, helping to remove excess NO_3^- from soil and aquatic systems (Seitzinger et al., 2006). However, the removal of NO_3^- from soil and water bodies through denitrification causes increase on nitrous oxide (N_2O), a harmful greenhouse gas (Butterbach-Bahl and Dannenmann, 2011), 310 times more powerful in global warming potential than the CO_2 (Thangarajan et al., 2013).

2.4.1 Nitrogen pollution

N pollution occurs in surface water bodies and in groundwater (Krause et al., 2008; Burt et al., 2010; Smith et al., 2010; Hutchins, 2012). In surface water bodies NO_3^- is one of the most problematic nutrients among all water pollutants, causing nutrient enrichment of water bodies and contamination of drinking water (Burt et al., 2010). Beyond these problems, N input may result in two additional environmental problems: water acidification and direct toxicity of inorganic nitrogenous compounds (NH_4 , NO_2 and NO_3) (Camargo and Alonso, 2006). According to these authors, eutrophication and toxicity of NH_4 , NO_2 and NO_3 can affect many aquatic ecosystems, but freshwater animals seem to be more sensitive to the toxicity of inorganic N compounds than seawater animals, with NO_3 being less toxic than NH_4 and NO_2 in any case. Extensive kills of invertebrates and fishes, are probably the most dramatic manifestation of hypoxia (or anoxia) in eutrophic and hypereutrophic aquatic ecosystems with low water turnover rates. Moreover, occurrence of toxic algae can significantly contribute to the extensive kills of aquatic animals. Cyanobacteria, dinoflagellates and diatoms appear to be the major responsible, which may be stimulated by inorganic N pollution (Camargo and Alonso, 2006). They suggest that TN levels lower than the range 0.5 - 1.0 mg/l might prevent aquatic ecosystems from developing acidification and eutrophication, at least by inorganic N pollution.

Bu et al. (2011) monitored N pollution in China. They verified a significant seasonal variation on N concentrations. $\text{NH}_4\text{-N}$ was the major N form during the spring season and $\text{NO}_3\text{-N}$ dominated N pollution during the summer and autumn seasons. For Bu et al. (2011), the relationships between N and physicochemical parameters showed that N pollution in the river was driven by nitrification and denitrification processes rather than by seasonal biological demand during the different sampling periods.

Drolc and Koncan (2008) assessing the N pollution in Slovenia concluded that the main sources of N originated from wastewater (62% from point sources and 4% from diffuse sources when compared to the total emission) and agriculture (3% from point sources and 28% from diffuse sources again compared to total emission). For the authors, atmospheric deposition of N contributes relatively in a small percentage of the total loading (3%). For Rogora et al. (2012), the role of atmospheric deposition as a N input to ecosystems will become more important in future, both as an acidifying agent and as a nutrient vehicle.

Bartley et al. (2012) studying N losses from about 514 different geographical sites covering 13 different land uses in Australia verified that the median of TN concentration were 32 mg/l for horticulture, 6.5 mg/l for cotton, 2.7 mg/l for bananas and 2.2 mg/l for pastures. Rothwell et al. (2010) found a positive relationship between NO₃-N concentration in surface water bodies and arable land area.

2.4.2 Strategies to mitigate N pollution

Grizzetti et al. (2013) quantified the N loss to the environment related to food waste at global scale consumption. They estimated a global loss of 2.7 Tg N/year due to food waste. The authors emphasized the necessity of more control policies related to nutrients, water, energy, climate, biodiversity and land use, as well as for the scenario analysis of societal change in diet, aiming to increase the efficiency and decrease the N pollution. N loss through leaching is not only of environmental and health concern, but also a matter of money sink for the farmers and society (Darwish et al., 2011). For these authors, regulations that simply limit N applications may not encourage farmers to consider other aspects of fertilizer and water management. Understanding the factors that influence leaching can help farmers save money and at the same time prevent groundwater pollution.

Sainju et al. (2009) examined the tillage impacts on N cycling in the USA verified that the frequency of tillage affect positively N losses through leaching, volatilization, and denitrification. For these authors, long-term no-till system increased crop grain productivity and biomass N, N soil storage, and potential N mineralization, and reduced N loss compared with the conventional system. In China, Nie et al. (2012) testing NO₃-N leaching from corn crop systems verified that inter-cropping systems involving corn decreased NO₃-N leaching compared with corn monoculture. According to Dawson and Hilton (2011), in order to reduce N pollution, farmers need to apply fertilizer correctly and increase N use efficiency. Also, N losses by animal excrement are high, therefore, it is necessary to recycle these N quantities as low as possible (Küstermann et al., 2010). Raymond et al. (2012) argue that in highly managed and productive watersheds, the export of N is directly controlled by the amount added by fertilization and modulated by water residence time, with water residence time being impacted by climate and agricultural practices, such as tile drainage, cropping system and

fertilizer input. For Drolc and Koncan (2008), besides the reduction of point sources by implementing nutrient removal technologies, the management of agricultural pollution should become a major task with the aim to reduce the total N load to river system.

Dawson and Smith (2010) discussed sources and the qualitative risk of diffuse pollutant production which impacts air and water quality. For the authors, an integrated diffuse pollution research that combines gaseous, dissolved and solid (particulate) physical phases is essential for understanding inter-relationships between different pollutant fates, and preventing unintentional pollutant swapping.

Saunders and Kalff (2001) compared the potential of N retention in wetlands, lakes and rivers. They concluded that wetlands retain the highest proportion of TN loading, followed by lakes and then, by rivers. According to Lind et al. (2013), $\text{NO}_3\text{-N}$ can be removed in wetland soils by denitrification which is the reduction of NO_3 to the gaseous forms nitrous oxide (N_2O) and dinitrogen (N_2). Pal et al. (2010) showed that peat soils which are rich in organic matter, have high potential for nitrification under oxic conditions and denitrification under anoxic conditions, but a high proportion of nitrate (30 - 50%) was converted to the greenhouse gas, N_2O . Testing the potential of denitrification of wetland soils, Lind et al. (2013) verified a rapid reduction of the NO_3 fluxes, supporting the effectiveness of wetlands for removal of N. However, during the reduction of NO_3 transient accumulation of N_2O was observed, confirming the capacity of wetlands to remove large amounts of N, but it also shown that substantial emission of N_2O might occur if the reduction of NO_3 is not complete. They showed that N_2O emissions from N loaded riparian areas are likely to be low provided that NO_3 availability is low as this promotes the reduction of N_2O to N_2 . Nevertheless, when diverting N rich water toward wetlands, the risk of atmospheric pollution cannot be excluded, especially in areas where fluctuations in the water level may disrupt the reduction of N_2O to N_2 . N removal via denitrification and plant uptake is often observed under the combination of aerobic followed by sustained anoxic conditions, the presence of a carbon source (organic material), and the presence of dense vegetation (Collins et al., 2010).

Thieu et al. (2011) showed that the implementation of classical management measures involving improvement of wastewater purification and “good agricultural practices” are not sufficient to obviate these problems. According to Collins et al. (2010), alternative control measures, such as bio-retention, filters, and wetlands, show greater promise in their ability to

remove N from storm water than the more conventional practices such as dry ponds and wet ponds.

Howden et al. (2011) assessed and modeled a long-term diffuse NO₃-N pollution in a rural catchment in UK. They suggested that N-loading increased by up to a factor of six over the period of 1930-2007. The main causes of this increase in NO₃-N is reported by Howden et al. (2011) as due to a combination of increased inputs from animal excreta, enhanced N mineralization following ploughing of permanent grasslands and fertilizer inputs to land. Gholamhoseini et al. (2013) assessing the interaction of corn yield, N use efficiency and NO₃ leaching showed that, from a certain amount of N, the yield corn productivity had not increased, but the loss of NO₃ through leaching increased considerably. Aquilina et al. (2012) estimated that the groundwater constitutes a N reservoir which should not be ignored since it represented about 10% of the TN input in the river system in France.

Nie et al. (2009) recommend the following effective methods for reducing N loss from farmlands: 1) use of best management practices, such as reduced irrigation and split application of N fertilizer; 2) use of controlled release fertilizers instead of conventional fertilizers; 3) adoption of high N use efficiency crop genotypes; 4) application of new tools such as modeling as well as N indexing and 5) use of deep-rooted crops in crop rotations systems.

2.5 Monitoring and assessment of water quality

The assessment and monitoring of N and P concentrations in the river systems provide critical information to catchment managers (Jaji et al., 2007; Bulut et al., 2010), allowing them to select the most suitable mitigation options to reduce N and P concentrations and eutrophication risks (Withers and Sharpley, 2008). In northern Germany, many studies have been carried out in lowland catchments to monitor and assess the river water quality (Schmalz et al., 2007; Schmalz et al., 2008b; Lam et al., 2010; Lam et al., 2011; Wu et al., 2011; Fohrer and Schmalz, 2012). However, there are very few studies that show the development of water quality over time because these long-term studies require a lot of resources. According to Bowes et al. (2009), long-term data sets help to understand the changes in catchment

characteristics and provides important information to future management decisions. Between 1991 and 1995, Ripl et al. (1996) coordinated the project called "Stör project I and II" at the upper river Stör catchment, a typical rural lowland catchment in Germany. In this project, water quality parameters at 128 sampling points were measured from March 1991 until March 1995. Thus, a consistent database of water quality is available to compare the development of water quality parameters over the last two decades.

In order to establish evidence of environmental changes in water quality, a lot of studies were conducted to verify the improvement in water quality over the time (Howden and Burt, 2008; Kronvang et al., 2008; Tisseuil et al., 2008; Iital et al., 2010; Rothwell et al., 2010; Bouraoui and Grizzetti, 2011). The majority of these studies used monthly or weekly water quality monitoring, minor number of studies used daily time series to assess water quality parameters (Alewell et al., 2004; Evans and Johnes, 2004; Oeurng et al., 2010). According to Lu et al. (2011), environmental monitoring programs need to include daily monitoring in water quality studies. The daily monitoring is important to verify the real dynamics of water quality, such as peaks of nutrient concentration at specific times, and could help to understand the water quality variability over time.

High frequency data collected at multiple sites can be used to more effectively quantify spatial and temporal variability in water quality constituent fluxes than through the use of low frequency water quality grab sampling (Horsburgh et al., 2010). The long-term monitoring of N and P concentrations in the river systems is needed to assess the impact of environmental policy and the sustainability of environmental measures (Burt, 2003; Howden et al., 2009; Bouraoui and Grizzetti, 2011). Additionally, it allows to select the most suitable mitigation options to reduce N and P concentration and eutrophication risks in the future (Iital et al., 2008; Withers and Sharpley, 2008; Bowes et al., 2009). Furthermore, in studies of modeling of hydrology and water quality, a consistent data set of environment monitoring is also important to achieve a good calibration of models (Burt et al., 2010).

The existence of long-term data sets of this type, across a range of river types, is vital for understanding the effectiveness of various mitigation strategies, and is particularly needed through the process of WFD (EC, 2000) implementation. Unfortunately, such monitoring programs are extremely expensive to fund and difficult to maintain over a decal time scale (Bowes et a., 2011). Furthermore, permanent monitoring stations are also required within the

river basins to evaluate the local implementation of measures, but the true integrated response of the river basin indicating if further efforts are needed to reduce nutrient concentration can only be measured at the outlet (Bouraoui and Grizzetti, 2011).

2.6 Hydrological, sediment and nutrient load modeling

Studies have used models to evaluate the impacts of soil erosion and sediment transport on receptors (water bodies), while others have been used to assess the potential effectiveness of management options, particularly through scenario analysis (Owens and Collins, 2006). Erosion and pollutant modeling have had various functions, as related by Owens and Collins (2006): improve the understanding of landscape evolution; predict erosion and sediment generation and transport; evaluate the likely impacts on receptors (such as water bodies); evaluate the effectiveness of management options. Laan et al. (2010) emphasized the importance of combining monitoring and modeling to estimate nutrients losses. According to the authors, the modeling will lead to more efficient and less environmentally threatening crop management practices.

According to Lane et al. (1988), description of mathematical models of overland flow and erosion are classified in three main types of models: empirical models, process based or physically based models, and conceptually based models.

2.6.1 *Empirical models*

Empirical models usually establish relationships between runoff, sediment yield and precipitation, plants, soil types, land use types, tillage styles, water conservation measures and so on (Blanco and Lal, 2010). They are still used because of their simple structure and ease of application. Since they are based on coefficients computed or calibrated from measurements and/or observations, they cannot describe or simulate the erosion process as a set of physical phenomena (Shen et al., 2009). The Universal Soil Loss Equation (USLE) is the most widely used empirical erosion model (Wischmeier and Smith, 1965). USLE is used to estimate soil erosion from an area simply as the product of empirical coefficients based on the following

parameters: rainfall erosivity, soil erodibility, topography, land cover and conservation practices (Wischmeier and Smith, 1978). As USLE did not consider surface runoff, the Modified Universal Soil Loss Equation (MUSLE) was developed by Williams (1975). Currently, the Revised Universal Soil Loss Equation (RUSLE, Foster et al., 2003) and MUSLE can be used at watershed scale.

2.6.2 Process based or physically based models

Process physically based models can describe with details the physical mechanism of sediment yield, and can simulate the individual components of the entire erosion process by solving the corresponding equations; and so it is argued that they have a wider range of applicability (Shen et al., 2009). The process-based watershed models can be useful to improve the understanding of interactions between land use change, water balance and water quality issues (Shao et al., 2013). The Water Erosion Prediction Project (WEPP) is a physically based model that simulates sediment yield and deposition using a spatially and temporally distributed approach (Flanagan and Nearing, 1995). The WEPP model simulates many of the physical processes important in soil erosion, including infiltration, runoff, raindrop and flow detachment, sediment transport, deposition, plant growth, and residue decomposition (Flanagan et al., 2007). Other physically model is the European Soil Erosion model (EUROSEM), it is a process-based erosion prediction model designed to predict erosion in individual events and to evaluate soil protection measures (Morgan et al., 1993, 1998). Also, EROSION 3D (Schmidt et al., 1999; Schob et al., 2006) and SHETRAN (Système Hydrologique Européen TRANsport, Ewen et al., 2000) can be used to model erosion, but, they are usually applied in small areas (Kliment et al., 2008). Beyond these models, Aksoy and Kavvas (2005) had reviewed about others physically models for erosion and sediment transport.

2.6.3 Conceptual models

The conceptual models lie somewhere between empirically and physically based models, and are based on spatially lumped forms of continuity equations for water and sediment and some other empirical relationships (Lane et al., 1988).

The LASCAM model (Viney et al., 2000), the Agricultural Non-Point Source pollution model (AGNPS, Young et al., 1989) and the Soil and Water Assessment Tool (SWAT, Arnold et al., 1998) are example of conceptual models. LASCAM is a conceptual model of nutrient mobilization and transport to predict diffuse sources of P and N at watershed scale (Viney et al., 2000). The AGNPS (Young et al., 1989) is an event-based model simulating runoff, sediment and transport of N, P and chemical oxygen demand resulting from single rainfall events. AGNPS model works with physically based equations and also with empirical method as well RUSLE (Foster et al., 2003) and curve number (SCS, 1972). The currently revision is the AnnAGNPS, the Annualized AGNPS model used by Bingner and Theurer (2005), it can be used for continuous simulations of hydrology, soil erosion and transport of sediment, nutrients and pesticides. It is designed to analyze the impact on the environment of non-point source pollutants from predominantly agricultural watersheds (Shrestha et al, 2006; Kliment et al., 2008).

The SWAT model (Arnold et al., 1998) is an ecohydrological model development by the US Department of Agriculture (USDA) Agricultural Research Service (Arnold et al., 1998; Neitsch et al., 2011). The SWAT model is in large parts physically based and consists of mathematical process descriptions (Arnold et al., 1998), however the SWAT model use the empirical model MUSLE (Williams, 1975) to predict sediment load. SWAT was developed to predict the impact of land management practices on water, sediment and agricultural chemical yields in large complex watersheds with varying soils, land use and management conditions over long periods of time (Neitsch et al., 2011).

2.6.4 Other types of classification

Lumped models treat the catchment as a single homogeneous unit, with state variables that represent averages over all the catchment area. On the other hand, distributed models are considered to provide a more realistic representation of the spatial heterogeneity of hydrological processes, arising from spatial variability in both precipitation and the physical properties within the watershed (Kling and Gupta, 2009). Semi-distributed models have been suggested to combine the advantages of both types of spatial representation. This type model does not pretend to represent a spatially continuous distribution of stable variables, rather it

separates the catchment to a degree thought to be useful by the modeler using a set of lumped models (Pechlivanidis et al., 2011).

Models can be classified as continuous simulation or event based models. Continuous models typically would take into account a time series of rainfall-runoff, while event based scale models take into account only one storm event (Pechlivanidis et al., 2011). Other classification is the space-scale. According to Singh and Frevert (2006), models can be classified in small catchments (up to 100 km²) medium-size catchment (100-1000 km²) and large catchments (greater than 1000 km²).

2.6.5 Watershed models

With the implementation of Geographic Information System (GIS) in hydrological and erosion models, it is possible to model hydrology, sedimentation and pollutants at the watershed scale. Watersheds models are useful tools and have been used widely on the globe to predict the long-term impact of BMPs application on water quality (Lam et al., 2011). In recent years, a large number of diffuse sources pollutions models have been developed to generalize the effects of environmental conditions and agricultural practices on nutrients losses (Borah and Bera, 2003).

An important aspect of nutrients pollution from diffuse sources is the pollution of river water, so the natural scale for studying N and P problems has often been the catchment scale (Liu et al., 2005). Often the catchment model includes the analysis of surface and subsurface pollution, and must be able to represent the application of N and P materials to the land surface, the N and P transformations in the soil which control the rate of nutrients production, and the transport of nutrients through the surface and subsurface zones of the catchment.

Various models, developed to predict N and/or P are used worldwide:

The Areal Non-point Source Watershed Environment Response Simulation (ANSWERS, Beasley et al., 1980) is a physically based model able to simulate runoff, sediment transport and nutrients (N and P). A mathematical model called EPIC (Erosion-Productivity Impact Calculator) was developed to determine the relationship between soil erosion and soil productivity (Williams et al., 1984). EPIC is composed of physically-based components for

simulating erosion, plant growth, and related processes determining optimal management strategies. The EPIC components include weather simulation, hydrology, erosion-sedimentation, nutrient cycling, plant growth, tillage, soil temperature, economics, and plant environment control (Williams et al., 1984).

The Generalized Watershed Loading Function (GWLF, Haith and Shoemaker, 1987) simulates runoff, sediment, and nutrient (N and P) loadings for source areas (land uses) within a watershed. It can also calculate septic system loads and point source discharge data. GWLF is a combined distributed/lumped parameter watershed model; the model does not spatially distribute the source areas, but simply aggregates the loads from each area into the watershed without spatial routing (Schneiderman et al., 2002). It is a continuous simulation model, which uses daily time steps for weather data and water balance calculations.

The Soil Moisture-based Runoff Model (SMRM), is a cell-based rainfall-runoff model which is integrated with GIS (Zollweg et al., 1996). The model combines elevation, soil and land use data within the GIS and predicts the spatial distribution of soil moisture, evapotranspiration, surface runoff and inter flow throughout a watershed (Frankenberger et al., 1999).

The Hydrological Simulation Program - Fortran (HSPF, Bicknell et al., 1997) is generally used to assess the effects of land use change, reservoir operations and point or non-point source treatment alternatives. HSPF simulates the catchment response by changes in water, sediment and nutrients (N and P).

The Spatially Referenced Regressions on Watershed Attributes (SPARROW) model (Smith et al., 1997) is capable to simulate total N and total P at regional scale. It is a budget-based modeling used to provide predictions of annual nutrient flux (mass per time) and can be applied to ungauged catchments (Oehler and Elliot, 2011).

According to Gassman et al. (2007), the SWAT model (Arnold et al., 1998) is originated from the model EPIC (Williams et al., 1984) and from the Simulator for Water Resources in Rural Basins (SWRRB) model (Arnold and Williams, 1987), which was designed to simulate management impacts on water and sediment movement for ungauged rural basins across the US. The SWAT model (Arnold et al., 1998) is applied in various watersheds of the world (Ndomba et al. 2008; Lam et al., 2010; Lee et al., 2010; Panagopoulos et al., 2011; Oeurng et al. 2011; Bieger et al., 2012a; Baker and Miller, 2013). The SWAT model is a conceptual,

continuous time model which was developed in the early 1990s to assist water resource managers in assessing the impact of management and climate on water supplies and non-point source pollution in watersheds and large river basins (Arnold et al., 1998; Arnold and Fohrer, 2005). The SWAT components include weather, hydrology, erosion/sedimentation, plant growth, nutrients, pesticides, agricultural management, stream routing and pond/reservoir routing (Arnold and Fohrer, 2005). It has to be adjusted for different weather, soil and local conditions (Gikas et al., 2006). The SWAT model has been extensively used to evaluate water balance (Abbaspour et al., 2007; Schuol et al., 2008, Schmalz and Fohrer, 2009; Lam et al. 2009), sediment load (Oeurng et al. 2011; Uzeika et al., 2012; Somura et al., 2012; Wu and Chen, 2012; Shao et al., 2013) and nutrients load (Panagopoulos et al., 2007; Schmalz et al. 2008b; Schilling and Wolter, 2009; Lam et al., 2010; Panagopoulos et al., 2012) and pesticides in streams (Luo and Zhang, 2009; Zhang and Zhang, 2011; Fohrer et al., 2013). SWAT is able to simulate the impact of climate changes on the hydrology (Ficklin et al., 2009; Mango et al., 2011; Lirong and Jianyun, 2012) and on water quality (Wilson and Weng, 2011). Recently, the SWAT model is used worldwide to test alternative scenarios to improve water quality through best management practices (BMPs), as related by Ullrich and Volk (2009), Lam et al. (2011), Laurent and Ruelland (2011), Dechmi and Skhiri (2013), Liu et al. (2013), Yenilmez and Aksoy (2013).

Huang et al. (2009) used the Soil and Water Integrated Model (SWIM, Krysanova et al., 1998) to simulate alternative land use scenarios in some catchments in Germany. Huang et al. (2009) showed that the optimal agricultural land use and management are essential for the reduction in nutrient load and improvement of water quality in order to meet the objectives of the WDF (EC, 2000). Hesse et al. (2008) successfully applied the SWIM model in a lowland catchment in Germany. According to Hesse et al. (2008) the simulation of the discharge behavior and water quality with ecohydrological catchment models is more difficult for regulated lowland rivers than for rivers in mountainous areas, due to the special characteristics of the former ones.

Recently, other models have been developed to assess hydrologic processes and/or nutrient load: Long-Term Hydrologic Impact Assessment (L-THIA) model (Bhaduri et al., 2000) has been developed using the curve number (CN) method. Long-term climatic records are used in combination with soils and land-use information to calculate average annual runoff and non-

point sources pollution at a watershed scale. The model is linked to GIS for convenient generation and management of input and output data of the model, and advanced visualization of model results.

The SHETRAN (Ewen et al., 2000) is a physically based spatially distributed model able to simulate sediment transport in watersheds. SHETRAN coupled with the Grid Oriented Phosphorus Component (GOPC, Nasr et al., 2005) is capable to simulate P detachment and transport. SHETRAN/GOPC is an example of a fully physically-based model which relies wholly on relationships derived from physical and chemical laws (Nasr et al., 2007). The Modeling Nutrient Emission in River Systems (MONERIS) is a model to quantify annual average of total N and total P emissions from catchments to surface waters (Behrendt et al., 2000, Venohr et al., 2005).

The Topography-based Nitrogen Transfer and Transformation model (TNT2) developed by Beaujouan et al., (2002) consists of hydrological modules of the integrated hydrological and N model, which was developed to study hydrological and N fluxes in small catchments.

The IWAN model is used for modeling water balance and nutrient dynamics of floodplains (Krause and Bronstert, 2005). The Dynamic Watershed Simulation Model (DWSM, Borah et al., 2001) simulates distributed surface and subsurface storm water runoff, propagation of flood waves, upland soil and stream bed erosion, sediment transport and agrochemical transport in agricultural and rural watersheds during single events. The Diffuse Nitrate Modeling Tool (DNMT) was developed for modeling the fate of $\text{NO}_3\text{-N}$ in urban areas (Liu et al., 2005). The DNMT works at the catchment scale and has a modular structure that consists of three components: the hydrological module, the N cycle module and the $\text{NO}_3\text{-N}$ transport module.

Bowes et al. (2008) developed the Phosphorus Load Apportionment Model, which can be used to define point and diffuse P load at catchment scale. It is a simple model and it does not require any knowledge of the land use, catchment size, population or livestock density to estimate total P load. Recently, a new Distributed Rainfall-Runoff (DR2) model was developed (Lópes-Vicente and Navas, 2012). The new model computes the volume of actual available water downwards from divides, taking into account the different configurations of the up slope contributing area, infiltration processes and climatic parameters.

Panagopoulos et al. (2011) showed that sediments and nutrients (N and P) loads could be adequately reproduced in large time steps (monthly or seasonal) with the SWAT model and that even with data limitations, the seasonal variation and the most critical areas of pollutant losses to waters could be adequately identified. Borah and Bera (2003) analyzing various watershed models verified that AnnAGNPS, ANSWERS, HSPF and SWAT are useful for long-term simulations and assessments of hydrological changes and watershed management practices, especially agricultural practices. AnnAGNPS, HSPF and SWAT are the long-term simulations models having all the three major components (hydrology, sediment and chemical) that are applicable to watershed scale (Borah and Bera, 2003). Nasr et al. (2007) tested three mathematical models, SWAT, HSPF and SHETRAN/GOPC to assess diffuse P pollution in three watersheds, and found out that the SWAT model gave the best calibration results for daily TP loads. Shen et al. (2009) used WEPP and SWAT for modeling sediment load and runoff in China. They verified that both models had acceptable performance. In addition, the computational efficiency of the SWAT model is convenient for parametric adjustment and multiple simulations implemented in minimal time (Arnold and Fohrer, 2005).

2.7 European legislation for water quality

In the last decades, the European Community has been taking various measures to prevent water pollution. Three important directives have been adopted, namely the Nitrate Directive (NO₃-Directive) (EEC, 1991a), the Urban Waste Water Treatment Directive (WWTP-Directive) (EEC, 1991b) and the Water Framework Directive (WFD) (EC, 2000). The main objective of the NO₃-Directive was to reduce water pollution caused or induced by NO₃⁻ from agricultural sources (EEC, 1991a). The objective of the WWTP-Directive was to protect the environment from adverse effects of wastewater discharges (EEC, 1991b). In 2000, the WFD was initiated to established good water quality and ecological status of all water bodies until 2015 in all European Union member states (EC, 2000). The response time of N pollution in water bodies in order to achieve some changes due to modifications of management practices can vary from 10 to 30 years (Behrendt et al., 2000; Fenton et al., 2011).

On behalf of sustainability and the climate change adaptation strategy of the German government, “green” energy has been promoted in recent years. The number of biogas plants

has grown rapidly since specific feed-in tariffs for “green” electricity were defined in the German Renewable Energy Sources Act in 2001 (Djatkov et al., 2012). From 2002 until 2009, the area of corn for silage increased 80% in the State of Schleswig-Holstein (Statistical Office Schleswig-Holstein, 1992-2013). Corn is the most important crop used as substrate for the digestion in agricultural biogas plants (Oslaj et al., 2010). The incentive to produce biogas may be contributing negatively to reduce N levels in the rivers. The potential of N pollution with biogas system is not only because the corn crop needs high levels of N, but according to Raven and Gregersen (2007) the manure produced at the biogas plants also requires to be redistributed at farming.

Management policies are required to achieve food, energy and water security concomitant with environmentally sustainable targets for preventing pollution of air, soils and waters (Dawson and Smith, 2010). According to Goodchild (1998) and Tunney (1994), a great degree of cooperation between the ministries of agriculture and environment is required to achieve the goals of the environmental directives. A deficient cooperation with agricultural and energy policies could adversely affect the environmental policies.

Regional land use change due to European market policy has far reaching consequences for various landscapes functions. Simulation models are mostly used to analyze the effect of management practices on water quality and quantity (Fohrer et al., 2001). In many European lowland rivers and riparian floodplains, diffuse nutrients pollution are causing a major risk for the surface waters and groundwater making them susceptible to not achieve a good status as demanded by the WFD (Krause et al., 2008). Due to the mean residence time of N in groundwater of 25 years, measures that are implemented to reduce N emission will take many years to have an evident beneficial effect (Wendland et al., 2010; Hirt et al., 2012). According to Hirt et al. (2012), it is possible that N loads from groundwater into surface waters can increase in short term despite of the implementation of environment measures, because the groundwater concentrations still reflect the nutrient surpluses of the last decades. According to Aquilina et al. (2012), the contribution of groundwater as source of N to river systems should be reduce the time to achieve a reduction of N concentration occasioned from best management practices in agriculture. Thus, an improvement of water quality is expected many years after the implementation of the environmental directives.

2.8 Changes in water quality

Diffuse pollution is one of the most challenging issues in catchment management (Chon et al., 2012). To reduce water pollution, public policies aim to change agricultural practices by supporting land use and management practices that limit the risks of sediment, N and P transfers to streams. According to Laurent and Ruelland (2011), these practices are called environment-friendly or best management practices (BMPs). The most frequent BMP consists of catch crops, reduced fertilization, conversion of arable land to pasture, grass filter strips, no tillage and conservation tillage systems (Ullrich and Volk, 2009; Laurent and Ruelland, 2011). Changes in land use and management are seen as the main factor responsible for changes in sediment and nutrient delivery to water bodies (Bartley et al., 2012). An accurate control of non-point pollution related to agriculture is not possible without considering soil and landscape management (Delgado and Scalenghe, 2008).

According to Kronvang et al. (2008) the successful reduction on N pollution in Denmark was due to three main policy instruments: i) mandatory requirements to improve treatment on WWTPs including nitrogen removal on larger WWTPs; ii) mandatory fertilizer and crop rotation plans, with limits on the plant-available N applied to different crops; iii) statutory norms for the proportion of manure N assumed to be available for plants. For Iital et al. (2005) the successful reduction on N pollution in Estonia was due to: i) a dramatic decrease in the use of organic and inorganic fertilizers and livestock numbers; ii) increased fraction of grassland and abandoned land at the expense of cultivated and ploughed areas; iii) better farm management practices.

Although N and P input to water bodies from agricultural non-point sources of pollutants are difficult to control, it is of prime importance to continually search for ways to reduce inputs of contaminants into surface waters (Larose et al., 2011). The reduction in fertilizer application is one of the most effective BMPs to minimize the nitrate pollution in agriculture areas (Schilling and Wolter, 2009; Yevenes and Mannaerts, 2011; Lam et al., 2011). Schilling and Wolter (2009) employing the SWAT model showed that the reduction in fertilizer applications from 170 to 50 kg/ha achieved 34.4% reduction in NO₃-N load in the Des Moines River watershed in USA. Yevenes and Mannaerts (2011) simulating land use alternative on NO₃-N load with the SWAT model in Portugal stated that a fertilizer reduction scenario was effectively implemented to evaluate remedial NO₃-N control policies in accordance with the

European Nitrate (EEC, 1991a) and Water Framework Directives (EC, 2000).

The effectiveness of BMPs for reduction of agricultural non-point sources of pollution is difficult to evaluate and the monitoring of such changes would be costly and time consuming (Liu et al., 2013). In this way, after an adequate nutrient calibration and validation of the SWAT model, new simulation with alternative BMP (Tong and Naramngam, 2007; Lam et al., 2011; Laurent and Ruelland, 2011; Liu et al., 2013; Yenilmez and Aksoy, 2013) or climate changes (Ficklin et al., 2009; Mango et al., 2011; Wilson and Weng, 2011; Lirong and Jianyun, 2012) can be modeled. According to Bartley et al., 2012, understanding how sediment and nutrient concentrations vary with land use is critical to understand the current and future impact of land use change on aquatic ecosystems.

Glavan et al. (2013) investigated the impact of a historical land use scenario on the river water quality in Slovenia. They showed that the lower extent of forest and higher extent of grassland and arable land resulted in higher concentrations of water pollutants. In addition, Glavan et al. (2013) related that tillage methods for arable use, such as ploughing or regular mulch and hoeing, are very invasive for the top soil horizon and consequently for soil erosion.

Gordon et al. (2010) reviewed the trade-offs among ecosystem services that have been generated by agriculture-induced changes to water quality and quantity in downstream aquatic systems, wetlands and terrestrial systems. They identified three main strategies: (i) The opportunity to improve management practices on agricultural lands to increase the efficiency with which water is used to produce food and to reduce water pollution including nutrient leakages. This can relieve some of the pressure from upstream water use on other ecosystems. (ii) The need to link agricultural water management and management of downstream aquatic systems in order to strike trade-offs, where necessary. Involving stakeholders who can negotiate unavoidable trade-offs between upstream food production and downstream ecosystem services is important in this process. There might be scope to reduce these trade-offs by paying more attention to how agriculture alters the dynamics (e.g., timing and variability) of water flows and how this can be better adapted to downstream ecosystem dynamics. (iii) Paying more attention to how water can be managed to create multifunctional ecosystems which can increase synergies among ecosystem services. This can only be done if ecological landscape processes are better understood, and the values of ecosystem services rather than food production alone are recognized. Since most ecosystem services do not have

a price on the market and are seldomly part of current agricultural decision making, this requires a considerable shift in thinking.

Historical land use maps are rarely used as an option for viable future land uses, especially in terms of environmental conditions. There are numerous reasons and these are closely related to uncertainties in past and future types of agricultural production technology and weather (precipitation) in the area (Glavan et al., 2013).

3 CHARACTERIZATION OF THE STUDY AREA

3.1 The Stör catchment

The river Stör, a tributary of the river Elbe is located in the lowland area of Schleswig-Holstein in Northern Germany (Fig. 3.1). In this study, 462 km² of the upper part of the Stör catchment up to the gauge Willenscharen were under investigation, because the lower part is already influenced by the tide of the North Sea. The topography is very flat and varies between 90 and 1 m above sea level (Fig. 3.1). The main tributaries of the upper Stör are Aalbek, Buckener Au, Bünzener Au, Dosenbek, Höllenau and Schwale (Fig. 3.1).

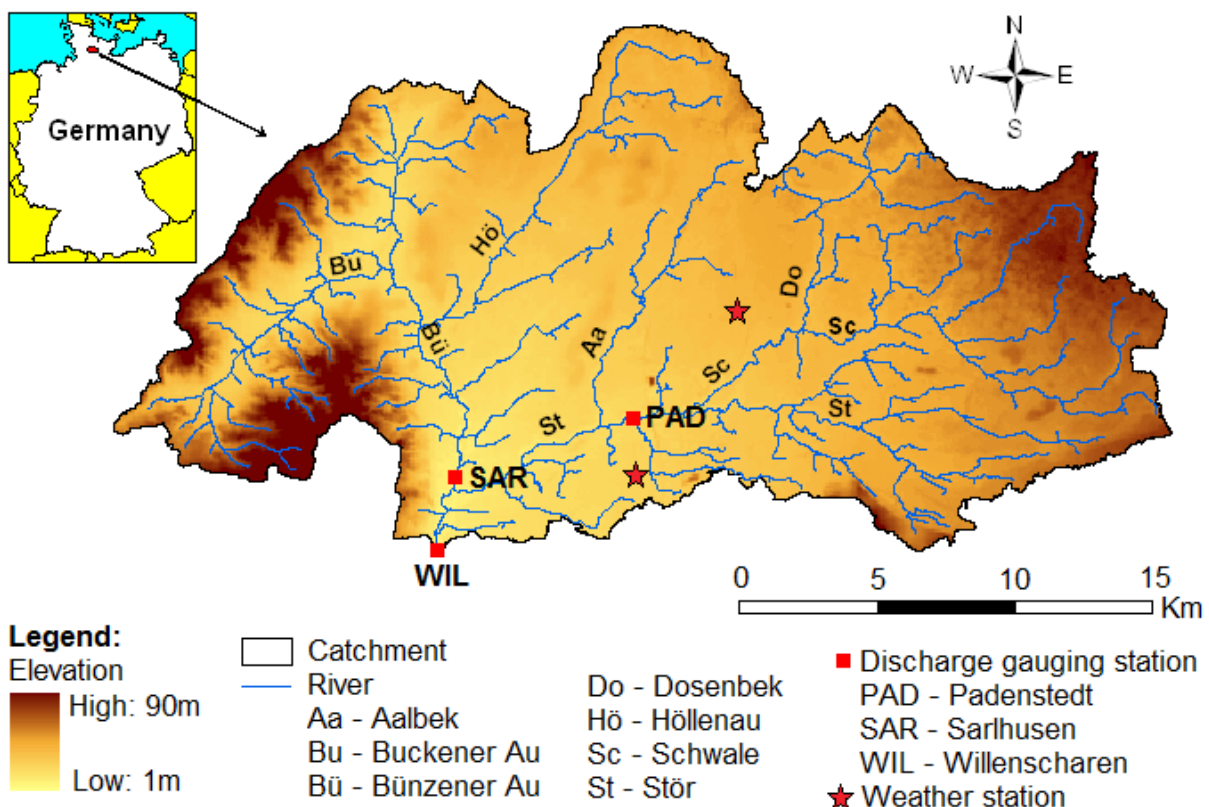


Fig. 3.1 Location of the upper Stör catchment, its main tributaries and the localization of the discharge gauging Stations (LVerMA, 2008).

Since 1880, the landscape and the river network changed considerably due to human activity.

The fraction of agricultural land increased with a growing population. Drainage systems were installed, many tributaries of the Stör catchment were straightened, deepened and canalized (Gessner et al., 2009). Around 1987, the restoration of the rivers from the Stör catchment started with a restoration project of the Buckener Au. The main restoration aim in the Stör catchment was the prevention of bank erosion with bundles of bushes along the river banks and the reinforcement of the embankments with stones (Dickhaut, 2005). In many parts of the catchment, the river profile was flattened and widened, also canalized sections were removed. Moreover, trees were planted along the river to provide shading and integrate the river in the landscape (Martini, 2000). In addition, the canalized sections were reopened and the meandering of the river was made possible, as described by Jensen (2009).

3.2 Soils

The main soils in the upper Stör catchment are Histosol, Gley, Gley-Podsol, Cambisol, Podsol, Planosol and Luvisol (Table 3.1). Soils are dominated by sandy types, with some Gleysols in the eastern parts and some peat soils along the streams. The peaty soils occupy about 3.4% of the total area (Finnern, 1997) and the most important wetland area is the natural reserve “Dosenmoor bog”. Fig. 3.2 represents the soils map in the upper Stör catchment.

Table 3.1 Proportion of the soil classes in the upper Stör catchment (Adapted from Finnern, 1997).

Soils	Area (ha)	Proportion (%)
Cambisol	1836	4.0
Luvisol	3504	7.6
Planosol	5460	11.8
Gley	5540	12.0
Histosol	5924	12.8
Gley-Podsol	9131	19.8
Podsol	14789	32.0

3.3 Climate

The mean annual precipitation is 851 mm and the mean annual temperature 8.2°C at the Padenstedt and Neumünster weather station (DWD, 2012). Fig. 3.3 shows the mean values of precipitation and discharge at the gauge Willenscharen.

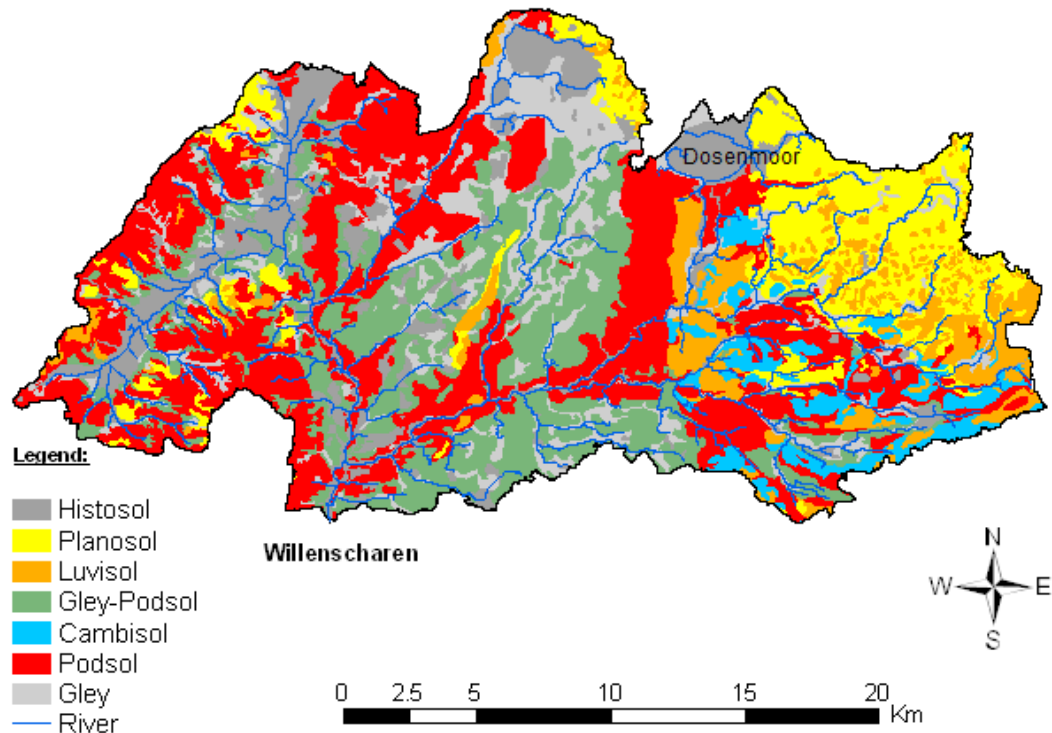


Fig. 3.2 Soils map (Adapted from Finnern, 1997).

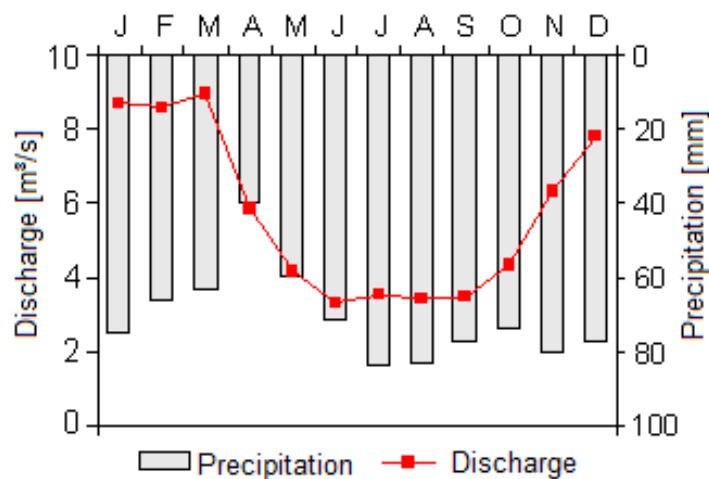


Fig. 3.3 Monthly precipitation in the upper river Stör catchment (weather station Neumünster and Padenstedt) and monthly discharge at the gauge station Willenscharen (Average from 1990 to 2010), (DWD, 2012, LKN, 2012).

3.4 Land use

Land use is dominated by arable land and pasture. In 1987, the pasture area was characterized by 20,7% and arable land by 56.7 of the total area (Ripl et al., 1996). According to Oppelt et al. (2011), in 2010 the pasture area was represented by 33.1%. In this same time the arable land decreased to 42.1%. The major crops used in agricultural areas are winter wheat (13.7%), rapeseed (1.8%) and corn for silage (26.6%) (Oppelt et al., 2011). Fig. 3.4 and Fig. 3.5 show the land use representation in 1987 and 2010, respectively. The urban area represents about 10% of the total area. The most important city is Neumünster with nearly 88,000 citizens. Fig. 3.6 shows the landscapes of the main land uses in the lowland rural Stör catchment.

With circa 521 ha, the big wetland area is represent by the "Dosenmoor bog". It is the largest regenerating and still partially preserved bog of Schleswig-Holstein. It is located near the city of Neumünster. Peat extraction was terminated at the end of the 70s and the area was put under nature protection in 1981 (Dosenmoor, 2013).

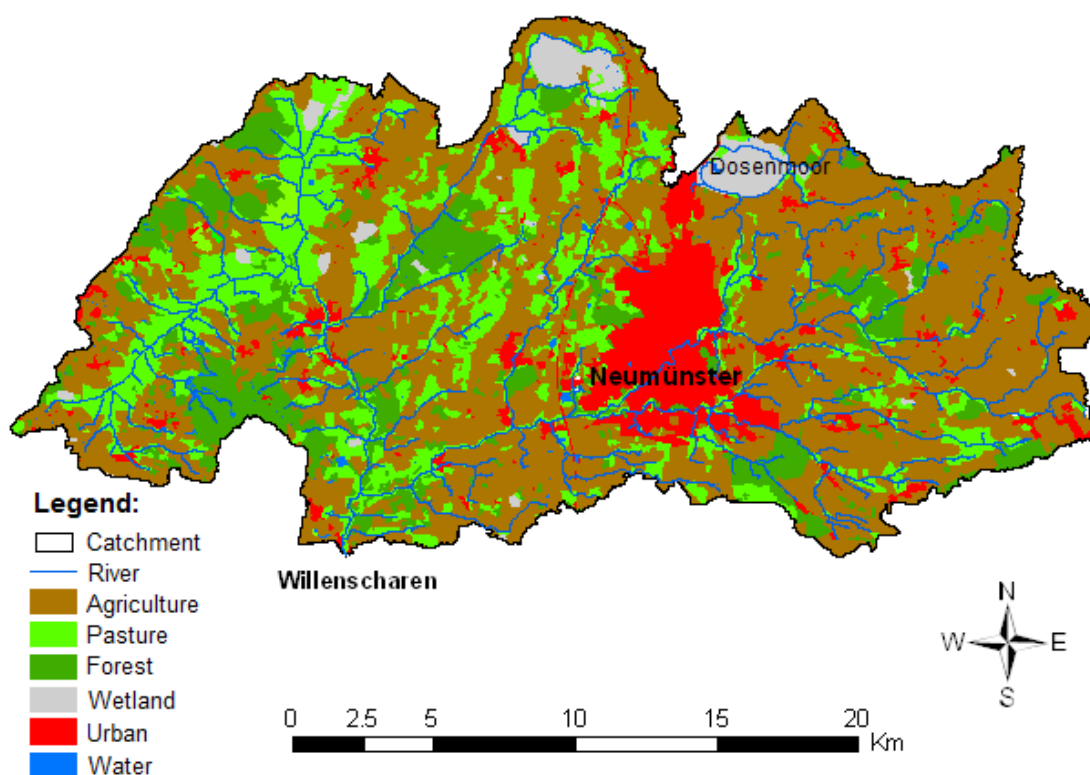


Fig. 3.4 Land use map from 1987 (Adapted from Ripl et al., 1996, based on Landsat 5 TM data, resolution 30 x 30 m).

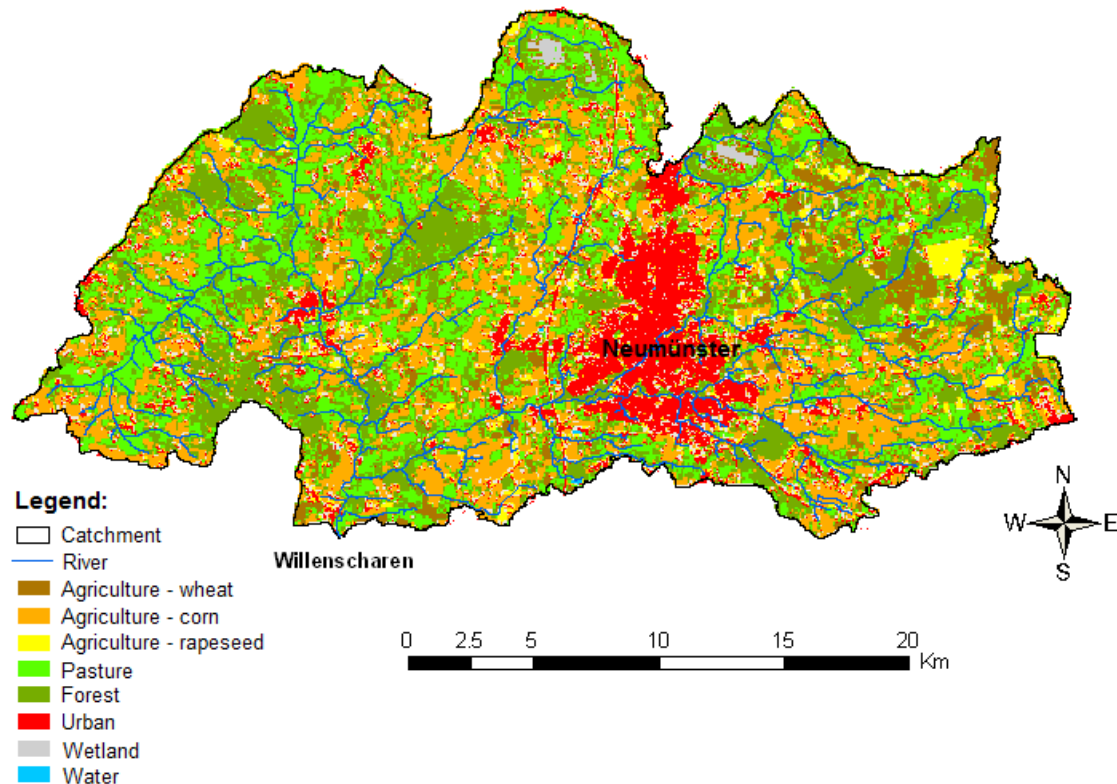


Fig. 3.5 Land use map from 2010 (Adapted from Oppelt et al., 2011, based on Landsat TM data, resolution 30 x 30 m).

3.5 Wastewater treatment plants

Wastewaters of the watershed are treated in twenty-three wastewater treatment plants (WWTPs) (LLUR, 2011). According to LLUR (2011), the WWTPs are classified into three main types: wastewater lagoons (WWTP-L), small WWTP with mechanical purification and biological activation (WWTP-MB), and WWTPs with tertiary treatment for further N and P elimination (WWTP-NP). The main characteristics of the WWTPs are presented in Table 3.2.

The majority of WWTPs in the catchment are WWTP-L, which is a method of semi-natural wastewater treatment, of which four are aerated technically, whereas 12 function with natural aeration (Redeker, 2011). They have between 34 and 1,140 population equivalents (PE) connected (Table 3.2). In Germany, the use of WWTP-L is usually restricted to rural areas, where a few thousand PE are connected (Mudrack and Kunst, 2003). There are five smaller technical WWTPs-MB which apply mechanical treatment and activation and have between 92 and 223 PE connected (Table 3.2). The two major WWTPs in Neumünster and Aukrug-Bünzen with

design capacities of 380,000 PE and 7,000 PE, respectively, and actually connected to 110,816 PE and 4,000 PE, respectively, are WWTPs-NP, which apply in addition to mechanical treatment and activation also nitrification, denitrification, biological and chemical P elimination processes.

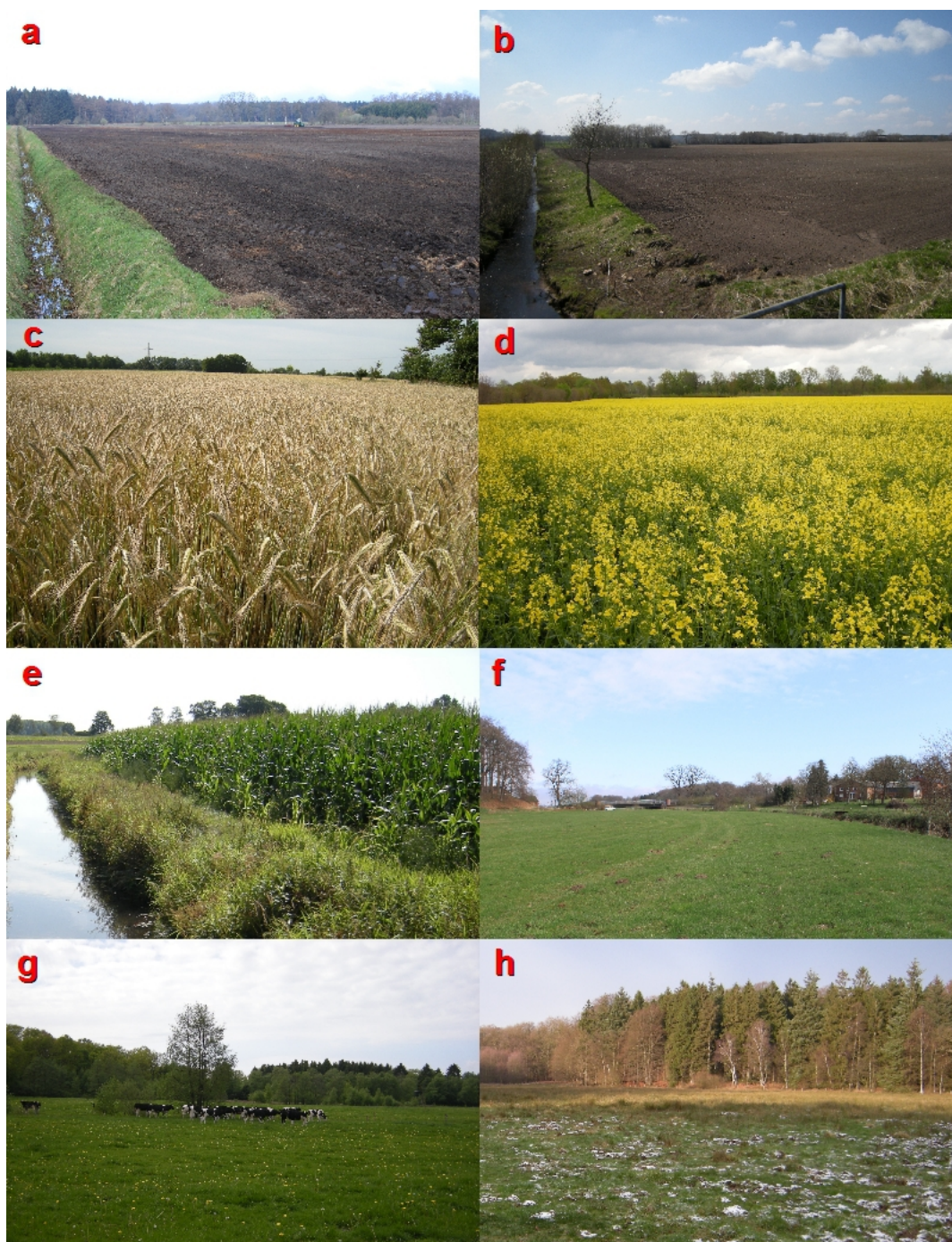


Fig. 3.6 Land uses in the lowland upper Stör catchment. a) arable land beside a drainage system; b) arable land beside the river; c) winter wheat; d) winter rape; e) corn for silage beside the river; f) pasture beside the river; g) pasture with dairy cattle during the spring; h) pasture area and forest during the winter.

Table 3.2 WWTPs location, capacity and building date.

WWTP-Nr.	Location	Design capacity (PE*)	Connected PE	Date of building	Building change
WWTP-L1	Gnutz	1200	1140	1982	
WWTP-L2	Mörel Ost	260	224	1987	2001
WWTP-L3	Mörel West	70	34	1987	
WWTP-L4	Tappendorf	410	342	1991	
WWTP-L5	Grael	360	230	1987	2002
WWTP-L6	Poyenberg	400	409	1983	
WWTP-L7	Aukrug-Homfeld	300	365	1985	
WWTP-L8	Groß Kummerfeld	790	831	1983	
WWTP-L9	Kleinkummerfeld	360	394	1991	
WWTP-L10	Kleinkummerfeld Bhf	220	171	1992	
WWTP-L11	Gönnebek Nord	220	211	1984	
WWTP-L12	Negenharrie	690	314	2002	
WWTP-L13	Willingrade	600	524	1983	
WWTP-MB1	Heinkenborstel	200	126	1999	
WWTP-MB2	Petersberg	150	103	1992	
WWTP-MB3	Hollenbek	340	223	1979	
WWTP-MB4	Schipphorst	150	150	2003	
WWTP-MB5	Hüttenwohld	140	92	1984	
WWTP-NP1	Aukrug-Bünzen	7000	4000	1974	2003
WWTP-NP2	Neumünster	380000	110816	1963	2001
ns ⁽¹⁾	Bokhorst	550	473	1979	
ns	Gönnebek Süd	400	400	1984	
ns	Braak-Siedlung	175	107	1982	

*PE: population equivalent. ⁽¹⁾ Not sampled. Adapted from LLUR (2011).

4 MATERIAL AND METHODS

4.1 Measurement campaigns

Three different measurement campaigns were carried out for this study: monthly water quality campaign, daily water quality campaign and wastewater treatment plants campaign.

4.1.1 Monthly measurement campaigns

The monthly water samples were taken at the outlets of 21 subbasins of the upper river Stör (Fig. 4.1). The selection criteria were i) the available data from the earlier measurement campaigns (Ripl, et al., 1996), ii) the accessibility (bridge, road) and iii) the different types of land use. The current monthly sampling campaign was done on Wednesdays from August 2009 to July 2011 on mid-month. The water samples were taken with a sampling beaker (Fig. 4.2) and conditioned in plastic bottles in coolbox until processed in the laboratory.

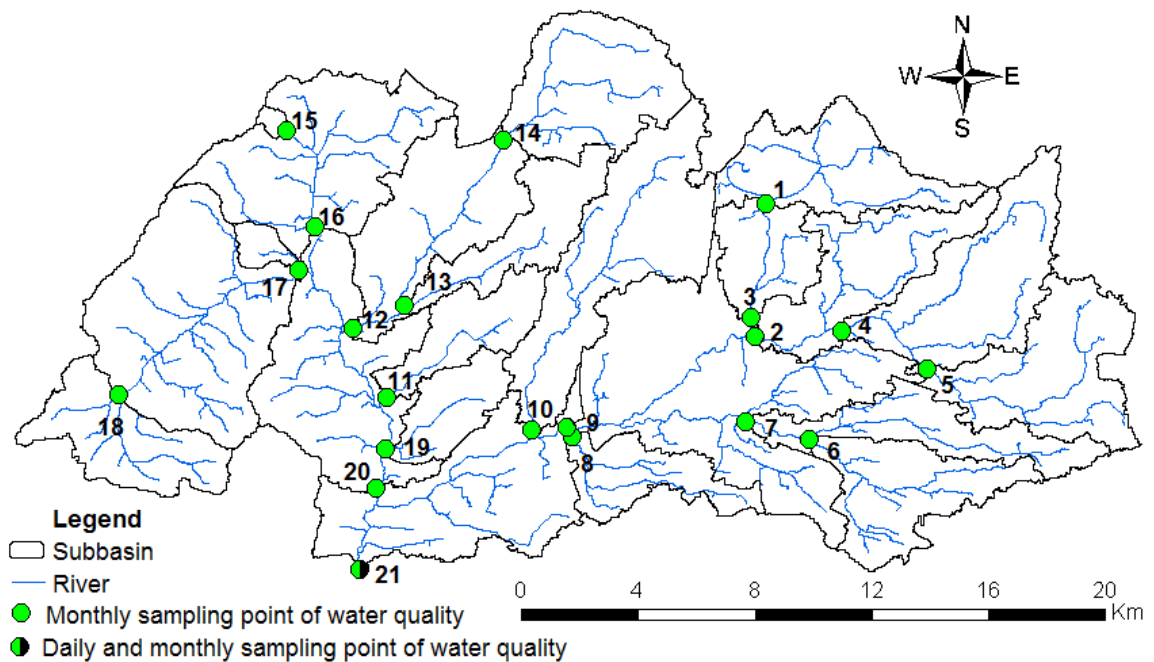


Fig. 4.1 Location of the monthly sampling points and the daily sampling point in the upper Stör catchment.



Fig. 4.2. Monthly manual water sampling.

4.1.2 Daily water quality monitoring

Daily mixed water samples were taken using an automatic water sampler MAXX SP III© at the gauge Willenscharen, the outlet of the upper Stör catchment (Fig. 4.3a). It is located at the site of the sampling point 21 (Fig. 4.1). The central computer was programmed to collect water samples at an interval of 72 min, making 20 subsamples per day (Fig. 4.3b). The water tube collector was installed into the river Stör at a distance of 2 m from the riverbank and at a depth of 0.30 m above the river bed, attached to a rock (Fig. 4.3c). The automatic water sampler had a storage capacity of up to 12 water bottles of 2.9 liters (Fig. 4.3d), the temperature in the sampler was kept constant between 3 and 5°C. The water samples were brought to the laboratory on Tuesdays and Fridays alternatively, resulting in a storage time of 10 to 11 days. Each daily mixed sample contained about 2 liters of water. On field sampling days, pH, dissolved oxygen (DO) and water temperature (WT) were determined in situ using a multiparameter water quality monitoring instrument (WTW Multiline©, Germany). The monitoring period lasted from August 8th 2009 until August 10th 2011.



Fig. 4.3 Automatic water sampler MAXX SP III© installed at the gauge Willenscharen (a), central computer and pump collector system (b), water tube collector installed into the river (c), view of the bottles into the automatic water sampler (d).

4.1.3 Wastewater treatment plant campaigns

The wastewater treatment plant (WWTP) campaigns were conducted in collaboration with Redeker (2011) and Honsel (2011). Redeker (2011) investigated 19 WWTPs during winter (December 2009, January and February 2010). Honsel (2011) analyzed 8 WWTPs in summer from June until August 2010. According to LLUR (2011), the WWTPs are ranked in three types: wastewater lagoons (WWTP-L), small WWTP with mechanical purification and biological activation (WWTP-MB), and WWTPs with tertiary treatment for further nitrogen and phosphorus elimination (WWTP-NP). The location of the WWTPs sampling points are shown in Fig. 4.4. At each WWTP, at least three sampling points were chosen: the first one in the river or ditch just upstream of the WWTP outlet, the second one directly from the effluent of the WWTP and the third one downstream of the outlet, where the effluent water appeared well mixed with the stream water (Honsel, 2011; Redeker, 2011).

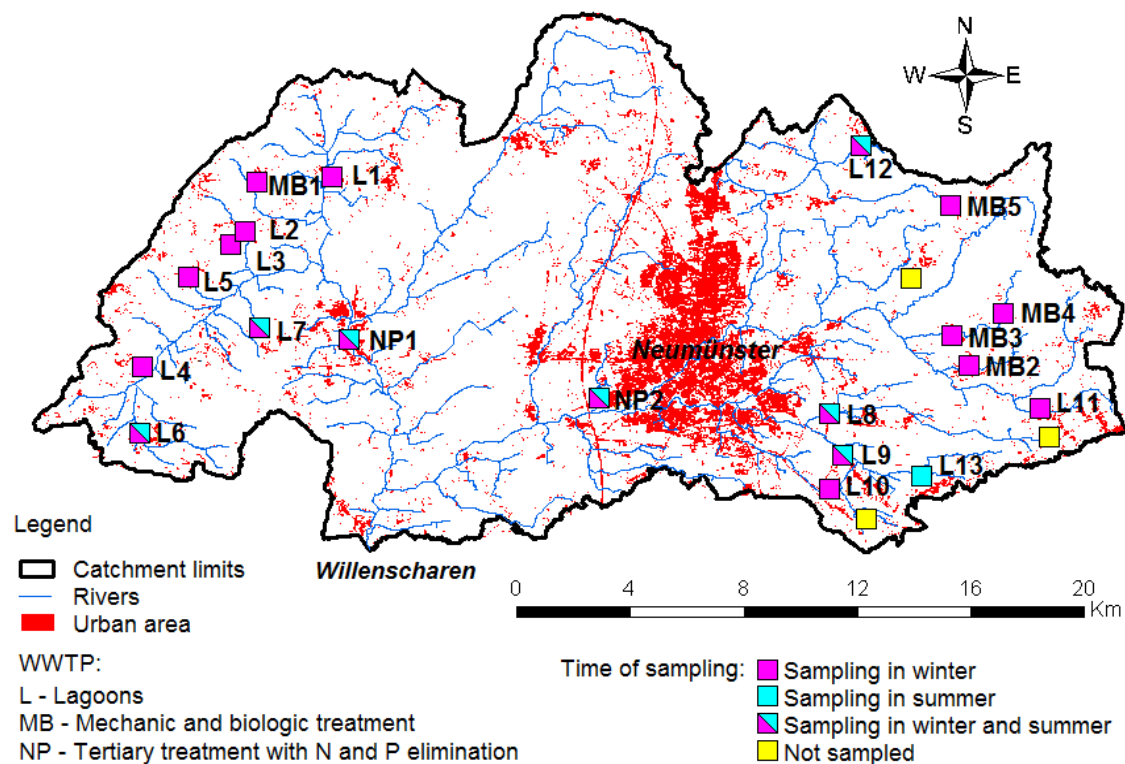


Fig. 4.4 Location of the WWTPs sampling points at the upper Stör catchment.

4.2 Water quality analyses

Water samples were prepared and analyzed in the laboratory of the Department of Hydrology

and Water Resources Management at Christian-Albrechts-University Kiel. Total phosphorus (TP), soluble orthophosphate-phosphorus ($\text{PO}_4\text{-P}$), total nitrogen (TN), nitrate-nitrogen ($\text{NO}_3\text{-N}$) and ammonium-nitrogen ($\text{NH}_4\text{-N}$) were analyzed. TP, $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ were determined by spectrophotometry, TN was determined by chemiluminescence detection using the DIMATEC-TOC-100©, and $\text{NO}_3\text{-N}$ was analyzed by ion chromatography. Particulate phosphorus (PP) represents the fraction adsorbed by soil particles and organic matter. It was calculated as the difference between TP and $\text{PO}_4\text{-P}$ (Sharpley and Halvorson, 1994). The ratio between dissolved inorganic N and dissolved P (DIN/DIP) helps to determine the limitation potential of these elements for phytoplankton growth (Jarvie et al., 1998; Nedwell et al., 2002; Lu et al., 2011). In this study, DIN represents the sum of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$, and DIP is the own value of $\text{PO}_4\text{-P}$. A relation of $\text{DIN/DIP} > 16$ represents P limitation, while $\text{DIN/DIP} < 16$ means limitation of N. Organic nitrogen (ON) was calculated as the difference between TN and DIN. Additionally, the total suspended sediment (TSS) concentration was determined by filtering 1.0 liter of water samples through $0.45 \mu\text{m}$ filter paper and drying at 105°C . In addition, pH, dissolved oxygen (DO) and water temperature (WT) were determined directly in situ using a multiparameter water quality monitoring instrument (WTW Multiline ©, Germany).

4.3 Assessment of water quality and statistical analysis

TP, $\text{PO}_4\text{-P}$, TN, $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ data set were used to determine the water quality according to the German LAWA (1998) classification, which consists of four classes and three subclasses. Table 4.1 shows the classes and the corresponding TP, $\text{PO}_4\text{-P}$, TN, $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ thresholds for the LAWA classification. The aim of WFD is to achieve a "good status", which corresponds to LAWA class II in all surface water bodies until the year of 2015 (EC, 2000). Other water classification also used in Germany is the RAKON (LAWA, 2007). In this study the LAWA (1998) classification was used because RAKON classification does not have a rating for nitrate $\text{NO}_3\text{-N}$. Also, RAKON ranges the water quality parameters with arithmetical average. As can be seen in the item 4.7 (Statistical analyses), the water quality data could not be normalized (Zar, 2010), but shown in its original form as box percentile plots, which permits show the 90 percentile, required by LAWA (1998) classification.

4.4 Water flow

In this study, daily discharge data set from 1991 until 2011 was used from three gauging stations (LKN, 2012). One is the Padenstedt gauging station where the discharge of the river Stör is measured at the Padenstedt village (Fig. 4.5a). Another gauge used in this study is the Sarlhusen gauging station located at the mouth of the Bünzener Au river at the Sarlhusen village (Fig. 4.5b). The third gauging station is located at the Willenscharen village (Fig. 4.5c) and represents the outlet of the study area.

Table 4.1 Water quality classes for surface water bodies according to German LAWA (1998) classification and their thresholds for TP, PO₄-P, TN, NO₃-N and NH₄-N.

Classes	Description	TP	PO ₄ -P	TN	NO ₃ -N	NH ₄ -N
----- mg/l -----						
I	unpolluted	≤ 0.05	≤ 0.02	≤ 1.0	≤ 1.0	≤ 0.04
I-II	lightly polluted	≤ 0.08	≤ 0.04	≤ 1.5	≤ 1.5	≤ 0.10
II	moderately polluted	≤ 0.15	≤ 0.10	≤ 3.0	≤ 2.5	≤ 0.30
II-III	critically polluted	≤ 0.30	≤ 0.20	≤ 6.0	≤ 5.0	≤ 0.60
III	heavily contaminated	≤ 0.60	≤ 0.40	≤ 12.0	≤ 10.0	≤ 1.20
III-IV	very heavily contaminated	≤ 1.20	≤ 0.80	≤ 24.0	≤ 20.0	≤ 2.40
IV	excessively contaminated	> 1.20	> 0.80	> 24.0	> 20.0	> 2.40

4.5 Historical database comparison

Aiming to assess the long-term evolution of water quality, the current monthly campaign was compared with the database of Ripl et al. (1996), who sampled 128 water sampling points in monthly time steps in the upper Stör catchment between 1991 and 1995. The current monthly campaign of measurement consisted of the same 21 sampling points where Ripl et al. (1996) had sampled in the first study. The historical database consisted of 35 to 44 monthly water samples from March 1991 until March 1995 (Ripl et al. 1996). Samples were taken in a monthly time step from February 1992 until October 1994. In 1991 and 1995, Ripl et al. (1996) used a bimonthly water sampling interval.

The following water quality parameters from Ripl et al. (1996) were used to compare the evolution of water quality with the current data: TP, TN, NO₃-N and NH₄-N. PO₄-P

concentration during the monthly campaign by Ripl et al. (1996) had not been measured.

The land use map from Ripl et al. (1996) was obtained from a Landsat 5 TM scene from August 7th 1987. The spatial resolution was 30 x 30 m. The differentiation of agricultural land was made between arable and grassland, fields without crop cover were assumed to be already harvested, plowed land or crops in the stage of yellow ripeness. The reported bogs were added interactively by a constant comparison with the topographic map (Ripl et al., 1996).



Fig. 4.5 View of location of the gauges Padenstedt (a), Sarlhusen (b) and Willenscharen (c).

4.6 Calculation of N and P loads

Monthly nutrient loads were calculated using the measured concentration of the nutrient data from the monthly campaign, which was multiplied by the mean monthly discharge data obtained by the gauging stations of LKN (2012). Daily load was calculated with the daily water quality data collected with the automatic water sampler installed at Willenscharen and the respective daily discharge of this gauge station (LKN, 2012).

Nutrient loads of the WWTPs were calculated with data of the water quality obtained from the measured campaign from Redeker (2011) and Honsel (2011). Monthly discharge data of the WWTPs were obtained by TBZ (2012) and LLUR (2011).

4.7 Statistical analyses

Statistical calculations were done with the R program (<http://www.r-project.org>). Box-percentile-plots were calculated to represent the 90th percentile, which is used to determine the LAWA (1998) class limits. T-test was used for the means comparison because the water quality data could not be normalized (Zar, 2010). Correlogram was used to represent the Pearson correlation among the water quality parameters. Autocorrelation (AC) plots were calculated with the function “acf” in R program. It was used to determine the correlation of each water quality parameter with itself through out a daily time series (Box et al., 2008). According to Alewell et al. (2004), high AC indicates a stable and foreseeable parameter. Land use maps from Rippl et al. (1996) and from Oppelt et al. (2011) were used for the correlation with N and P data set from 1991-1995 and 2009-2011 periods, respectively. All time series data was aggregated to values based on the hydrological year with winter from November 1st until April 30th and summer from May 1st until October 31st. Hierarchical cluster analysis using the average method was also performed to further explain the similarities of P fractioning from the sampling points.

4.8 SWAT modeling

4.8.1 SWAT model description

In this study, the software ArcSWAT2009 (version 2009.93.7b Revision Nr. 488) was used to simulate water discharge, sediment and N and P nutrients. It is a SWAT interface for ESRI ArcGIS 9.3.1 SP2 (<http://swat.tamu.edu>). The SWAT model is a continuous model for long-term observations, which run on daily, monthly or annual time steps (Neitsch et al., 2011). In this study, water discharge was simulated in daily time steps. Sediment, NO₃-N and TP load were simulated in daily and monthly time steps.

The model represents the large-scale spatial heterogeneity of the study area by dividing the watershed into subbasins. The subbasins are then further subdivided into hydrologic response units (HRUs) based on homogeneous soils, land use and slopes (Neitsch et al., 2010). The major components of the SWAT model include weather, hydrology, soil, topography, plant growth, nutrients, pesticides, bacteria and land management (Neitsch et al., 2010). The details of all components can be found by Arnold et al. (1998) and Neitsch et al. (2010, 2011).

The hydrologic cycle in the SWAT (Arnold et al., 1998) is based on the water balance equation (Equation 1):

$$SW_t = SW_0 + \sum_{i=1}^t (R_{day} - Q_{surf} - E_a - W_{seep} - Q_{gw}) \quad (1)$$

where: SW_t is the final soil water content (mm H₂O); SW_0 is the initial soil water content on day i (mm H₂O); t is the time (days); R_{day} is the amount of precipitation on day i (mm H₂O); E_a is the amount of evapotranspiration on day i (mm H₂O); W_{seep} is the amount of water entering the vadose zone from the soil profile on day i (mm H₂O); Q_{gw} is the amount of return flow on day i (mm H₂O).

Soil water processes include evaporation, surface runoff, infiltration, plant uptake, lateral flow and percolation to lower layers (Arnold et al., 1998; Neitsch et al., 2011). The surface runoff from daily precipitation is estimated with a modification of the SCS (1972) curve number method from the United States Department of Agriculture Soil Conservation (USDA SCS) (Neitsch et al., 2011).

The different N processes modeled by SWAT in various pools of N in the soil are shown in Fig. 4.6. Plant use of N is estimated using the supply and demand approach described by Neitsch et al. (2011) and represented in the cycle of N of the SWAT model (Fig. 4.7). In addition, $\text{NO}_3\text{-N}$ and organic N may be removed from the soil via mass flow of water. Amounts of $\text{NO}_3\text{-N}$ contained in runoff, lateral flow and percolation are estimated as products of the volume of water and the average concentration of $\text{NO}_3\text{-N}$ in the layer. The loading function estimated the daily organic N runoff loss based on the concentration of organic N in the top soil layer, the sediment yield and the enrichment ratio. The enrichment ratio is the concentration of organic N in the sediment divided by that which is in the soil (Neitsch et al., 2011).

The P cycle used in SWAT is shown in Fig. 4.8 and the different processes modeled by SWAT in different pools of P in the soil are depicted in Fig. 4.9. Soluble P and organic P may be removed from the soil via mass flow of water. The amount of soluble P removed in runoff is predicted using a solution of P concentration in the top 10 mm of soil, runoff volume and a partitioning factor. Sediment transport of P is simulated with a loading function as described in organic N transport (Neitsch et al., 2011).

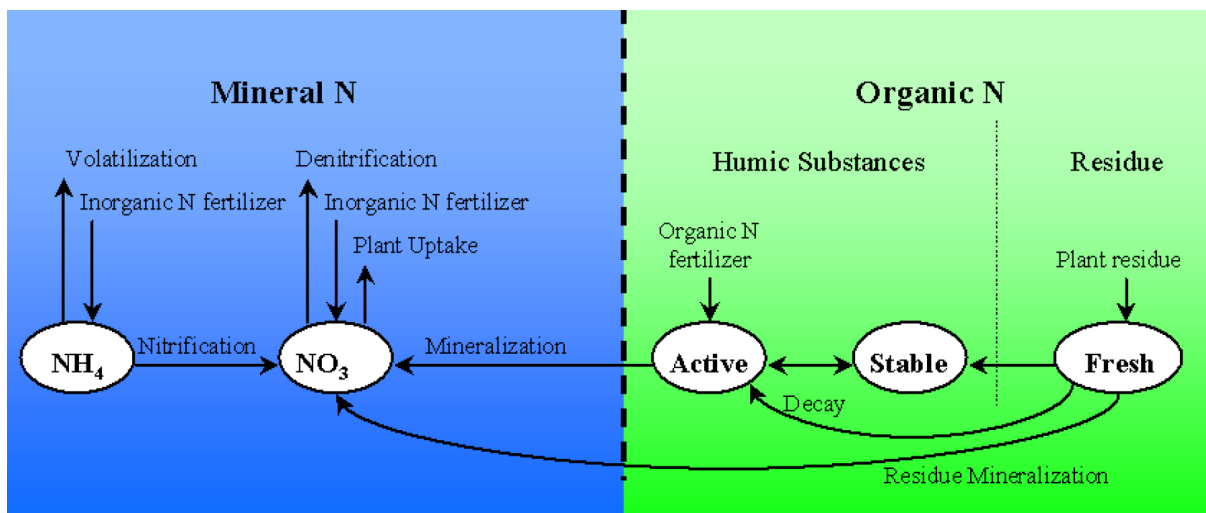


Fig. 4.6 Partitioning of N in SWAT model (Neitsch et al., 2011).

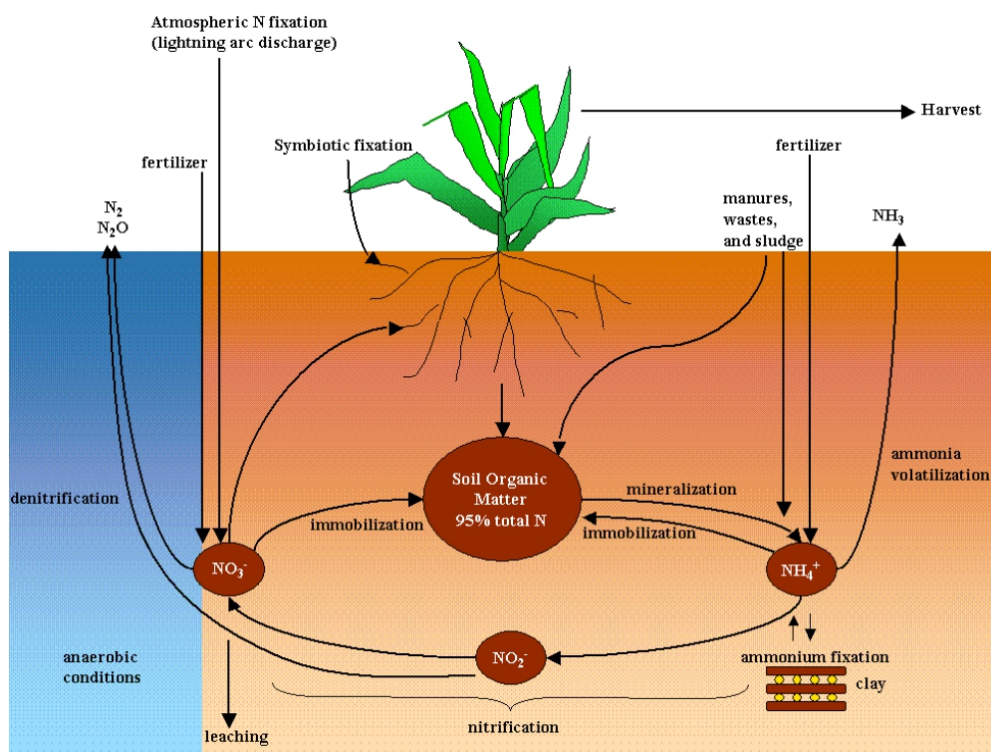


Fig. 4.7 The nitrogen cycle (Neitsch et al., 2011).

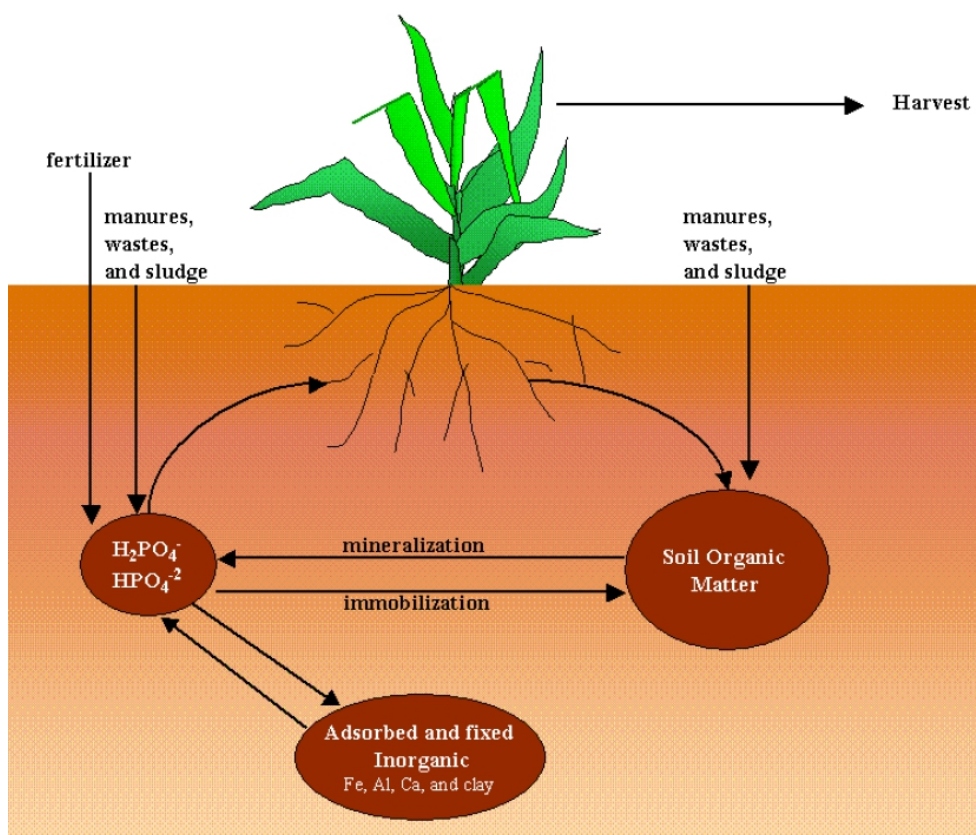


Fig. 4.8 The phosphorus cycle (Neitsch et al., 2011).

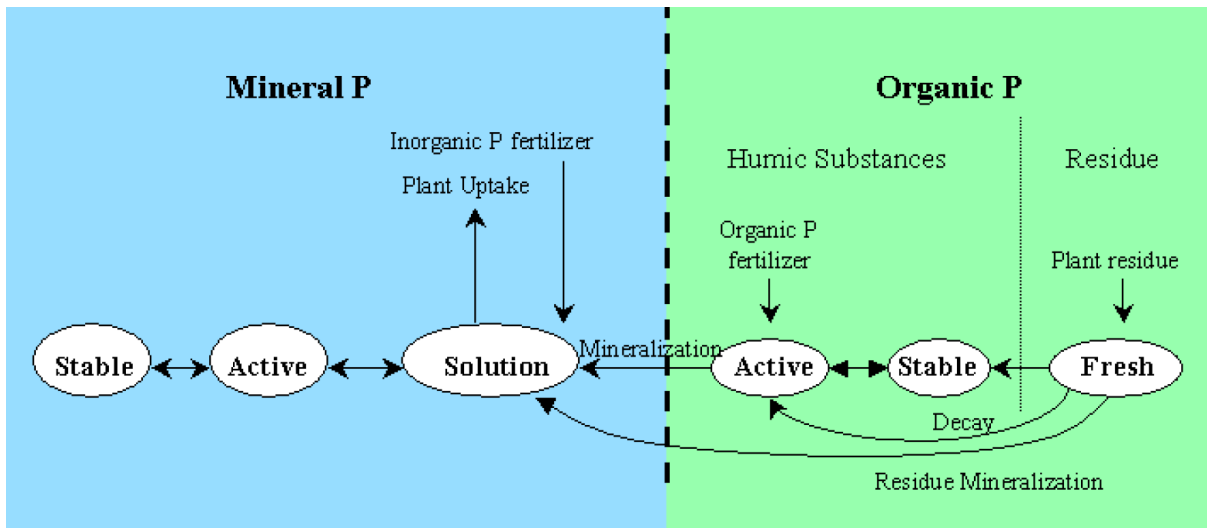


Fig. 4.9 Partitioning of P in SWAT model (Neitsch et al., 2011).

4.8.2 Performance of the model

The reliability of results from a model is based on performance of the calibration and validation. Calibration is the process of estimating model parameters by comparing model predictions (output) for a given set of assumed conditions with observed data for the same conditions. Validation involves running a model in a study period different of the calibration and using input parameters measured or determined during the calibration process (Moriasi et al., 2007). A good performance of nutrient modeling is dependent of the water cycle balance and sediment load simulation. According to Neitsch et al. (2011), the calibration should be conducted preferably in the sequence: discharge, sediment and nutrient load.

To evaluate the performance of a model, measured and simulated values need to be compared. Two methods were applied in parallel to calibrate the SWAT model. Firstly, the measured and simulated values were subjected to a graphical comparison, in addition, the adjustment by statistical analyzes was assessed.

The most important statistical index parameters used in this study to evaluate the performance of the SWAT model were:

Coefficient of determination (R^2) describes the degree of collinearity between simulated and measured data. R^2 ranges from 0 to 1, with higher values indicating less error variance. Equation 2 describes R^2 .

Nash-Sutcliffe efficiency (NSE) is a normalized statistic that determines the relative magnitude of the residual variance compared to the measured data variance (Nash and Sutcliffe, 1970). NSE is calculated as shown in Equation 3.

Percent bias (PBIAS) measures the average tendency of the simulated data to be larger or smaller than their observed counterparts (Gupta et al., 1999). Zero is the optimal value for PBIAS. Positive values indicate model underestimation bias, and negative values indicate model overestimation bias. PBIAS is calculated with Equation 4.

Root mean square error (RMSE) is an index statistic. However Singh et al. (2004) developed the RMSE standard deviation observations (STDEV) ratio named RSR. RSR standardizes RMSE using the standard deviation observations and it combines both an error index. RSR is calculated as the ratio of the RMSE and STDEV of measured data, as shown in Equation 5.

$$R^2 = \left[\frac{\sum_{i=1}^n (Y_i^{obs} - \bar{Y}^{obs})(Y_i^{sim} - \bar{Y}^{sim})}{\sqrt{\sum_{i=1}^n (Y_i^{obs} - \bar{Y}^{obs})^2} \sqrt{\sum_{i=1}^n (Y_i^{sim} - \bar{Y}^{sim})^2}} \right]^2 \quad (2)$$

$$NSE = 1 - \left[\frac{\sum_{i=1}^n (Y_i^{obs} - Y_i^{sim})^2}{\sum_{i=1}^n (Y_i^{obs} - \bar{Y}^{obs})^2} \right] \quad (3)$$

$$PBIAS = \left[\frac{\sum_{i=1}^n (Y_i^{obs} - Y_i^{sim}) \times 100}{\sum_{i=1}^n (Y_i^{obs})} \right] \quad (4)$$

$$RSR = \frac{RMSE}{STDEV_{obs}} = \frac{\sqrt{\sum_{i=1}^n (Y_i^{obs} - Y_i^{sim})^2}}{\sqrt{\sum_{i=1}^n (Y_i^{obs} - \bar{Y}^{obs})^2}} \quad (5)$$

where: Y^{obs} is the measured value; Y^{sim} is the simulated value; \bar{Y} is the arithmetical mean; n is the number of values.

Table 4.2 shows the statistical index parameters ranked according to Moriasi et al. (2007) to determine the quality performance of the simulations.

Table 4.2 General performance rating for recommended statistics for a monthly time steps (Adapted from Moriasi et al., 2007).

Performance rating	RSR	NSE	PBIAS (%)		
			Stremflow	Sediment	Nutrients (N and P)
Very good	$0 \leq \text{RSR} \leq 0.5$	$0.75 < \text{NSE} \leq 1.0$	$\text{PBIAS} < \pm 10$	$\text{PBIAS} < \pm 15$	$\text{PBIAS} < \pm 25$
Good	$0.5 < \text{RSR} \leq 0.6$	$0.65 < \text{NSE} \leq 0.75$	$\pm 10 \leq \text{PBIAS} < \pm 15$	$\pm 15 \leq \text{PBIAS} < \pm 30$	$\pm 25 \leq \text{PBIAS} < \pm 40$
Satisfactory	$0.6 < \text{RSR} \leq 0.7$	$0.50 < \text{NSE} \leq 0.65$	$\pm 15 \leq \text{PBIAS} < \pm 25$	$\pm 30 \leq \text{PBIAS} < \pm 55$	$\pm 40 \leq \text{PBIAS} < \pm 70$
Unsatisfactory	$\text{RSR} > 0.7$	$\text{NSE} \leq 0.50$	$\text{PBIAS} \geq \pm 25$	$\text{PBIAS} \geq \pm 55$	$\text{PBIAS} \geq \pm 70$

4.8.3 Input data

The basic data sets required to set up the model inputs are: topography, soil, land use and climatic data set (Arnold et al., 1998; Neitsch et al., 2011). The input data are described in Table 4.3. In this study, the SWAT model was subdivided in 21 subbasins and 1402 HRUs. The outlet of the subbasin was the same as the one where the water quality samples were collected.

The inclusion of drainage parameters in SWAT was based on information from Venohr (2000), who estimated the drained areas in the river Stör basin, of those with groundwater at a depth below 1.5 m. Thus, drainage systems were included in the area of soils Histosol, Gley, Gleyposol, Planosol and Luvisol in the areas of agriculture, pasture and forest on slopes of 0 to 2%. The drainage parameters used in this study are listed in Table 4.9.

The soil data was used from Finnern (1997) and from AG Boden (2005). The classification of the hydrologic soil group (HYDGRP) was ranked as suggested by Neitsch et al. (2010, 2011). Table 4.4 summarizes the main soil parameters used in the SWAT model.

For the simulation of nutrient balance, the information on management options and fertilizer applications are essential (Lenhart et al., 2003). The management schedules for the crop rotation and fertilizer application for the calibration and validation period were created with

information from Kühling (2011), KTBL (2008) and LWK (2011). The main information for crop rotation and fertilizer application is shown in Table 4.5. In this study, the organic manure parametrization in the SWAT model was set to 0.4 and 0.2% of N and P₂O₅, respectively.

The data of the WWTP campaigns (Honsel, 2011; Redeker, 2011) was implemented in the SWAT model to simulate the point pollution in the upper Stör catchment. Table 4.6 and Table 4.7 show the mean discharge and nutrient values from the different WWTPs used in the SWAT model, respectively.

Table 4.3 Model input data sources for the upper Stör catchment.

Data type	Data description	Source
Topography map	Digital elevation model (DEM), a grid size of 5 m x 5 m	LVerma (2008)
Soil map	Soil map and soil physic properties	Finnern (1997)
Land use maps	Land use classification, resolution 30 m x 30 m	Ripl et al. (1996), based on Landsat 5 TM data from 1987. Oppelt et al. (2011), based on Landsat TM data from 2010.
Climate data	Daily data from temperature, precipitation, wind speed, humidity (1975 - 2012)	DWD (2012)
Wastewater	Water quality data set of WWTPs Discharge of WWTPs	Redeker (2011); Honsel (2011) TBZ (2010, 2012)

Table 4.4 Soil parameters used in the SWAT model in the upper Stör catchment.

Soil	HYDGRP ⁽¹⁾	ANION_EXCL	SOL_Z	SOL_BD	SOL_AWC	SOL_K	SOL_CBN	USLE_K
Cambisol	B	0.47	261	1.30	0.084	42.9	2.33	0.0624
			753	1.37	0.075	44.4	1.30	0.0731
			1360	1.30	0.070	41.8	0.33	0.1616
			2000	1.30	0.075	41.0	0.10	0.1000
Gley	B	0.44	314	1.50	0.279	32.7	2.25	0.1311
			941	1.50	0.270	36.2	3.00	0.1302
			2092	1.60	0.27	35.0	2.00	0.1244
Gley- Podsol	B	0.43	314	1.30	0.158	119	5.3	0.1218
			523	1.30	0.130	122	4.7	0.1218
			1307	1.30	0.075	128	0.75	0.1500
			2000	1.30	0.080	110	0.05	0.1567
Histosol	A	0.55	209	1.10	0.56	24.5	10	0.1525
			837	1.10	0.372	33.8	10	0.1525
			2092	1.30	0.120	146	2	0.1240
Luvisol	B	0.43	418	1.50	0.177	23.4	1.16	0.1384
			1255	1.70	0.158	11.7	0.58	0.1640
			2092	1.70	0.140	14.0	0.05	0.1675
Planosol	B	0.40	366	1.30	0.200	35.0	2.57	0.1354
			837	1.56	0.158	23.2	1.04	0.1613
			1255	1.50	0.140	23.2	0.71	0.1667
			2000	1.50	0.150	20.0	0.10	0.1729
Podsol	A	0.41	314	1.35	0.167	140	1.85	0.0654
			523	1.32	0.140	142	0.96	0.0833
			1167	1.33	0.13	128	0.46	0.0801
			2000	1.30	0.14	105	0.29	0.0821

¹⁾ HYDGRP: Soil hydrologic group; ANION_EXCL: Fraction of porosity from which anions are excluded; SOL_Z: Depth from soil surface to bottom of layer (mm); SOL_BD: Moist bulk density (g/cm³); SOL_AWC: Available water capacity of the soil layer; SOL_K: Saturated hydraulic conductivity (mm/h); SOL_CBN: Organic carbon content (% soil weight); USLE_K: USLE equation soil erodibility factor.

Table 4.5 Crop and fertilizer information used for the calibration and validation period with the SWAT model in the upper Stör catchment.

Crop	Date	Operation	Quantity (kg/ha)*	
			Mineral soils ^[1]	Organic soils ^[2]
Silage corn	March 1 st - 10 th	Manure application	25000	15000
	April 5 th	P ₂ O ₅ application	50	50
	April 10 th	Tillage operation		
	April 20 th	Time of planting		
	April 20 th - 29 th	N application	30	20
	May 20 th - 29 th	N application	90	80
	September 20 th	Harvest		
	November 1 st - 10 th	Manure application	25000	15000
Winter rape	August 10 th	P ₂ O ₅ application	50	
	August 20 th	Time of planting		
	October 10 th - 19 th	Manure application	20000	
	March 1 st - 10 th	N application	80	
	April 10 th - 19 th	N application	70	
	August 1 st	Harvest		
Winter wheat	September 10 th	P ₂ O ₅ application	75	50
	September 20 th	Tillage operation		
	October 1 st	Time of planting		
	October 1 st - 10 th	N application	20	0
	February 25 th - March 6 th	N application	60	60
	April 14 th - 19 th	N application	60	60
	June 10 th - 19 th	N application	60	50
	August 1 st	Harvest		
Pasture	February 20 th - March 1 st	Manure application	20000	15000
	March 1 st	Time of planting		
	March 10 th - 19 th	N application	60	50
	June 15 th	Harvest		
	June 15 th - 24 th	N application	60	50
	November 1 st - 10 th	Manure application	20000	15000
	December 1 st	Harvest		

^[1] Mineral soils for this study: Gley, Gley-Podsol, Cambisol, Podsol, Planosol and Luvisol

^[2] Organic soil for this study: Histosol.

* Values based on Kühling (2011), KTBL (2008) and LWK (2011).

Table 4.6 Mean values of discharge of the WWTPs used in the SWAT model.

WWTP-Nr.	Q [m ³ /s]*
WWTP-L1	233.7
WWTP-L2	45.9
WWTP-L3	7.0
WWTP-L4	70.1
WWTP-L5	47.2
WWTP-L6	83.8
WWTP-L7	74.8
WWTP-L8	170.4
WWTP-L9	80.8
WWTP-L10	35.1
WWTP-L11	43.3
WWTP-L12	64.4
WWTP-L13	107.4
WWTP-MB1	25.8
WWTP-MB2	21.1
WWTP-MB3	45.7
WWTP-MB4	30.8
WWTP-MB5	18.9
WWTP-NP1	820
WWTP-NP2	22706

*Values calculated with base on the discharge of the WWTP-NP2 (TBZ, 2012) and the equivalent population of each WWTP (LLUR, 2011).

Table 4.7 Mean values of NO₃-N, NH₄-N, TN, PO₄-P and TP concentrations of the WWTPs used to characterize the point pollution in the SWAT model.

WWTP type	NO ₃ -N [mg/l]		NH ₄ -N [mg/l]		TN [mg/l]		PO ₄ -P [mg/l]		TP [mg/l]	
	Winter ⁽¹⁾	Summer ⁽²⁾	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
Actual period of 2009 - 2011										
WWTP-L ⁽³⁾	0.72	0.20	12.70	11.00	4.70	0.0	2.48	1.50	3.13	2.18
WWTP-MB ⁽³⁾	12.9	12.9	12.7	12.7	19.1	19.1	6.36	6.36	7.34	7.34
WWTP-NP1 ⁽³⁾	0.44	0.35	0.08	1.07	1.05	0.12	0.96	0.96	1.14	1.14
WWTP-NP2 ⁽³⁾	5.91	2.40	1.10	0.82	4.70	0.94	0.03	0.03	0.10	0.08
Historical period of 1991 - 1995										
WWTP-L ⁽³⁾	0.72	0.20	12.70	11.00	4.70	0.0	2.48	1.50	3.13	2.18
WWTP-MB ⁽³⁾	12.9	12.9	12.7	12.7	19.1	19.1	6.36	6.36	7.34	7.34
WWTP-NP1 ⁽³⁾	0.44	0.35	0.08	1.07	1.05	0.12	0.96	0.96	1.14	1.14
WWTP-NP2 ⁽⁴⁾	20.4	18.9	1.10	0.82	26.2	20.7	-	-	0.54	0.35

¹⁾ Winter corresponding from November 1st until April 30th.

²⁾ Summer corresponding from May 1st until October 31st.

³⁾ Adapted from Honsel (2011) and Redeker (2011).

⁴⁾ Adapted from TBZ (2010).

4.8.4 Model calibration and validation

According to Neitsch et al. (2011), the calibration should be conducted in the respective order: discharge, sediment and nutrients load. The standard procedure for the simulation is to use a period of time for the calibration and a subsequent time for validation. For this study, the validation in an antecedent time was used, as shown in Table 4.8. This division was carried out aiming to fit the actual land use map dated from July 2010 (Oppelt et al., 2011) for the calibration period. Furthermore, it is important that the water balance (calibrated by the discharge) has a long time simulation (Burt et al., 2010). For all simulations, a period of five years warm up of the model was used, aiming to stabilize the main water and nutrient processes that occur in the SWAT model.

Table 4.8 Calibration and Validation bank set used for discharge, sediment and nutrient load.

Bank data	Calibration	Validation
Discharge	January 1 st 2006 - December 31 st 2011	January 1 st 2001 - December 31 st 2005
Sediment	August 8 th 2010 - August 7 th 2011	November 1 st 2009 - August 7 th 2010
Phosphorus	August 8 th 2010 - August 7 th 2011	August 8 th 2009 - August 7 th 2010
Nitrogen	August 8 th 2010 - August 7 th 2011	August 8 th 2009 - August 7 th 2010

The daily discharge calibration was done with the assistance of the software SWAT-CUP (Abbaspour, 2011) which is able to calibrate multiple parameters simultaneously. The SWAT-CUP works with different methods of calibrations and uncertainty analysis procedures: Generalized Likelihood Uncertainty Estimation (GLUE), Parameter Solution (ParaSol), Sequential Uncertainty Fitting algorithm (SUFI-2), and a Bayesian framework implemented using Markov chain Monte Carlo (MCMC) and Importance Sampling (IS) techniques. In this study, the discharge calibration was carried out using the method SUFI-2 for data set of discharge from the gauges Padenstedt (PAD), Sarlhusen (SAR) and Willenscharen (WIL), simultaneously. Therefore, some parameters have different values depending on the location of the subbasins, whether belonging to the subbasins of the gauges PAD, SAR or WIL (Table 4.9). The measured discharge data set from the three gauge stations (PAD, SAR and WIL) was provided by LKN (2012).

Table 4.9 Main variables used for discharge calibration using SWAT-CUP method SUFI-2.

SWAT Input file	Variable name	Description	Allowable range	Value used
BSN ⁽¹⁾	SURLAG	Surface runoff lag coefficient	0 - 24	1
	SMTMP	Snow melt base temperature (°C)	-5 - 5	0.01
	SFTMP	Snowfall temperature (°C)	-5 - 5	2
	SMFMX	Melt factor for snow on June 21	0 - 10	9.8
	SMFMN	Melt factor for snow on December 21	0 - 10	3.1
	TIMP	Snow pack temperature lag factor	0.01 - 1	0.1
GW	GW_DELAY	Groundwater delay time (days)	0 - 500	114 [PAD] ⁽³⁾ 68 [SAR] 80 [WIL]
	ALPHA_BF	Base flow alpha factor	0 - 1	0.07 [PAD] 0.13 [SAR] 0.06 [WIL]
	GWQMN	Threshold depth of water in the shallow aquifer required to occur the return flow (mm)	0 - 5000	232 [PAD] 242 [SAR] 260 [WIL]
	GW_REVAP	Groundwater REVAP coefficient	0.02 - 0.2	0.07 [PAD] 0.04 [SAR] 0.05 [WIL]
	REVAPMN	Threshold depth of water in the shallow aquifer for REVAP or percolation to the deep aquifer to occur (mm)	0 - 500	254 [PAD] 270 [SAR] 185 [WIL]
	RCHRG_DP	Deep aquifer percolation fraction	0 - 1	0.08 [PAD] 0.05 [SAR] 0.07 [WIL]
	RTE	CH_N2	Manning's "n" value for the main channel	0 - 0.3
CH_K2		Effective hydraulic conductivity in main channel alluvium (mm/h)	0 - 150	20 [PAD] 4 [SAR] 12 [WIL]
HRU	Dep-Imp ⁽²⁾	Depth to impervious layer in soil profile (mm)	0 - 5000	1500
	ESCO	Soil evaporation compensation factor	0.01 - 1	0.03 [PAD] 0.03 [SAR] 0.16 [WIL]
	EPCO	Plant uptake compensation factor	0.01 - 1	0.89 [PAD] 0.18 [SAR] 0.37 [WIL]
MGT	DDRAIN	Depth to subsurface drain (mm)	0 - 2000	900
	TDRAIN	Time to drain soil to field capacity (h)	0 - 72	36
	GDRAIN	Drain tile lag time (h)	0 - 100	72
	CN2	Initial SCS runoff curve number for moisture condition II	35 - 98	62.2 [agriculture] 40.3 [pasture] 39.7 [wetland] 38.5 [forest]

¹⁾ BSN: Basin; GW: Groundwater; RTE: Main channel; HRU: hydrologic response units; MGT: Management. ²⁾ The Dep-Imp parameter was used in the same areas that was drained. ³⁾ PAD: Padenstedt; SAR: Sarlhusen; WIL: Willenscharen.

Daily and monthly calibration was carried out for the data set of sediment. Table 4.10 shows the sensitive parameters used for the calibration of the sediment load. The calibration was done only at the gauge station Willenscharen because TSS was analyzed only with water samples collected with the automatic water sampler MAXX SP III© in this gauge station. The SWAT-CUP method SUFI-2 was also used to calibrate the sediment data set from Willenscharen.

For the TP and NO₃-N calibration, SWAT-CUP method SUFI-2 associated to manual calibration was carried out using daily and monthly time steps. The main parameters which were sensitive for N and P simulation with SWAT are represented in Table 4.11. In addition, for the BSN input data it was used the option Algae/CBOP/Dissolved oxygen as inactive.

Table 4.10 Main variables used for sediment load calibration at the gauge station Willenscharen in the SWAT model.

SWAT Input file	Variable name	Description	Allowable range	Value used
BSN ⁽¹⁾	PRF	Peak rate adjustment factor for sediment routing in the main channel	0 - 2	0.35
	ADJ_PKR	Peak rate adjustment factor for sediment routing in the subbasin	0.5 - 2	1.83
	SPEXP	Exponent parameter for calculating sediment reentrained in the channel sediment routing	1 - 2	1.09
	SPCON	Linear parameter for calculating the maximum amount of sediment that can be reentrained during channel sediment routing	0.0001 - 0.01	0.00089
RTE	CH_COV_1	Channel erodibility factor	0 - 1	0.15
	CH_COV_2	Channel cover factor	0 - 1	0.50
MGT	USLE_P	USLE equation support practice factor	0 - 1	0.9

¹⁾ BSN: Basin; RTE: Main channel; MGT: Management.

Table 4.11 Main variables used for NO₃-N and TP load calibration with the SWAT model.

SWAT Input file	Variable name	Description	Allowable range	Value used
BSN ⁽¹⁾	RCN	Concentration of nitrogen in rainfall	0 - 15	2.3
	CMN	Rate factor for humus mineralization of active organic nutrients (N and P)	0.001-0.003	0.002
	CDN	Denitrification exponential rate coefficient	0 - 3	0.0137
	SDNCO	Denitrification threshold of water content	0 - 1	0.85
	N_UPDIS	Nitrogen uptake distribution parameter	0 - 100	95
	P_UPDIS	Phosphorus uptake distribution parameter	0 - 100	100
	NPERCO	Nitrate percolation coefficient	0.01 - 1	0.68
	PPERCO	Phosphorus percolation coefficient	10 - 17.5	17.5
	PHOSKD	Phosphorus soil partitioning coefficient	100 - 200	100
	PSP	Phosphorus availability index	0.01 - 0.7	0.4
HRU	ERORGP	Phosphorus enrichment ratio for loading with sediment	0 - 5	1
SOL	ANION_EXCL	Fraction of porosity from which anions are excluded	0.1 - 1	0.43 [GLPO, LUVI ⁽²⁾] 0.40 [PLAN] 0.41[PODS] 0.50 [CAMB, GLEY, HIST]
GW	H LIFE_NGW	Half-life of nitrate in the shallow aquifer (days)	0 - 200	1 [PAD] 16 [SAR] 7 [WIL]
	GWSOLP	Concentration of soluble phosphorus in groundwater contribution to stream flow from the subbasin		0.1 [GLPO, LUVI, PLAN, PODS, CAMB, GLEY] 0.5 [HIST]

¹⁾ BSN: Basin; HRU: hydrologic response units; SOL: Soil; GW: Groundwater.

²⁾ GLPO: Gley-Podsol; LUVI: Luvisol; PLAN: Planosol; PODS: Podsol; CAMB: Cambisol; GLEY: Gley soil, HIST: Histosol.

4.8.5 *Simulation of the historical scenario*

The daily discharge simulation of the historical scenario was considered for the period from January 1st 1991 until December 31st 1999, i.e. nine years. The historical scenario corresponds to the decade of 1990, when Ripl et al. (1996) assessed the water quality at the upper Stör catchment during 1991-1995. For the NO₃-N and TP load, monthly time steps from February 1992 until October 1994 were simulated. The variables used for calibration and validation of discharge (Table 4.9), sediment (Table 4.10) and nutrient (Table 4.11) were also used to simulate the historical scenario. Only the land use map (Ripl et al., 1996) and the management operations were modified for the historical scenario, aiming to describe the characteristics of crop rotation, management operations and fertilization of the 1990s. A 30 x 30m resolution map from July 1987 (Ripl et al., 1996) was used to characterize the land use distribution for the historical scenario. The historical land use map (Fig. 3.4, Ripl et al., 1996) contemplated only one class for agriculture use. In order to represent the various crops in the agriculture area, statistical data from Statistical Office Schleswig-Holstein (1992-2013) was used. In this way, the agricultural area from the historical scenario was characterized by 12% silage corn, 29% rapeseed and 59% wheat, randomly distributed in different HRUs with agriculture.

The management schedules for crop rotation and fertilizer application for the historical scenario were performed according to information of KTBL (1995) and LWK (1991, 1998). Table 4.12 shows the crop and fertilizer information used for simulation of the historical scenario.

Table 4.12 Crop and fertilizer information used for the historical scenario with the SWAT model in the upper Stör catchment.

Crop	Date	Operation	Quantity (kg/ha)*	
			Mineral soils ^[1]	Organic soils ^[2]
Silage corn	March 1 st - 10 th	Manure application	25000	25000
	April 5 th	P ₂ O ₅ application	50	50
	April 10 th	Tillage operation		
	April 20 th	Time of planting		
	April 20 th - 29 th	N application	30	20
	May 10 th - June 20 th	N application	90	80
	September 20 th	Harvest		
	December 1 st - 10 th	Manure application	25000	25000
Winter rape	August 10 th	P ₂ O ₅ application	50	
	August 20 th	Time of planting		
	September 20 th - 29 th	N application	60	50
	December 11 th - 19 th	Manure application	20000	20000
	March 4 th - 27 th	N application	50	40
	April 6 th - 24 th	N application	40	30
	August 1 st	Harvest		
Winter wheat	September 10 th	P ₂ O ₅ application	75	50
	September 20 th	Tillage operation		
	October 1 st	Time of planting		
	November 1 st - 10 th	N application	70	60
	March 6 th - 19 th	N application	60	50
	June 10 th - 19 th	N application	70	60
	August 1 st	Harvest		
Pasture	January 20 th - 29 th	Manure application	20000	20000
	March 1 st	Time of planting		
	March 10 th - 19 th	N application	40	33
	June 15 th	Harvest		
	June 15 th - 24 th	N application	40	33
	September 1 st - 10 th	N application	40	33
	December 8 th - 19 th	Manure application	30000	30000
	December 1 st	Harvest		

^[1] Mineral soils for this study: Gley, Gley-Podsol, Cambisol, Podsol, Planosol and Luvisol

^[2] Organic soil for this study: Histosol

* Values based on KTBL (1995) and LWK (1991, 1998).

4.8.6 *Simulation of Best Management Practices scenarios for the current situation*

After calibration and validation of discharge, sediment, NO₃-N and TP, scenarios were simulated using the principle of best management practices (BMPs). BMP are used broadly as field measures which reduce the negative impact of agriculture on water quality of a river network (Lam et al., 2011). Changes in nutrient load among the scenarios compared to the baseline scenario (current calibrated and validated), provided the percentage of reduction in N and P pollution in the upper Stör catchment. The simulated BMPs scenarios were implemented for the period of January 1st 2009 to December 31st 2011 using the same climatic conditions of the calibration and validation periods. According to Rao et al. (2009), BMPs are potentially most effective when they are located in areas that produce the majority of the runoff. The main BMPs scenarios tested in this study are described in Table 4.13.

Table 4.13 Scenarios simulation based in BMPs to reduce N and P pollution at the upper Stör catchment.

New Scenario code	Description of the new scenarios
DMA20	Decrease of organic manure application in 20%
DMA50	Decrease of organic manure application in 50%
DFA20	Decrease of mineral fertilizer application in 20%
CSC	Cultivation system in contour considering USLE_P=0.5 for agriculture in areas with more than 2% of slope.
WFS10	Use of field filter strip with width of 10 m
WFS30	Use of field filter strip with width of 30 m
CMB1	Combination of the scenarios DMA20, DFA20, and WFS30
CMB2	Combination of the scenarios DMA50, DFA20 and WFS10

5 RESULTS AND DISCUSSION

5.1 Land use and management changes

Based on the maps of Ripl et al. (1996) and Oppelt et al. (2011), land use in the upper Stör catchment has changed considerably. Table 5.1 shows the distribution of land use in both periods. Over the past 20 years, the agricultural area decreased from 56.7 to 42.1% and the pasture area increased from 20.7 to 33.1% (Table 5.1). However, according to the Statistical Office Schleswig-Holstein (1992-2013), a slight increase in agricultural area occurred over the past 20 years in the State of Schleswig-Holstein in Germany, especially with an increase of silage corn area, as can be seen in Fig. 5.1. This difference of agricultural area of both maps can be attributed to imprecision of satellite images of the land use maps, especially in the determination of pasture areas (Yuan et al., 2005; Numuta et al., 2008). The accuracy of the land use maps is dependent on the accuracy of the individual classifications and is subject to error propagation (Yuan et al., 2005). According to Numuta et al. (2008), heterogeneous pastures, amount of biomass and type of species can influence on the assessment of Landsat images.

Table 5.1 Distribution of land use in 1991-1995 and 2009-2011 in the upper Stör catchment.

Land use area [%]	1991-1995 ⁽¹⁾	2009-2011 ⁽²⁾
Agriculture	56.7	42.1
- wheat		13.7
- rapeseed		1.8
- corn		26.6
Pasture	20.7	33.1
Forest	12.7	14.0
Urban	7.6	10.0
Wetland	2.3	0.8

¹⁾ Adapted from Ripl et al. (1996)

²⁾ Adapted from Oppelt et al. (2011)

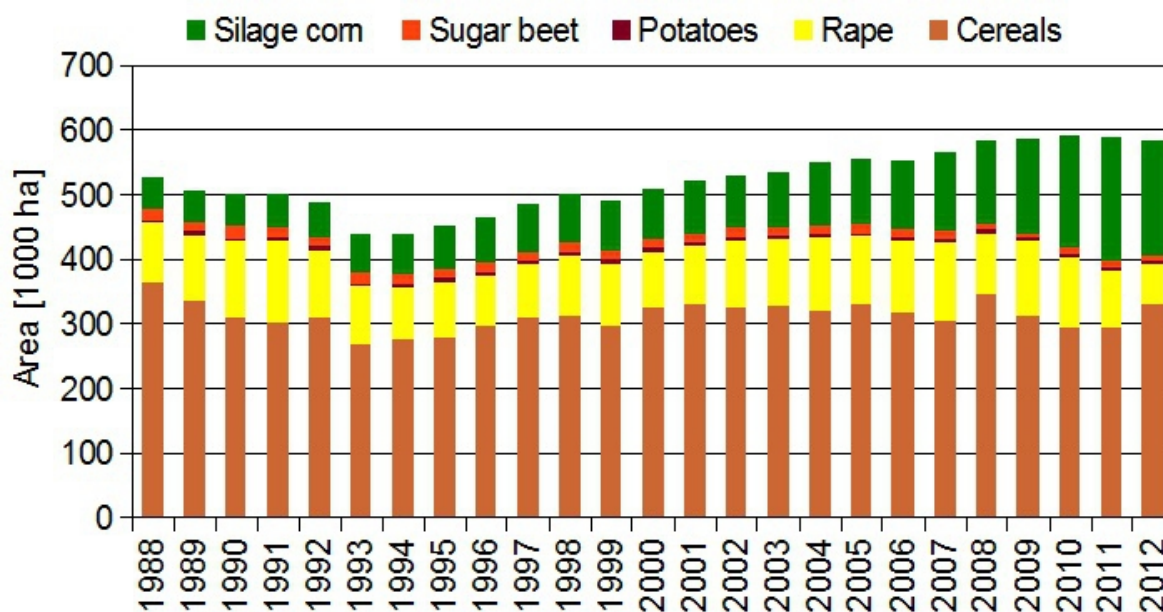


Fig. 5.1 Evolution of area of crop production between 1988 and 2012 in the State of Schleswig-Holstein (Statistical Office Schleswig-Holstein, 1992-2013), Germany.

In Fig. 5.2 is possible to observe the distribution of land use in each subbasin calculated with the land use maps from Ripl et al. (1996) and Oppelt et al. (2011), respectively for the periods of 1991-1995 and 2009-2011. In a general way, a decrease of agricultural area occurred in the major part of the subbasins followed by the increase in pasture areas.

The sum of the proportion of agriculture and pasture area is 77.4% and 75.2% from the 1991-1995 and 2009-2011 periods, respectively, indicating a slight increase of these areas in the current period. This information appear to have greater agreement with the increase in the areas of production of Fig. 5.1.

Fig. 5.3 shows the evolution of mineral N fertilizer (Fig. 5.3a) and P fertilizer (Fig. 5.3b) use in Germany during the years from 1991 until 2011. The amount of mineral N application decreased in Germany from an average of 108.6 kg/ha during the period of 1991-1995 to an average of 97.1 kg/ha during the years 2009-2011, corresponding to a reduction of circa 10.6% (Fig. 5.3a). The mineral P application decrease is more evident compared to N fertilizer, with a decrease from an average of 33.3 kg/ha of P_2O_5 in the period of 1991-1995 to an average of 13.8kg/ha of P_2O_5 in the period of 2009-2011, corresponding to a reduction of P use of circa 58.6% (Fig. 5.3b).

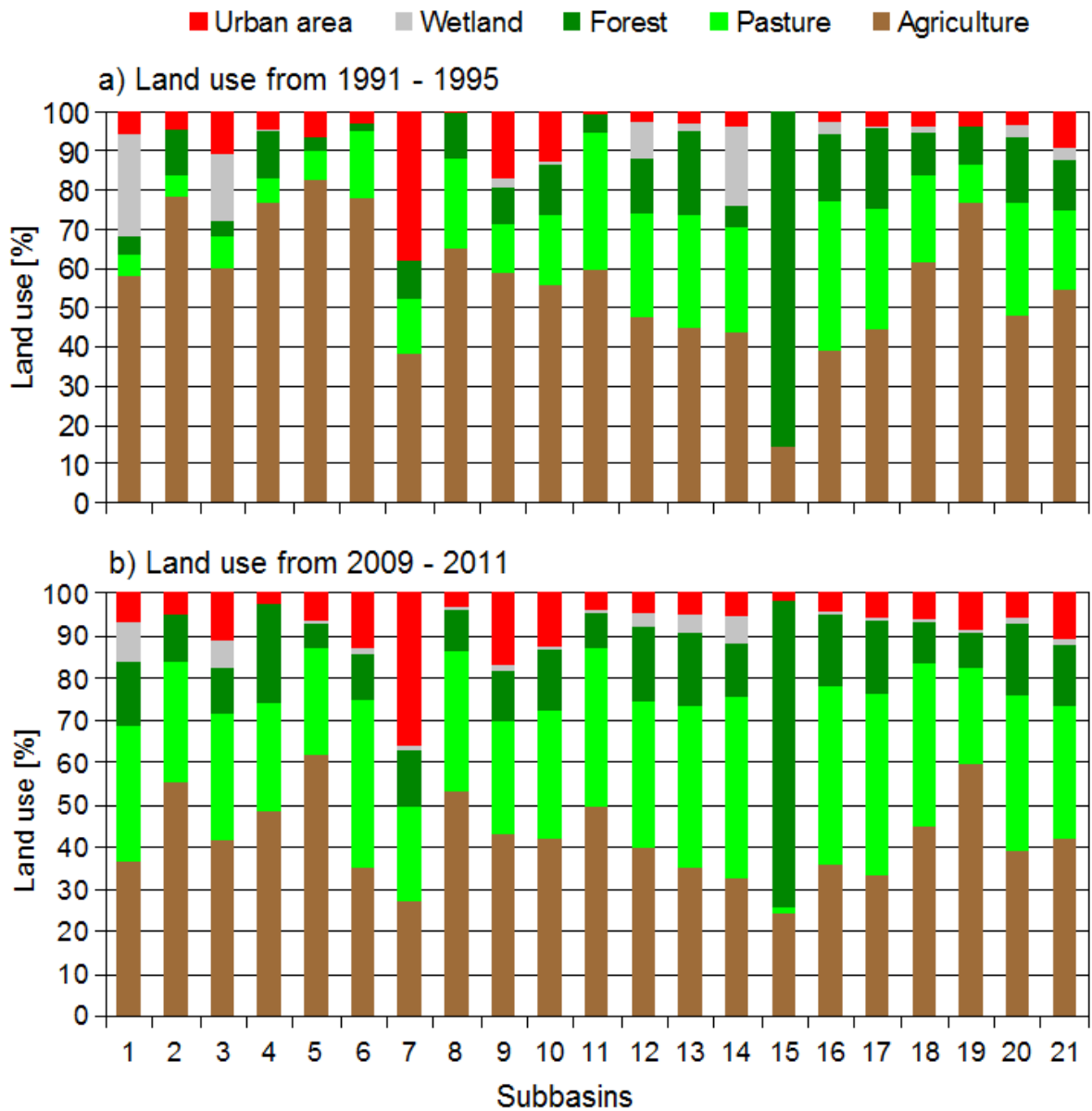


Fig. 5.2 Distribution of land use in each subbasin in the periods 1991-1995 and 2009-2010. Adapted from Ripl et al. (1996) and Oppelt et al. (2011).

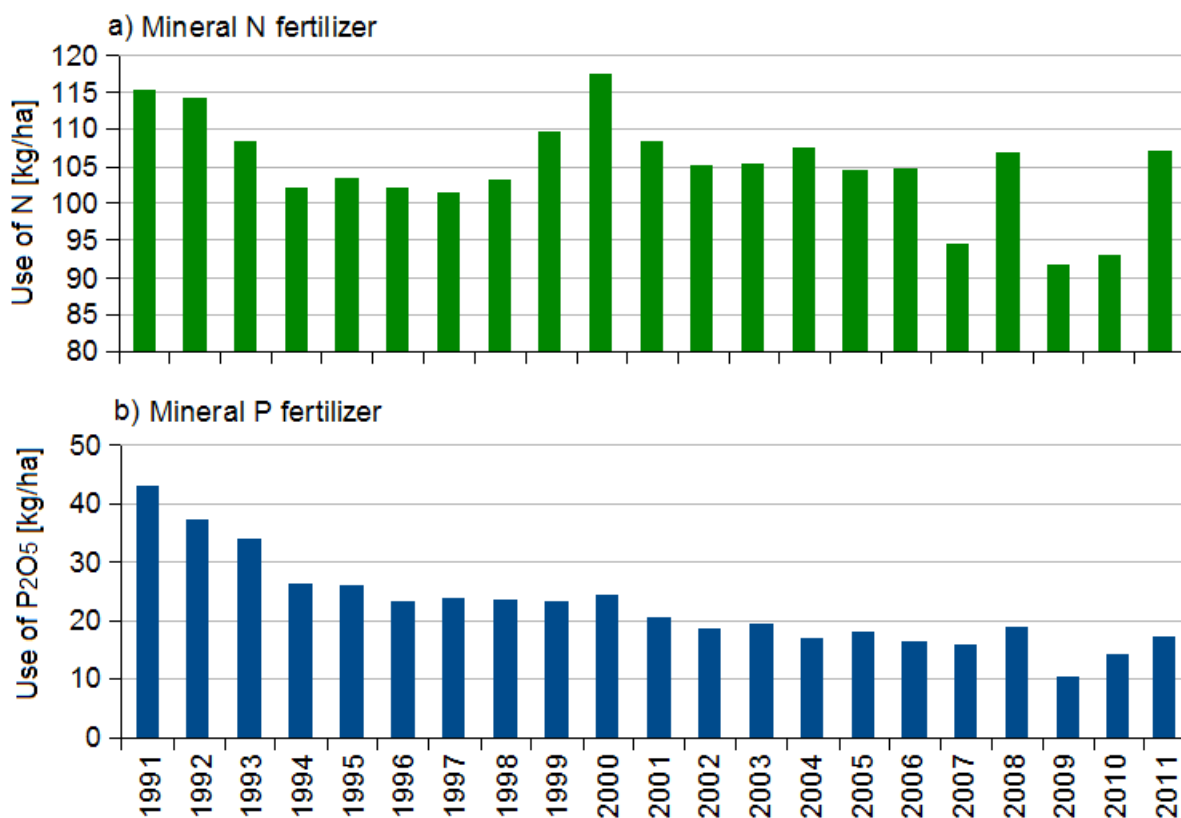


Fig. 5.3 Annual mean of fertilizer used in Germany. a) Mineral P fertilizer use; b) Mineral N fertilizer use (Adapted from Federal Statistical Office, 1992-2012).

5.2 Evolution of Nitrogen and Phosphorus pollution

5.2.1 General assessment of N and P

The general assessment of TP, PO₄-P, TN, NO₃-N and NH₄-N concentrations using the data of the 21 monthly sampling points of the upper Stör during 2009-2011 and 1991-1995 periods are shown in Fig. 5.4. TP, TN and NO₃-N concentrations from the 21 monthly sampling points of the upper Stör catchment decreased significantly from 1991-1995 to 2009-2011. According to the LAWA (1998) classification, TP concentration in water during both study periods was higher than 0.15 mg/l characterized as critically polluted (determined by the 90th percentile, Fig. 5.4), although there was an improvement of the TP concentration during the past 20 years. The 90th percentile of the PO₄-P concentration from 2009-2011 fits into class II (Fig. 5.4). Unfortunately, the PO₄-P concentration during the first campaign by Ripl et al. (1996), from 1991-1995, had not been measured. The decrease of TP concentration (Fig. 5.4) in the

past 20 years was also observed by Behrendt et al. (2000) in other German catchments from 1993 to 1997. The decrease of agricultural area (Table 5.1) as well as the reduction of mineral P fertilizer use in the last 20 years (Fig. 5.3), together with some restoration projects, such as shore stabilization and riparian vegetation (Dickhaut, 2005; Gessner et al., 2009) can explain, in part, the decrease of TP concentration in the upper Stör catchment (Fig. 5.4). Grimvall et al (2000), assessing the long-term P pollution in Western Europe verified a decrease of P load emission into rivers after 1985. They showed that P can be rapidly reduced from high to moderate levels, whereas a further reduction, may take decades. In Estonian, Iital et al. (2010) verify a trend of reduction of P concentration in rivers systems. They explained the improvement in water quality due to improvements in municipal wastewater treatment, a decrease in the number of inhabitants in rural areas, and, in particular, better handling of manure and fertilizers.

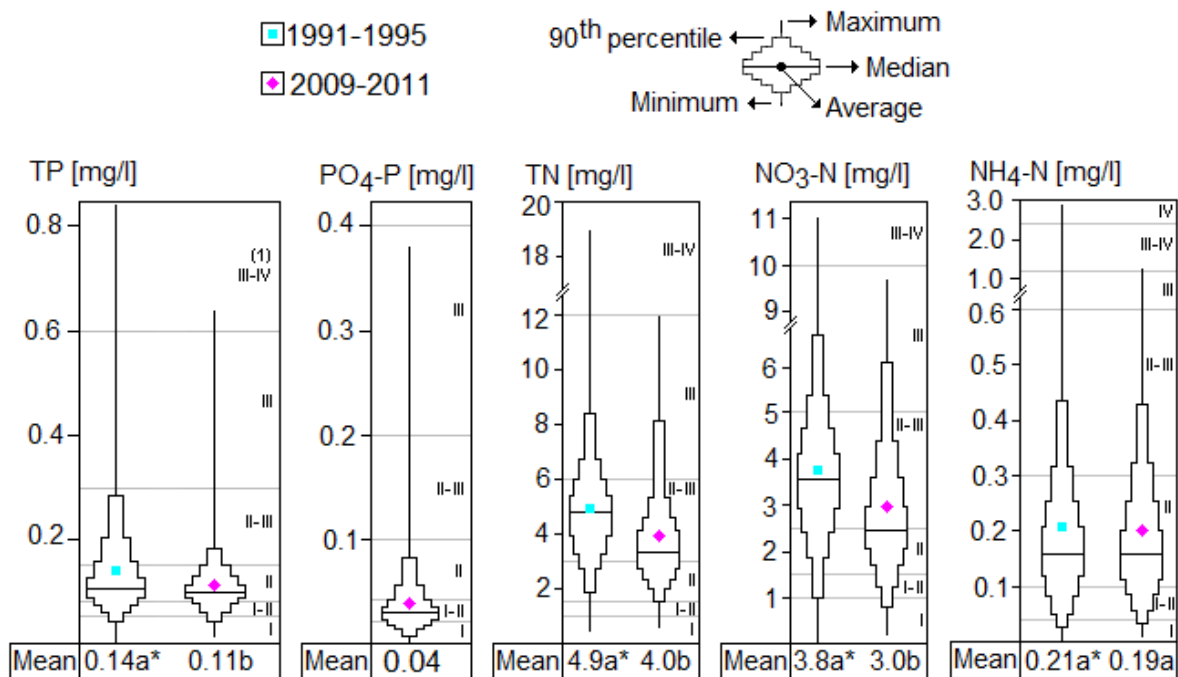


Fig. 5.4 Box-percentile-plots of TP, PO₄-P, TN, NO₃-N and NH₄-N concentration from 1991-1995 and 2009-2011 at all sampling points. *Means followed by different letter differ by T-test ($p < 0.001$). ⁽¹⁾ Letters at the right side indicate the LAWA (1998) water quality classes.

Pastuszak et al. (2012) investigating long-term response of P pollution in Poland verify that the reduction in P loads was particularly pronounced, which was a result of efficient management systems aiming at the mitigation of nutrient emission from point sources and to a

greater extent of structural changes in agricultural sector during the period of 1988 to 2008. The water quality of the River Frome in England has seen a rapid improvement over the last decade, due primarily to improvements in P removal at the major sewage treatment plants in the catchment (Bowes et al., 2011).

TN and NO₃-N concentrations from the 21 sampling points of the upper Stör catchment decreased significantly from 1991-1995 to 2009-2011, while the NH₄-N concentration remained constant (Fig. 5.4). According to the LAWA (1998) classification, water quality classes did not change for all N parameters (determined by the 90th percentile, Fig. 5.4). TN and NO₃-N were ranked as heavily contaminated (class III) and NH₄-N was ranked as critically polluted (class II-III). The decrease of NO₃-N and TN concentrations in the last 20 years can be attributed mostly to the decrease in mineral N fertilizer use (about 10.6% according to Federal Statistical Office (1992-2012, Fig. 5.3) and to the land use changes. However, the decrease of agricultural area from 56.7% to 42.1% and the increase from 20.7% to 33.1% in pasture areas (Table 5.1) apparently did not influence the N parameters as much as P. The decrease of erosion caused by the conversion from agriculture to grassland did not influence the N transport, because NO₃-N is mostly dissolved and not associated with soil particles. It is easily leached into the soil and into the groundwater, especially in flat lowland areas. Furthermore, the response time of N to changes in input can vary from 10 to 30 years (Behrendt et al., 2000; Howden et al., 2011). Howden et al. (2011) modeling a long-term NO₃-N load in UK suggested that the time delay necessary between N-loading from land to fluvial response in NO₃-N concentrations would be greater than previously expected. According to the authors, the recent efforts to limit NO₃-N pollution of freshwater may not be effective in many areas for several decades. They suggest that in the Alton Pancras catchment in UK, reduced inputs from 1990 will not reduce river water nitrate concentrations until around 2027.

Kay et al. (2012) assessing the effectiveness of agricultural stewardship for improving water quality at the catchment scale in UK verified a significant trend in decreasing winter nitrate peaks in some streams, which was attributed to recent reduced inorganic fertilizer application as a result of increasing prices. They concluded that these findings indicate that agricultural stewardship measures have the potential to improve water quality at the catchment scale, but that voluntary schemes with insufficient financial reward or regulatory pressure are unlikely to be successful.

In countries of Eastern Europe, the decreased use of fertilizer started in the late 1980s, and the concentrations of nutrients in the rivers did not reduce at the same rate because a large amount of N is stored in the soil and is slowly mineralized (Grimvall et al., 2000; Stålnacke et al., 2004; Sileika et al., 2006). McGovern et al. (2013) suggested that the soils have been relatively resistant to the large changes in the environmental pressures experienced in the past forty years. Moreover, the unsaturated zone in lowland catchments can prevent control of nitrate levels because NO_3^- is not reduced to N_2 via denitrification (Jackson et al., 2008). Cherry et al. (2008) reported that due to catchment buffering and long transit time, the effect of management changes will not be visible until 2015 in many water bodies in Europe. Taking into account this slow reaction, the observed change in TN and $\text{NO}_3\text{-N}$ concentrations in the upper Stör catchment seems to be quite satisfactory, even if the low levels required by the WFD (EC, 2000) could not be reached yet. Policy makers and catchment managers must take account of the delay in catchment response to N mitigation. This delay is both due to the necessary time for farmers to change their behavior and to the natural hydrologic delay in catchments characterized by a high baseflow index (Kronvang et al., 2008).

5.2.1.1 Status of P pollution in 21 subbasins

The interpretation of an overall assessment of water quality (Fig. 5.4) is often misleading, because any sampling point with high P concentration can be outside the 90th percentile, especially when there is a large amount of water samples. Fig. 5.5 shows the TP concentration of the 21 sampling points from 1991-1995 and 2009-2011 and the $\text{PO}_4\text{-P}$ concentration from 2009-2011. From 1991 to 1995, four sampling points (1, 14, 16 and 18) were ranked in class III (heavily contaminated) according to LAWA (1998). From 2009 to 2011, only one sampling point (18) was ranked in the same class, thus showing a moderate improvement in water quality. According to the map from Ripl et al. (1996) for 1991-1995, the land use of subbasin 1 was 58% agriculture, 5% pasture and 5% forest areas, respectively (Fig. 5.2). These values changed to 35% agriculture, 30% pasture and 14% forest in the period of 2009-2011 (Oppelt et al., 2011), showing a decrease in agricultural areas and an increase in pasture and forest land. Subbasin 14 showed a similar decrease. In subbasin 16 we observed a slight decrease of agricultural land use and a small increase in pastures and forests. As well as the tendency for subbasin 16, subbasin 18 had the highest percentage of area with a slope steeper than 2%

(72%) which could lead to higher erosion and P losses as observed by Haggard et al. (2005). In this subbasin we also observed rill erosion on agricultural areas without soil cover (Fig. 5.6) and a large accumulation of sediment in the river bed.

For the $\text{PO}_4\text{-P}$ concentrations in 2009-2011, four sampling points (subbasins 1, 14, 16 and 18) were characterized as critically polluted (class II-III). These subbasins also showed the highest decrease in TP concentration over the last 20 years (Fig. 5.5).

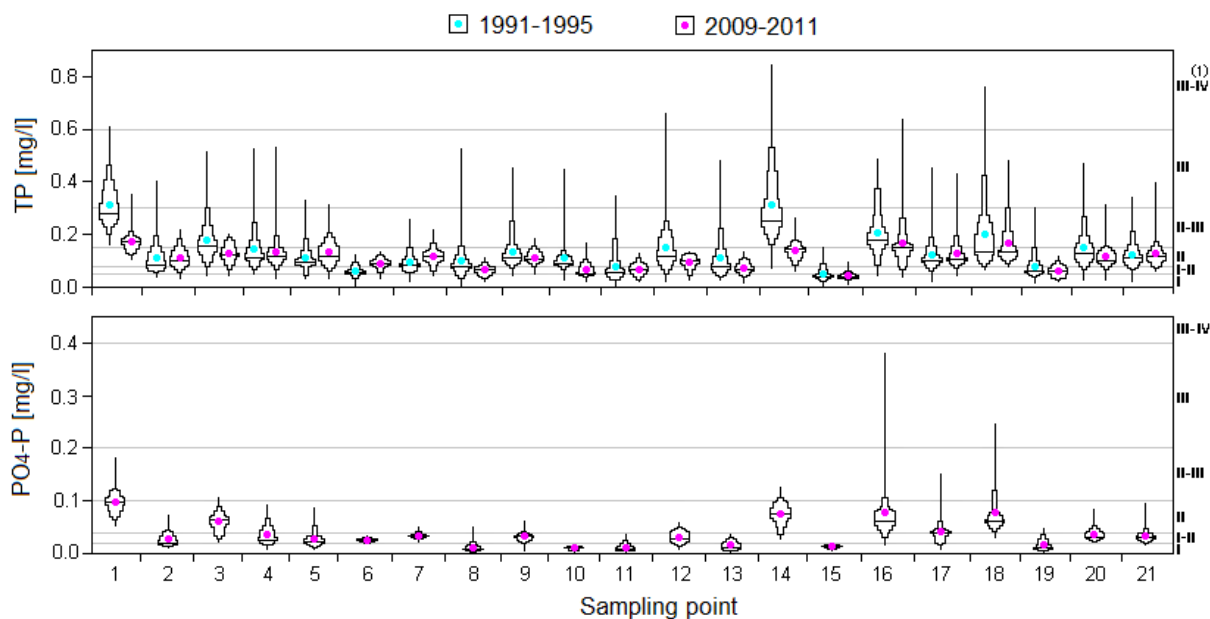


Fig. 5.5 Box-percentile-plots of TP and $\text{PO}_4\text{-P}$ concentration from the 21 sampling points from the upper Stör catchment in 1991-1995 and 2009-2011. ⁽¹⁾ Letters at the right side indicate the LAWA water quality classes. Number of observations at each sampling point: $n(1991-1995)= 35$ to 44 , $n(2009-2011)=24$.



Fig. 5.6 Erosion in agricultural area in the upper Stör catchment (April 2011).

5.2.1.2 Status of N pollution in 21 subbasins

Fig. 5.7 shows TN, NO₃-N and NH₄-N concentrations of the 21 sampling points from 1991-1995 and 2009-2011. For the TN parameter from 1991 to 1995, only one sampling point (8) was ranked in class II, while eleven and nine sampling points were ranked in classes III and II-III, respectively. Twenty years later, four sampling points were ranked in class II, while six and eleven sampling points were ranked in the classes III and II-III, respectively. For the NO₃-N parameter, between 1991 and 1995, three sampling points were ranked in class II, eight in class II-III, nine in class III and one in class III-IV. From 2009 to 2011, six sampling points were classified as class II, one as class I-II, eight as class II-III and six as class III. The results show a trend of decrease of TN and NO₃-N concentrations at most sampling points in the catchment, indicating that the objectives of the Nitrate Directive (EEC, 1991a) were partly achieved. However, the moderate decrease was not enough to achieve the target class II, the “good status”, in all sampling points.

For NH₄-N (Fig. 5.7) between 1991 and 1995, ten sampling points were ranked in class II, one in class I-II, seven in class II-III and three in class III. Twenty years later, six sampling points

were ranked in class II, one in class I-II, thirteen in class II-III and one in class III. Although differences between both periods are not statistically significant (Fig. 5.3), we could observe an increase of $\text{NH}_4\text{-N}$ concentration in more than 59% of the sampling points (Fig. 5.7). Ammonia is not only influenced by input, but also by pH (Erickson, 1985; Randall and Tsui, 2002). At pH 7 or below, most of the ammonia will be ionized (NH_4^+), at higher pH levels the fraction of NH_3 will increase and can reach levels which are toxic for fish (Novotny and Olem, 1993). The sampling point 9 corresponds to the outlet of the major part with urban area (Neumünster city), where the largest WWTP is installed (WWTP-NP2). This sampling point had clearly reduced $\text{NH}_4\text{-N}$ concentration compared to 20 years ago. Jin et al. (2009) verified that $\text{NH}_4\text{-N}$ concentration was higher near cities than in rural areas.

5.2.2 Daily mixed sampling of water quality

The time series of precipitation (PCP), discharge (Q), TSS, TP, PP, $\text{PO}_4\text{-P}$, TN, $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and WT are shown in Fig. 5.8. The highest peaks of Q are associated with PCP events, which are more evident in the winter months. TSS, TP, PP, $\text{PO}_4\text{-P}$, TN, $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, DO concentrations have a distinct seasonal trend with higher concentrations in winter. The daily monitoring data set allows us to show the concrete dynamics of N and P pollution in the upper river Stör (Fig. 5.8, 6.12 and 6.13). During the summer, Q is quite stable and is less directly influenced by PCP events (Fig. 5.8). In summer, P concentrations are lower than in winter, when the precipitation affects discharge more directly (Fig. 5.8) and peaks of P concentration can be seen.

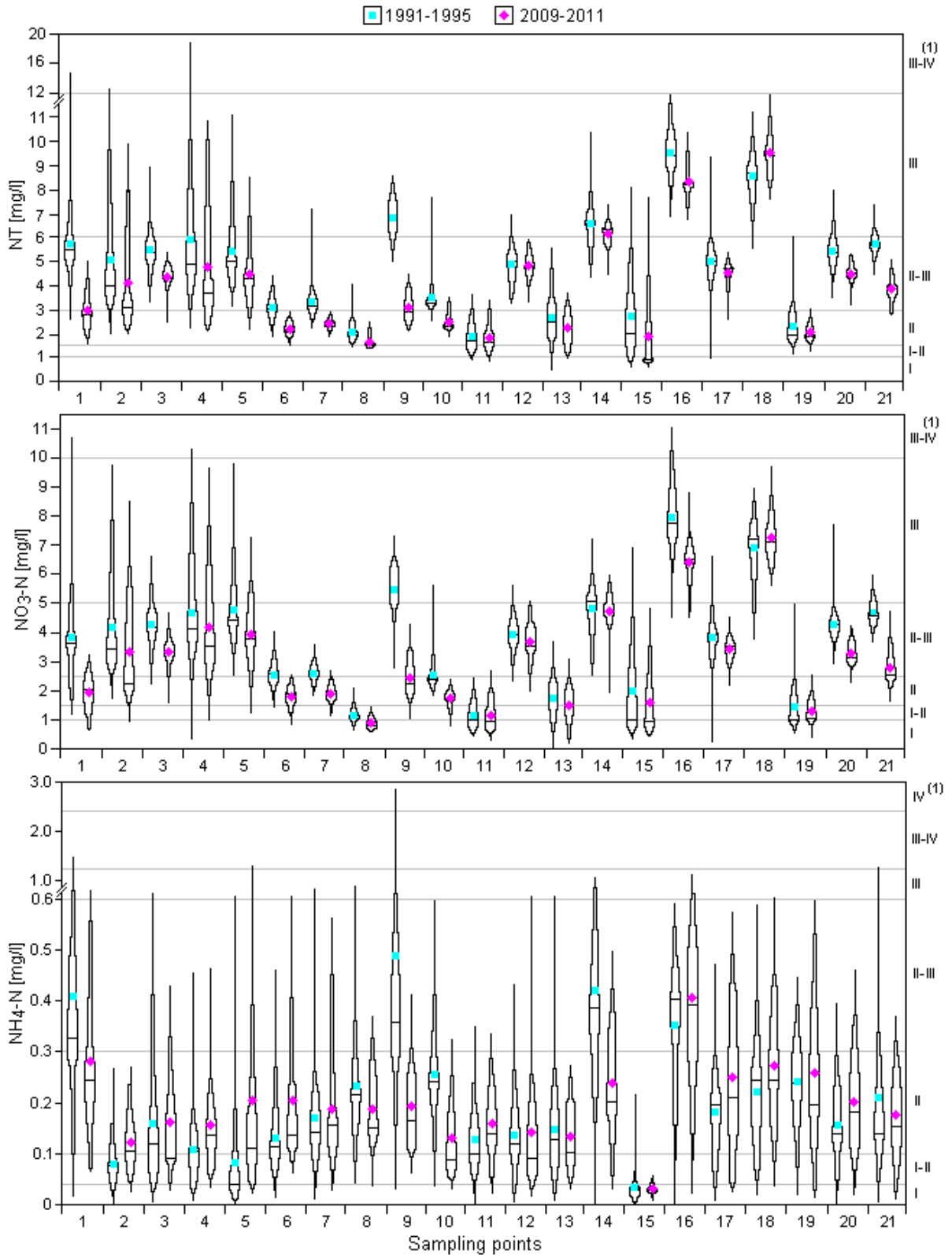


Fig. 5.7 Box-percentile-plots of TN, NO₃-N and NH₄-N concentration from the 21 sampling points from 1991-1995 and 2009-2011. (1) Water quality classes from LAWA (1998). Number of observations at each sampling point: n(1991-1995)= 35 to 44, n(2009-2011)=24.

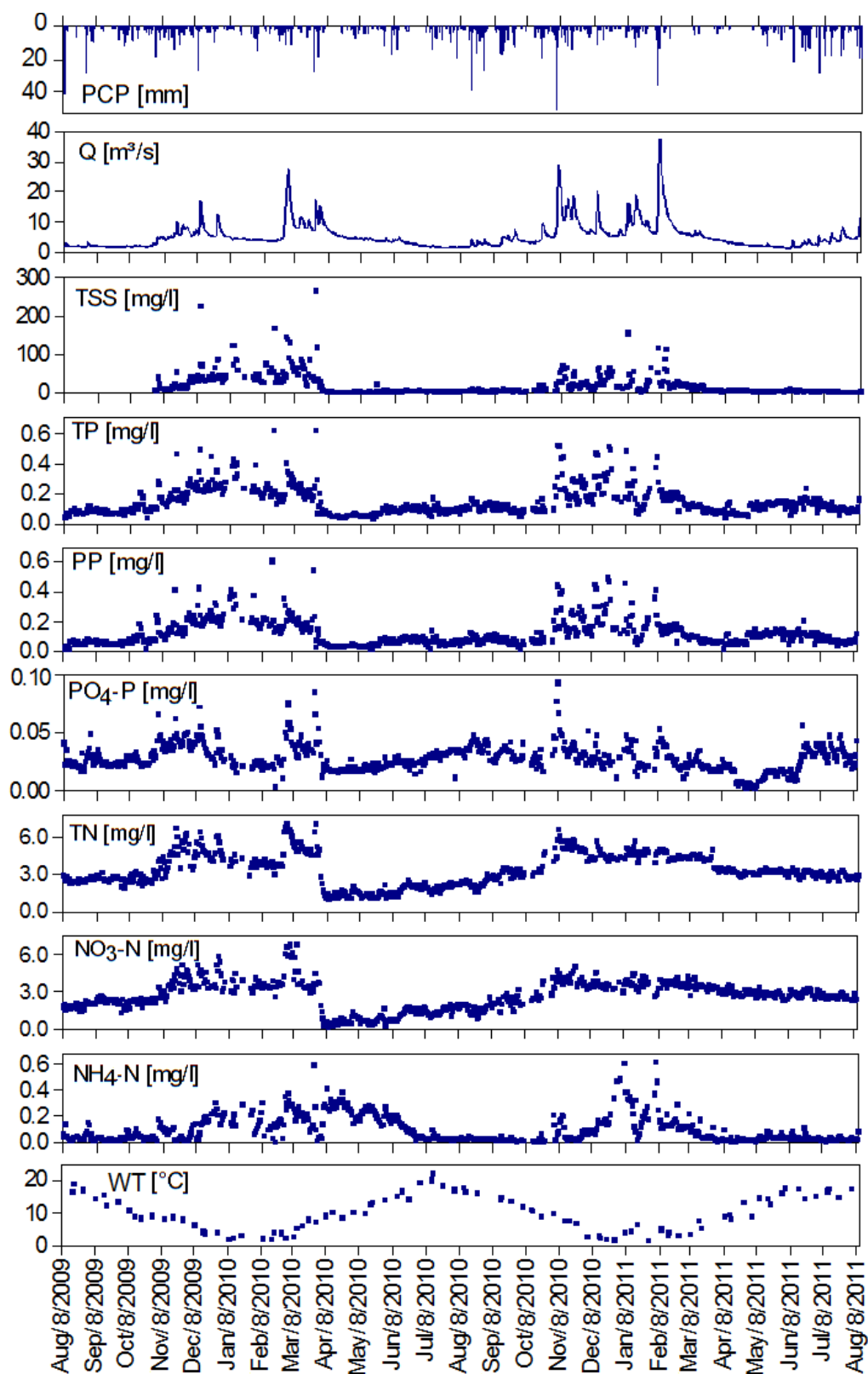


Fig. 5.8 Daily time series of PCP, Q, TSS, TP, PP, PO₄-P, TN, NO₃-N, NH₄-N and WT of the upper river Stör at the gauge station Willenscharen from August 8th 2009 until August 10th 2011.

5.3 Seasonality of N and P pollution

Fig. 5.9 shows the TP and PO₄-P concentrations of the 21 sampling points for winter and summer. Only the sampling points 1, 15 and 18 show higher TP concentrations in summer from 1991 to 1995 (Fig. 5.9a). All other points show higher TP concentrations in the winter. The same trend is visible from 2009 to 2011 (Fig. 5.9b). The PO₄-P concentrations at points 1 and 18 were also higher in summer, while for the other points they were higher in winter (Fig. 5.9c).

Fig. 5.10 shows N fractions for winter and summer. Data from the 21 sampling points of TN, NO₃-N and NH₄-N are grouped to represent the seasonality because unlike P, all sampling points showed the same tendency. TN, NO₃-N and NH₄-N from 1991-1995 and 2009-2011 are significantly higher in winter than in summer. In summer of the years 2009-2011, NO₃-N and NH₄-N concentrations decreased and reached the LAWA classes II-III and II, respectively. Therefore, in summer 2009-2011, NH₄-N concentrations were in accordance with the WDF (EC, 2000).

Seasonality was tested in the daily database of Willenscharen, which the daily time series were aggregated to seasonal values (Fig. 5.11) based on the hydrological year with winter corresponding from November 1st until April 30th and summer from May 1st until October 31st. TSS, TP, PP, PO₄-P, TN, NO₃-N, NH₄-N, DIN/DIP, DO, pH and WT values are significantly different based on T-test for the winter months when compared to the summer months. According to the 90th percentile (Fig. 5.11), TP is ranked in class III (heavily contaminated) in winter and class II (moderately polluted) in summer, thus TP reached the "good status" desired by EC (2000). PO₄-P is ranked in class II (moderately polluted) in winter and class I-II (lightly polluted) in summer. TN and NO₃-N are ranked in class II-III in both periods. NH₄-N is ranked in class II-III in winter and class II in summer, achieving the goals of the WDF (EC, 2000).

In general, most problems with N and P pollution occur in winter (Fig. 5.9, Fig. 5.10 and Fig. 5.11). Oeurng et al. (2010) also found lower NO₃⁻ concentrations from summer to early autumn, and a higher NO₃⁻ concentration from late winter to spring in an agricultural catchment. Higher N concentration in winter may be attributed to a lower growth of plants and lower adsorption of NO₃⁻ to soil particles, consequently NO₃⁻ can be washed off by runoff

and leaching. Tisseuil et al. (2008) found in a study of water quality in lowland catchments of France, that the NO_3^- concentrations in river systems exhibit a seasonal pattern, with peak concentrations coinciding with fertilizer applications in spring and a minimum concentration in summer, when terrestrial and aquatic uptake of plants were higher. Lower levels of $\text{NH}_4\text{-N}$ in summer can be attributed to the higher rate of nitrification at higher WT (Fig. 5.12c), being the optimum between 20 and 25°C (Novotny and Olem, 1993). On the other hand, the decrease of DO caused by increase of WT (Fig. 5.12c) could lead to denitrification and thus reduce the $\text{NO}_3\text{-N}$ levels in the summer.

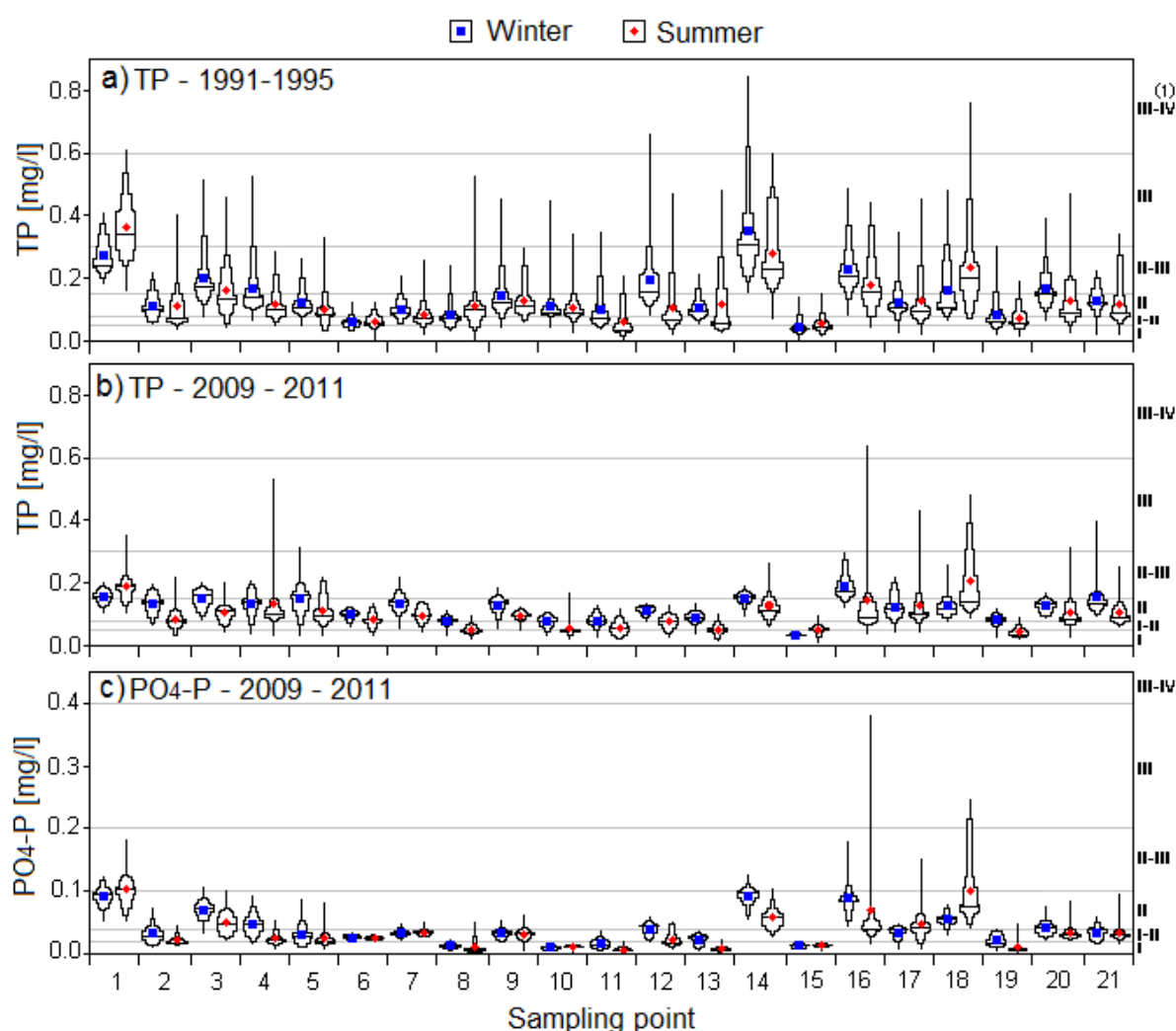


Fig. 5.9 Box-percentile-plots of P concentration in winter and summer. a) TP concentration from the 21 sampling points from 1991-1995. b) TP concentration from the 21 sampling points from 2009-2011. c) $\text{PO}_4\text{-P}$ concentration from the 21 sampling points from 2009-2011.

⁽¹⁾ Letters at the right side indicate the German LAWA (1998) water quality classes.

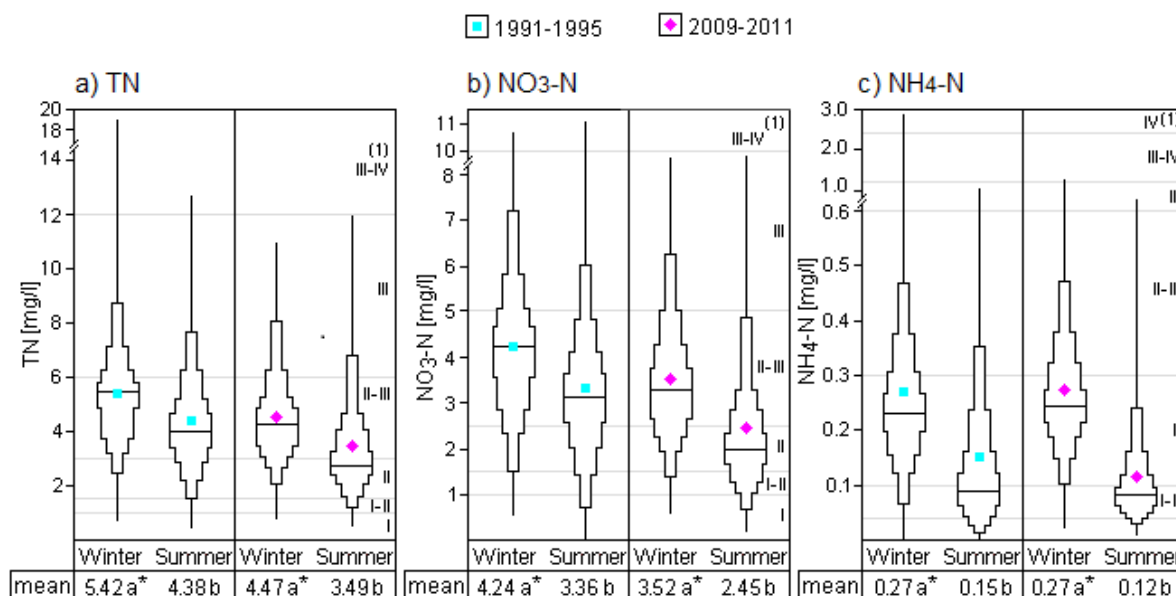


Fig. 5.10 Box-percentile-plots of TN (a), NO₃-N (b) and NH₄-N (c) concentrations in winter and summer from 1991-1995 and 2009-2011. ⁽¹⁾ Water quality classes from LAWA (1998). *Means followed by different letter differ by T-test ($p < 0.001$).

Higher TP and PO₄-P concentrations in winter are linked to higher river flow (Fig. 5.8), which causes more sediment transport (Evans and Johnes, 2004) and erosion along the river banks (Walling and Amos, 1999; Kessler et al., 2013). Jarvie et al. (2002) also observed higher P concentration in winter in their study of P dynamics in a lowland catchment in England. They explained it with a mobilization of PO₄-P from diffuse sources during higher river flows. Moreover, plants grow less in winter, causing less P uptake and consequently more potential to P losses by runoff. In summer TP and PO₄-P losses are lower due to a higher P uptake by terrestrial plants and by aquatic macrophytes (Schulz et al., 2003; Evans and Johnes, 2004; Gao et al., 2009).

Higher TP and PO₄-P concentrations in summer seem also to be related to peaty soils. Subbasin 1 has a large area of peaty soils (Finnern, 1997), the nature reserve “Dosenmoor bog“ covers 26% (521 ha) of the subbasin. The P fluxes in subbasin 1 seem to be dominated by typical wetland processes. According to Reddy et al. (1995), wetlands can be a sink or sources of P. The sink function of wetlands is used for treatment of wastewater (Novotny and Olem, 1993; Braskerud, 2002; Kadlec and Wallace, 2009; Yates and Prasher, 2009). High P concentrations in summer near wetland areas observed in this study appear to be mainly

associated with redox potential. In general, the water pH is higher in summer and the oxygen concentration is lower (Fig. 5.12b). The lower pH values in winter can explain the higher $\text{PO}_4\text{-P}$ concentrations of most sampling points, at least for the subbasins with mostly agricultural land use. The low concentration of oxygen caused by high summer temperature can increase the redox potential at the wetland areas, thereby increasing the solubility of $\text{PO}_4\text{-P}$ in summer, especially at the sampling point 1 (Fig. 5.12d).

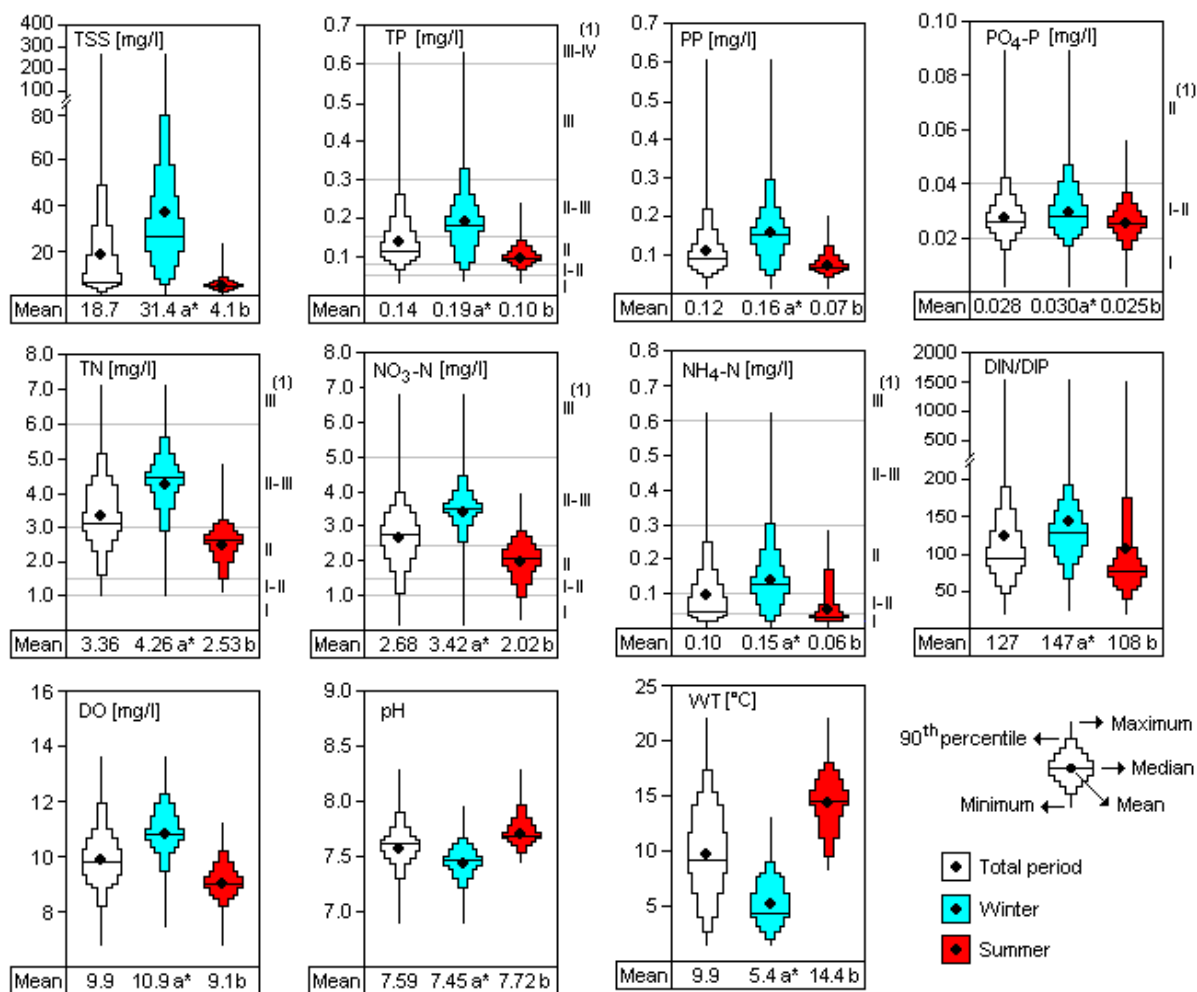


Fig. 5.11 Box-percentile-plots from TSS, TP, PP, $\text{PO}_4\text{-P}$, TN, $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, DIN/DIP, DO, pH and WT values of the upper river Stör at the gauge Willenscharen. *Means followed by different letter differ by T-test ($p < 0.001$). ⁽¹⁾ Water quality classes from German LAWA (1998) classification.

Howden et al. (2009) suggested that the major challenge is to characterize and control P input which is predominant during the late spring and summer, characterized by low-flow period, coinciding with the peak of primary biological production, thus presenting the major

challenge to achieving ‘good’ ecological status under the WFD (EC, 2000). Considering that the risk of eutrophication is higher during spring and summer with low flows and high biological activity (Neal et al., 2006), this analyzed catchment with high N and P concentrations in winter is less vulnerable to eutrophication.

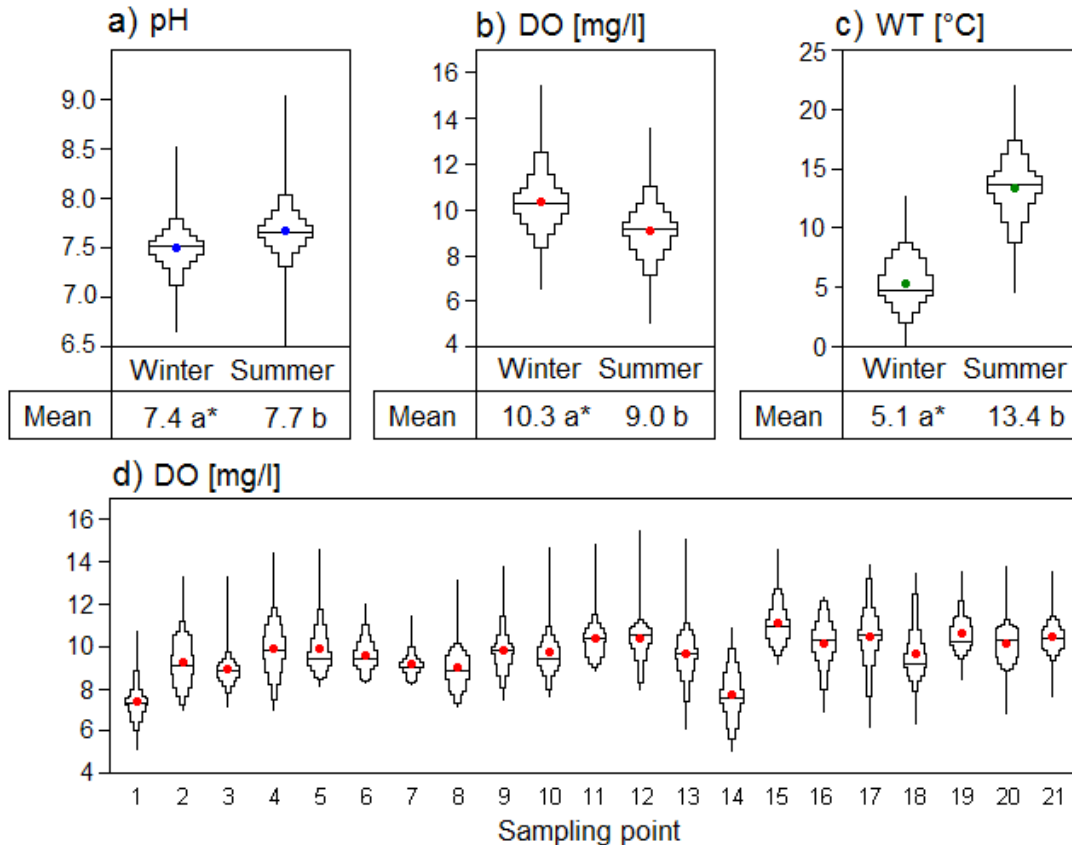


Fig. 5.12 pH (a), Dissolved oxygen (b) and Winter temperature (c) from 2009-2011 of all sampling points from the monthly campaign. d) DO at 21 sampling points from the monthly campaign. *Means followed by different letter differ by T-test at 0.001 level.

5.4 Sources of N and P pollution

5.4.1 Point pollution

Concentrations of N and P parameters from the upstream, downstream and from effluents of WWTPs are shown in Fig. 5.13. In WWTPs without P elimination steps, P is removed by primary sedimentation and microbial activity (Yeoman et al. 1988). A higher concentration of TP (Fig. 5.13a) and PO₄-P (Fig. 5.13b) can be observed for WWTPs without tertiary treatment, the highest concentrations comes from the small WWTP-MB. According to

Redeker (2011), the lower concentration of TP and $\text{PO}_4\text{-P}$ from the WWTP-L compared to the WWTP-MB is due to the dilution effect of rain water. Both P parameters show lower concentrations in summer due to the lower microbial activity caused by low temperatures in winter (Redeker, 2011). At downstream points after the river water dilution, TP (Fig. 5.13a) and $\text{PO}_4\text{-P}$ (Fig. 5.13b) were lower and the water quality was better than directly at the effluent points. Wastewater from point sources have not only high P concentrations but also have a large proportion of bioavailable P (Edwards and Withers, 2008).

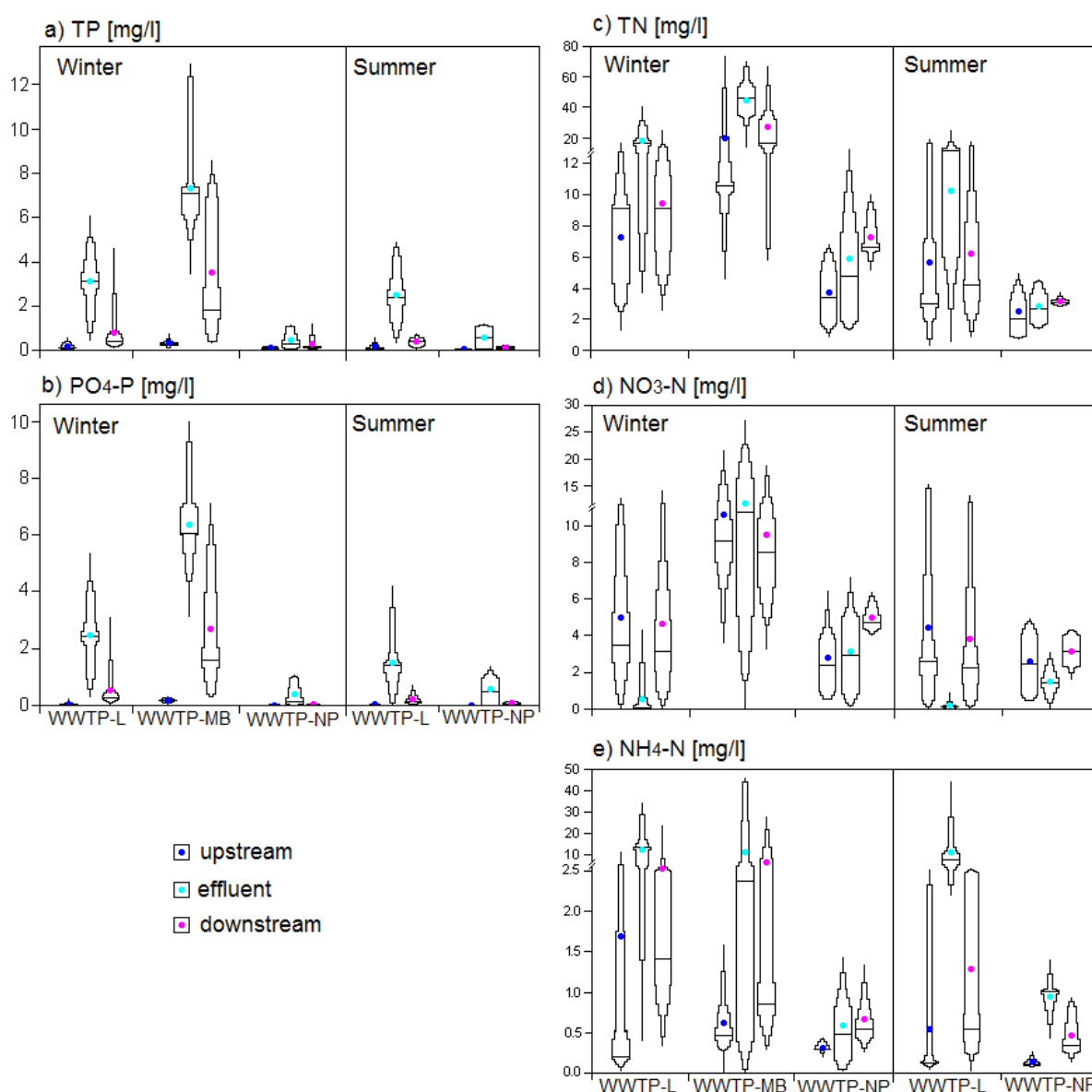


Fig. 5.13 Box-percentile-plots of N and P parameters from WWTPs in winter and summer. Number of observations: $n(\text{WWTP-L, winter})=31$, $n(\text{WWTP-MB, winter})=11$, $n(\text{WWTP-NP, winter})=6$, $n(\text{WWTP-L, summer})=17$, $n(\text{WWTP-NP, summer})=6$. Adapted from Redeker (2011) and Honsel (2011).

NO₃-N (Fig. 5.13d) from WWTPs is lower at the effluent than at the upstream section in the WWTP-L, indicating an efficient removal of N (Fig. 5.13d). The NO₃-N levels of the WWTP-MB are higher and make this type of WWTP an important source of NO₃-N pollution. The WWTP-NP has only a lower concentration of NO₃-N in the effluent in the summer. The high NH₄-N concentrations in the effluent of all WWTP types show that there is still the necessity for technical improvement.

Lower temperatures together with lower levels of dissolved oxygen in winter (Table 5.2) are favorable to inhibition of the nitrification process (Novotny and Olem, 1993). The conventional wastewater treatment technology does not always provide suitable solutions for heavily polluted sewage waters (Iital et al., 2010). In the WWTP-L, where only natural processes clean the water, the lack of oxygen causes anaerobic processes like denitrification of NO₃-N, which can be seen at Fig. 5.13d with lower NO₃-N concentration at the effluent than at upstream. However, without oxygen, the nitrification process is stopped and NH₄-N remains high, which can be seen in Fig. 5.13e with high values of NH₄-N in the WWTPs-L. The sources of NH₄-N and NO₃-N of the upper Stör catchment follow the same trend as observed by Jin et al. (2009), who found patterns of N fractions: NH₄-N concentration decreased with increasing distance from cities and NO₃-N concentration increased with the increasing of farmland areas in the catchments.

Table 5.3 shows the calculated N and P loads from diffuse and point sources. The point pollution represents 10.6% and 8.4% of TN and TP load of the upper Stör catchment, respectively, indicating that diffuse pollution represents the major part of TN and TP load. NH₄-N load represents only 3.3% of the the TN load in the upper Stör catchment, however, the major part (61%) is originated from the WWTPs. With regards to P, PO₄-P load represents only 16.2% of TP, but a representative part (44.2%) is originated from point pollution. These results are in accordance with Bartley et al. (2012) and Jin et al. (2009), who link PO₄-P (Bartley et al., 2012) and NH₄-N (Jin et al. 2009) pollution to urban land use. In lowland areas in UK, agriculture sources and wastewater are responsible for the most part of NO₃-N and PO₄-P load, respectively (Neal et al., 2008).

Table 5.2 Average of pH, dissolved oxygen concentration (DO) and water temperature (WT) from the WWTP types.

Parameter	WWTP type	Winter	Summer
pH	WWTP-L	7.3 a***	7.6 b
	WWTP-MB	7.4	ns ⁽¹⁾
	WWTP-NP	7.0 a*	7.5 b
DO [mg/l]	WWTP-L	4.7 a***	7.6 b
	WWTP-MB	5.3	ns ⁽¹⁾
	WWTP-NP	4.9 a**	7.5 b
WT [°C]	WWTP-L	2.0 a***	19.8 b
	WWTP-MB	7.7	ns ⁽¹⁾
	WWTP-NP	6.1 a***	20.7 b

*Means followed by different letter on the line differ by T-test at 0.05 level.

** Means followed by different letter on the line differ by T-test at 0.01 level.

*** Means followed by different letter on the line differ by T-test at 0.001 level.

¹⁾Not sampled.

Table 5.3 Calculated N and P load from diffuse and point pollution (WWTPs) in the upper Stör catchment for the 2009-2011 period.

Source of pollution	Unit	TN	NO ₃ -N	NH ₄ -N	TP	PO ₄ -P
Total load in the upper Stör catchment	t/a	705	557	23	32	5.2
Part of WWTP pollution	t/a	75	35	14	2.7	2.3
	%	10.6	6.3	61.0	8.4	44.2
Part of diffuse pollution	%	89.4	93.7	39.0	91.6	55.8
	kg/ha	13.6	11.30	0.20	0.63	0.06

With respect to WWTPs in the catchment, only a single one was built after the upcoming of the WWTP-Directive (EEC, 1991b) and two were built after the implementation of the WFD (EC, 2000) in the upper Stör catchment (Table 3.2). As a consequence of the WFD, four WWTPs were modified, among them the two largest WWTPs, which processes of removal of N and P were implemented. According to MLUR-SH (2011), the investment of improvement on WWTPs was carried out in accordance with the WFD (EC, 2000), where WWTPs with

more than 10,000 inhabitants were prioritized. Most part of the WWTPs-L and WWTPs-MB have already a shelf life between 20 and 30 years (Table 3.2). New technologies should be considered in the WWTPs with small populations in order to improve water quality, especially regarding $\text{NH}_4\text{-N}$ pollution, at the catchment in the future.

5.4.2 *Influence of land use on water quality*

The possible influence of land use on water quality is shown in Table 5.4 as correlation of TP, $\text{PO}_4\text{-P}$, PP, TN, $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ with agriculture, pasture and forest area. Table 5.4 also shows the correlations with peaty soils fraction and P and N parameters. Positive correlations were found among agricultural area and TP and PP concentrations, indicating that agriculture is a main factor for diffuse P pollution. However, the correlation between agricultural area and $\text{PO}_4\text{-P}$ concentration is low and can be attributed to the dynamics of soil P, due to the high P adsorption by the soil particles (Sharpley, 1995; Hoseini and Taleshmikael, 2013) and the decreasing of use of phosphate fertilizer during the past 20 years (Fig. 5.3b, Federal Statistical Office, 1992-2012). The pasture areas have also a positive correlation with TP and PP, but the correlation with $\text{PO}_4\text{-P}$ has statistical high significance, suggesting that pasture areas are more effective to control the PP pollution than agricultural areas. There are significant negative correlations between forest area and PP concentration, indicating that forest can reduce soil erosion and runoff transport of PP. Morgan and Kline (2011) found significant positive relationship between agricultural area TP (0.40) and negative relationship between TP and forest land cover ($r=-0.33$). The peaty soils also have positive correlation with $\text{PO}_4\text{-P}$ concentration, indicating that the soluble fraction of P is released from the wetland areas. In this study the wetlands function as a source of P for the river.

Significant positive correlations were found among agricultural area and concentrations of TN and $\text{NO}_3\text{-N}$ for both study periods. Positive correlations were found among pasture areas and TN, $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$, respectively. It shows the negative impact of farmland on water quality and confirms the results of Iital et al. (2005), Lassaletta et al. (2009) and Morgan and Kline (2011). Iital et al. (2005) found significant positive relationship between TN concentration in river and arable land. Lassaletta et al. (2009) found positive relationship ($r=0.83$) between $\text{NO}_3\text{-N}$ concentration in rivers and agricultural cover. Morgan and Kline (2011) found significant positive relationship between agricultural area and TN ($r=0.81$) and

negative relationship between forest area and TN ($r=-0.71$). A significant negative correlation was found between forest area and $\text{NH}_4\text{-N}$ concentration (Table 5.4), suggesting that the forest area can reduce $\text{NH}_4\text{-N}$ linked to soil erosion and runoff transport of sediment, thus confirming Pereira et al. (2009) and Wang et al. (2010). Wang et al. (2010) verified a high relationship between $\text{NH}_4\text{-N}$ and suspended sediment in rivers indicating a very high adsorption of this cation by the soil particles.

Table 5.4 Pearson correlation (r) between TP, $\text{PO}_4\text{-P}$, PP, TN, $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations with agriculture, pasture, forest area and peaty soil, in the period of 1991-1995 and 2009-2011.

Period	Land use	TP	$\text{PO}_4\text{-P}$	PP	TN	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$
1991-1995	Agriculture ⁽¹⁾	0.45 *			0.64 **	0.62 **	0.08
	Pasture ⁽²⁾	0.31			0.37	0.35	0.23
	Forest	-0.33			-0.16	-0.15	-0.36
	Peaty soil	0.88 ***			0.20	0.03	0.50
2009-2011	Agriculture ⁽¹⁾	0.67 ***	0.53 *	0.74 ***	0.63 **	0.67 ***	0.18
	Pasture ⁽²⁾	0.74 ***	0.72 ***	0.50 *	0.73 ***	0.68 ***	0.54 **
	Forest	-0.36	-0.17	-0.48 *	-0.17	-0.14	-0.45 *
	Peaty soil	0.34	0.69 ***	-0.53 *	0.14	0.02	0.26

* Correlation is significant at 0.05 level. ** Correlation is significant at 0.01 level.

*** Correlation is significant at 0.001 level. ⁽¹⁾ Agricultural area with more than 2% slope.

⁽²⁾ Pasture area with more than 2% slope.

5.4.3 Spatial distribution of N and P pollution according to the German LAWA classification

With water quality data of the monthly campaign and WWTPs campaign, pollution maps of N and P were carried out in Fig. 5.14 and 6.10, respectively. The maps of P pollution in winter and summer from 1991-1995 and 2009-2011 are shown in Fig. 5.14. Twenty years ago there were higher inputs of TP in winter than in summer. With the maps, it is possible to summarize the water quality for the parameter P: in 1991-1995 looking at TP concentration only 11.1 and 15.5% of the total area were classified below the class moderately polluted (class II) in winter and summer, respectively; in 2009-2011 TP concentrations are reduced and ranked in the class below moderately contaminated with 26.1 and 47.1% in winter and summer, respectively; in 2009-2011, 84.0 and 92.2% of the areas are lower than class II of

PO₄-P concentration, in winter and summer, respectively. Despite the fact that WWTPs represent high P point pollution, the dilution of P from the WWTPs along the waterways keeps the status of water quality in the subbasin lower than the level found in the effluent of WWTPs. Only the WWTP-NP located at the subbasin 9 had lower P values of the effluent of their own subbasin, indicating that only this WWTP was working well concerning nutrient elimination.

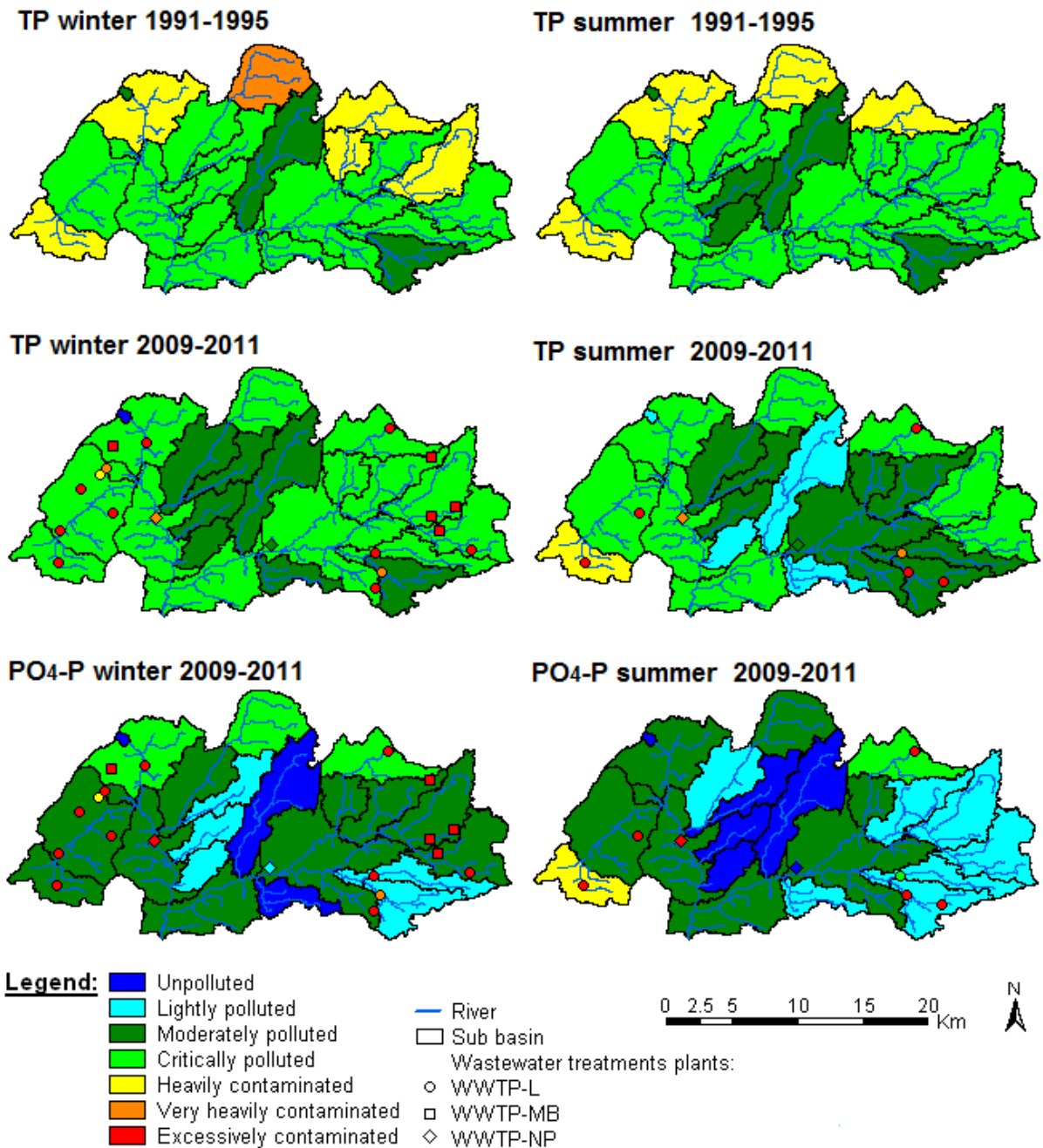


Fig. 5.14 Point and non-point P pollution maps from the upper Stör catchment.

Fig. 5.15 shows N pollution maps of the upper Stör catchment based on the data of the monthly campaign from 1991-1995 and 2009-2011 and of the WWTPs campaign. With the maps, it is possible to summarize the water quality as expressed by the N fractions: in 1991-1995, only 2.4% of the total area was classified below the class moderately polluted (class II) for TN concentrations. In 2009-2011 TN concentrations are reduced and 11.6% of the area was ranked in the class II. For $\text{NO}_3\text{-N}$, 6.8% and 24% of the area were classified below the class II in 1991-1995 and 2009-2011, respectively. Despite the low percentage ranked in class II, TN and $\text{NO}_3\text{-N}$ concentrations improved over the last 20 years. For $\text{NH}_4\text{-N}$, 49.0% and 27.8% of the area were classified below the class II in 1991-1995 and 2009-2011, respectively, indicating a decrease of water quality for this parameter.

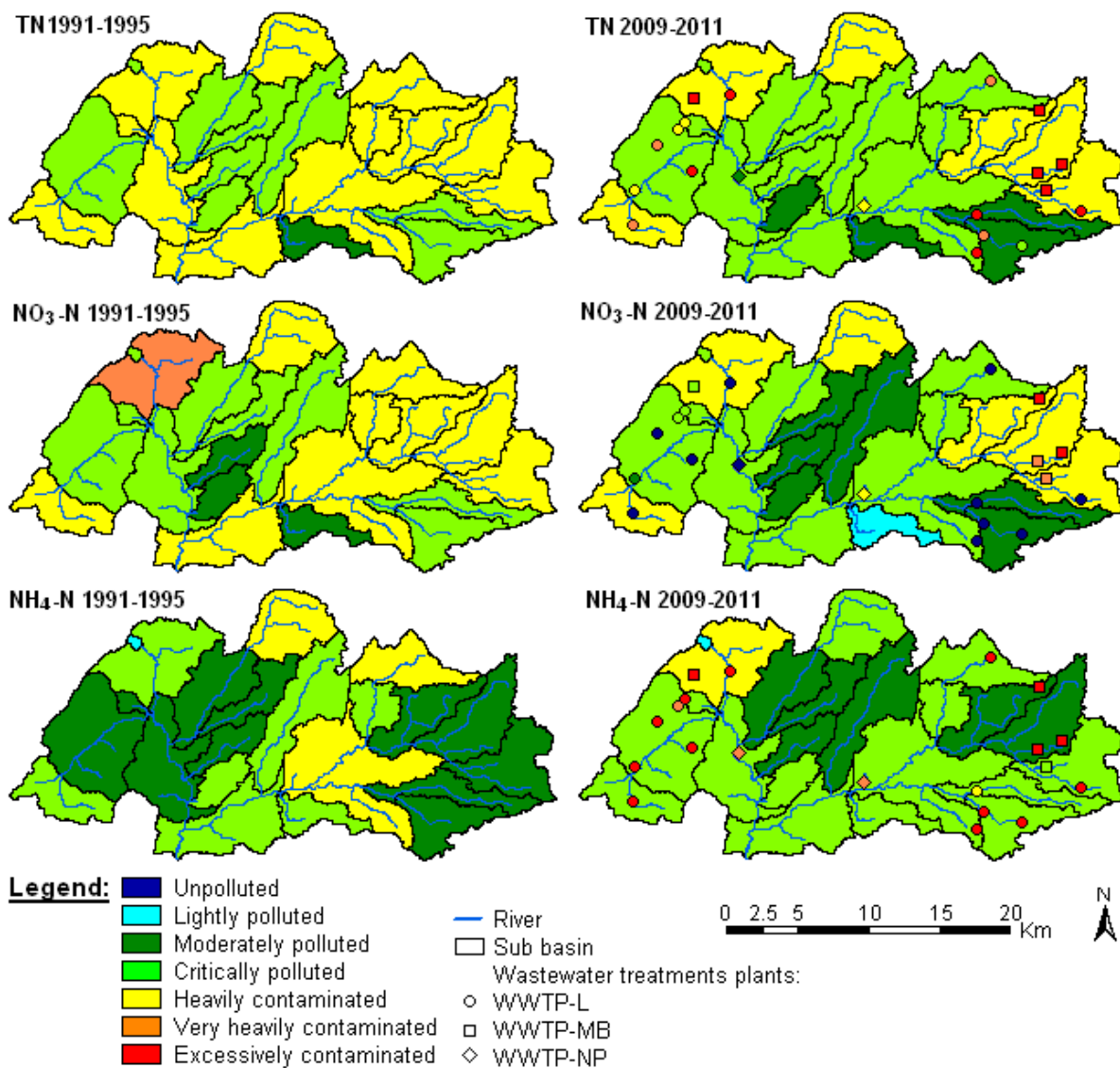


Fig. 5.15. Point and non-point N pollution maps from the upper Stör catchment.

The $\text{NO}_3\text{-N}$ of the WWTPs has lower concentration for most WWTP-L than non-point pollution sources. On the other hand, the $\text{NH}_4\text{-N}$ of WWTPs-MB shows a higher concentration than the diffuse pollution. With respect to TN, most WWTPs have higher concentrations than areas with diffuse pollution sources (Fig. 5.15), indicating that the point sources have high participation on N pollution. However, the results of Table 5.3 indicate that the point pollution (WWTPs) represent only 10.6% of the TN load in the upper Stör catchment.

5.5 Characteristics of nutrient pollution

5.5.1 Characteristics of P pollution

The fractionation of P is important to determine the predominant form of P from each water sample. Fig. 5.16a shows the P fractionation of the 21 sampling points from 2009-2011. Only the sampling points 1 and 14 have a higher fraction of $\text{PO}_4\text{-P}$. The points 3, 16 and 18 have a similar concentration of PP and $\text{PO}_4\text{-P}$, and the other sampling points have a higher concentration of PP. At the subbasins 1 and 14, the increase of the $\text{PO}_4\text{-P}$ fraction may be caused by the peat soil, which covers 26% and 21% of the area of each subbasin, respectively. According to Oliver et al. (2011), P solubility is regulated under aerobic and anaerobic conditions, especially when the link with iron (Fe) dominates the dynamics of $\text{PO}_4\text{-P}$. According to Reddy et al. (1995), $\text{PO}_4\text{-P}$ interactions with Fe can be significant in wetlands where Fe^{3+} in the oxidized zone is a sink for P, and the anaerobic zone is a source. Thus, it can explain why there is more $\text{PO}_4\text{-P}$ in summer at the sampling point 1 (Fig. 5.9). Wang et al. (2013) verified that the most important factor to sink P in wetland areas were the links Fe-P and Al-P. For these authors, riparian wetland can retain P from agricultural soil circa of 30 times more than the area of itself. According to Statham (2012) the role of sediments as sources or sink of P is highly dependent on the physical and chemical conditions prevalent at a particular time and it is thus difficult to generalize about exchanges across the sediment-water interface.

A similar fraction between PP and $\text{PO}_4\text{-P}$ at the sampling point 3 is caused by water with high $\text{PO}_4\text{-P}$ concentration coming from subbasin 1. A similar proportion between PP and $\text{PO}_4\text{-P}$ found at the sampling points 16 and 18 can also be attributed to wetland areas which cover

about 8% and 1% of these subbasin areas. The peaty soil of subbasin 18 represents only 1% of the area, but is located only a few meters from the sampling point. In addition, we observed a dark yellow “black tea” (Fig. 5.17) color in the water samples of subbasins 1, 3, 14, 16 and 18 after periods of low rainfall, which is typical for high iron and organic components. At all other points, PP concentration is higher than PO₄-P, meaning that most P is bound to the sediment and can stay in the river system for a long time according to Kerr et al. (2011). The subbasins 8, 10, 11, 13 and 19 are characterized as rural subbasins and are not influenced by wetlands and WWTPs. Subbasin 15 stands out with over 70% of forest area (Fig. 5.2b). Low proportion of PO₄-P when compared to PP concentration (Fig. 5.16) in most rural areas can be explained by the low mobility of P within the soil solution and the high adsorption of P in the soil (Sharpley, 1995; Oliver et al., 2011).

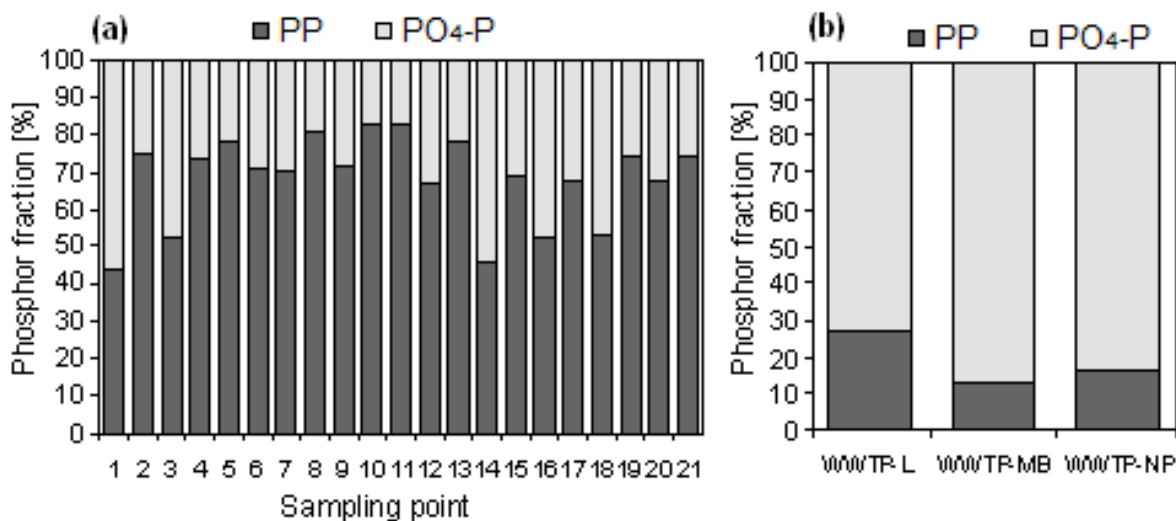


Fig. 5.16 Fractionation of P. a) P of the 21 sampling points from the period 2009-2011. b) P of the WWTP types.



Fig. 5.17 Color yellow "black tea", indicating P link with iron in subbasin 1 and 3.

The Fig. 5.18 shows a cluster dendrogram of the fraction of PP and $\text{PO}_4\text{-P}$. Two distinct clusters were found, one includes the sampling points that have a higher fraction of PP, the other includes the sampling points 1, 3, 14, 16 and 18, the subbasins influenced by natural wetlands. This results confirms wetland areas as a source of $\text{PO}_4\text{-P}$ in this lowland catchment, fact also verified by Palmer-Felgate et al. (2011) in constructed wetland in UK.

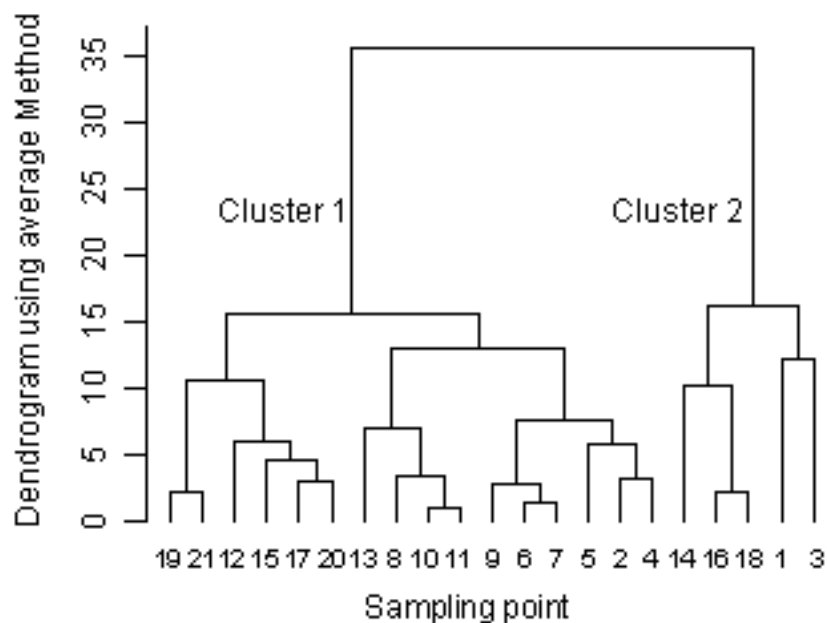


Fig. 5.18 Cluster dendrogram showing the grouping of sampling points based on fraction (%) of PP and $\text{PO}_4\text{-P}$.

The P fractionation of the three types of WWTPs in Fig. 5.16b shows that $\text{PO}_4\text{-P}$

concentration is higher than the PP concentration. This is in accordance with Puig et al. (2010), because the first step in a WWTPs is the sedimentation phase where P bound to sediment is removed. Jarvie et al. (2010) also found that wastewater was associated with soluble form of P. Jarvie et al. (2006) monitored P concentration in many lowland catchments systems in UK in order to examine the risk of eutrophication from point and diffuse sources. They evidenced that point sources (effluent from wastewater) rather than diffuse (agricultural) sources of P afford the most significant risk for river eutrophication, even in rural areas with high agricultural phosphorus losses. In addition, Jarvie et al. (2006) in UK identified that the most important form of P was the $\text{PO}_4\text{-P}$, representing 67% of the TP, which was originated from point sources. Bartley et al. (2012) verified that the urban land use had the highest concentrations of $\text{PO}_4\text{-P}$ in water bodies compared with agricultural land uses.

The results of this study are in accordance with literature, which relate that PP pollution is originated most diffuse sources with agriculture and pasture use (Morgan and Kline, 2011) and $\text{PO}_4\text{-P}$ pollution is most originated by wastewater from point sources and from wetland areas (Jarvie et al., 2006, 2010; Palmer-Felgate et al., 2011; Bartley et al., 2012).

5.5.2 Characteristics of N pollution

The fractionation of N is shown in Fig. 5.19a and Fig. 5.19b for the 21 sampling points and for the WWTPs, respectively. For the 21 sampling points, $\text{NO}_3\text{-N}$ was the major component of 56.1 to 81.5% of the TN. $\text{NH}_4\text{-N}$ had a share of only by 1.4 to 12.7 % of TN from the monthly monitoring campaign. Regarding N pollution, $\text{NO}_3\text{-N}$ is the most important form of N found in the upper Stör catchment.

For the effluent of the different WWTPs, $\text{NO}_3\text{-N}$ has a share of 2.8, 29 and 53.5% of TN, for WWTP-L, WWTP-MB and WWTP-NP, respectively. $\text{NH}_4\text{-N}$ corresponds to 80.4, 28.4 and 17.5% of TN for WWTP-L, WWTP-MB and WWTP-NP (Fig. 5.16d). These results show that the main problems with $\text{NH}_4\text{-N}$ pollution are originated by WWTPs.

The results of Fig. 5.19 indicated that the major part of $\text{NO}_3\text{-N}$ concentration comes from rural areas and the largest part of $\text{NH}_4\text{-N}$ concentration originates from WWTPs. This means that the high levels of $\text{NO}_3\text{-N}$ concentrations at the gauge station Willenscharen comes from

diffuse pollution. Morgan and Kline (2011) verified that $\text{NO}_3\text{-N}$ represented 71 to 91% of TN in a predominantly rural watershed with agricultural, pasture and forest areas.

Bu et al. (2011) verified that $\text{NH}_4\text{-N}$ dominated TN during the spring season, while $\text{NO}_3\text{-N}$ dominated during the summer and autumn seasons. For these authors, N pollution in the river was driven by nitrification and denitrification processes rather than by seasonal biological demand during the different sampling periods. In the upper Stör, same processes also occurred as can be seen at the sampling point 1 and 8, which had the minor % of $\text{NO}_3\text{-N}$ (Fig. 5.19) and had also the low values of DO (Fig. 5.12), meaning that the denitrification is high in these subbasin, consequently, $\text{NH}_4\text{-N}$ has greater proportion (Fig. 5.19).

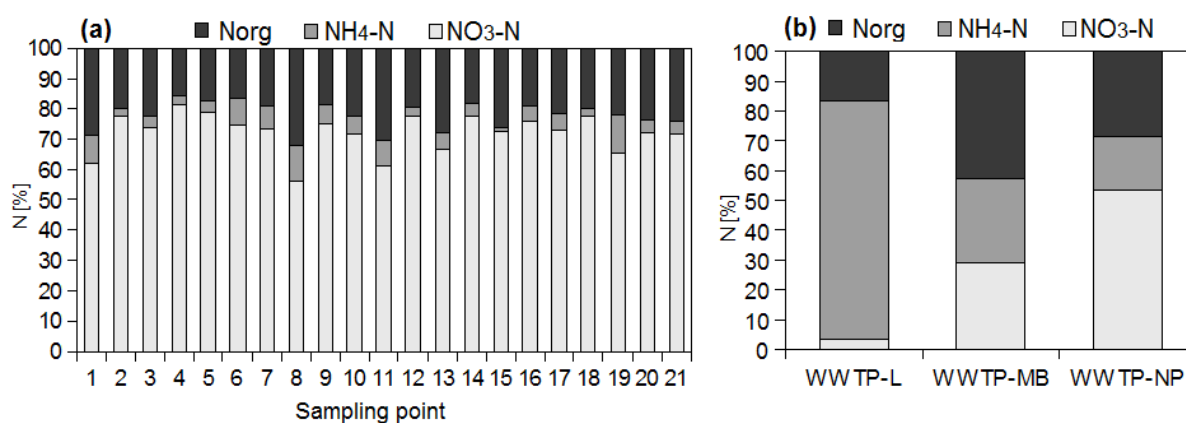


Fig. 5.19 Fractionation of N. a) N of the 21 sampling points from the period 2009-2011. b) N of the WWTP types.

5.5.3 Relation DIN/DIP

DIN/DIP ratio (average of $\text{DIN/DIP}=126$) indicates a great abundance of N in the upper river Stör throughout the year (Fig. 5.11). According to Yin et al. (2011) and Lu et al. (2011), a relation of $\text{DIN/DIP} > 16$ represents P limitation. Ma et al. (2011) verified algae blooms 8 times per year with a ration of TN/TP of 13.2 in China. Although there are high levels of N concentration, the risk of eutrophication is limited by the low concentration of DIP, especially in summer, when the potential of biological growth is high (Neal et al., 2006).

5.5.4 *Relationships between the water physicochemical parameters*

Fig. 5.20 shows the correlogram between the physicochemical parameters of daily data of the upper river Stör at the gauge Willenscharen. Two stronger statistical correlations were found, one between TP and PP ($r=0.99$), another one between TN and $\text{NO}_3\text{-N}$ ($r=0.95$). These demonstrate that PP represents the major part of TP (on average 77%) and $\text{NO}_3\text{-N}$ is the dominant part of TN (on average 78%). This fact also explains the similarity of the time series of TP and PP and of TN and $\text{NO}_3\text{-N}$ in Fig. 5.8. TSS had also a strong positive correlation with TP and PP showing that P is strongly bound to soil particles. Tao et al. (2010) also verified a strong correlation between TP and TSS ($r=0.97$). This means that P is originated especially from transport of sediment by erosion from agricultural areas and from riverbank erosion. Kiesel et al. (2009) modeling sediment load with the SEPAL model (Sediment Entry Pathway Assessment in Lowlands) in the German lowland Kielstau, verified that the proportion of sediment input into the river were 71% from river banks, 15% from agricultural drains and 14% from adjacent fields.

Discharge (Q) had a significant positive correlation with all N and P parameters. Statistically negative correlations were found between WT and all other physicochemical parameters, confirming the effect of seasonality verified in the Fig. 5.11. In the other hand, the strong positive correlation between TSS and TP means that P is adsorbed to soil particles, which can work as a sink of P in stream systems, as observed by Jarvie et al. (2006) and Cao et al. (2011b). In lowland, the channel erosion consists of streambed and stream bank erosion (Aksoy and Kavvas, 2005; Kiesel et al., 2009).

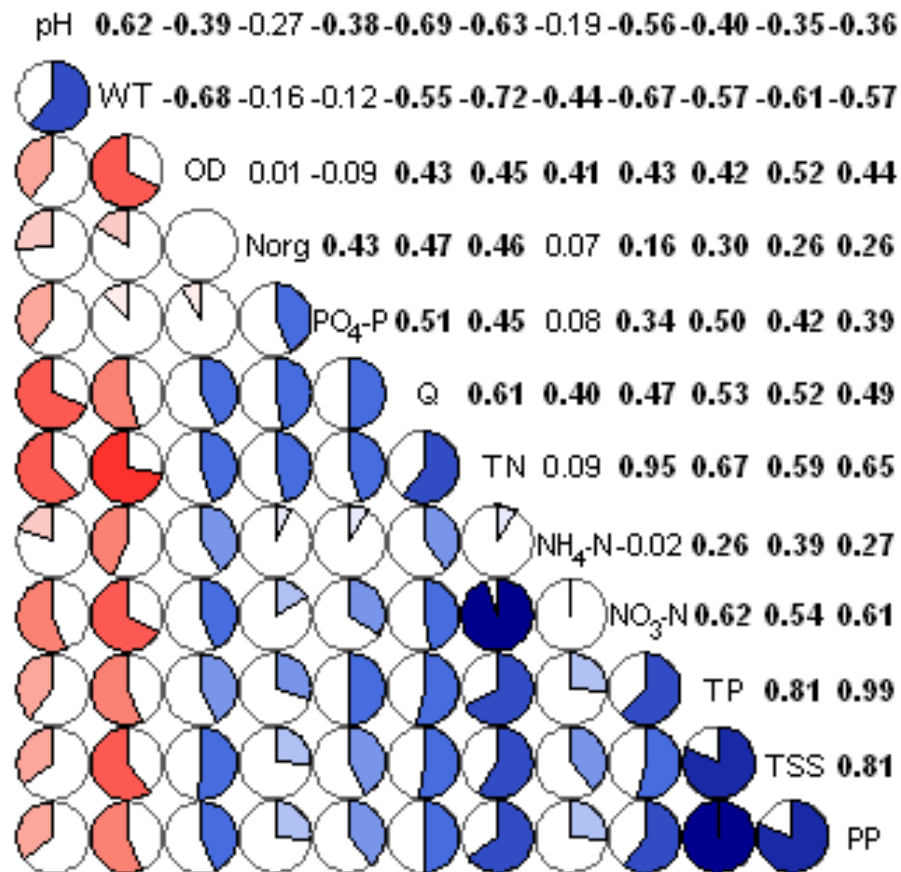


Fig. 5.20 Correlogram between the physicochemical parameters of the upper river Stör at the gauge Willenscharen. Bold numbers represent statistical significant correlation ($p < 0.001$).

The higher TSS concentration in winter may be related to a higher erosion potential, when many agricultural fields are uncovered (Fig. 5.6). In addition, water absorption and nutrient uptake by terrestrial plants and aquatic macrophytes during the winter are lower (Schulz et al., 2003; Evans and Johnes, 2004; Desmet et al., 2011), causing a higher runoff flow which in turn leads to surface and riverbank erosion (Fig. 5.21). In summer the riparian vegetation also plays an important role in the minimization of the TSS transport into the river (McKergow et al., 2003) and the macrophyte stands represent an important P sink in water bodies (Kleeberg et al., 2010).



Fig. 5.21 Riverbank erosion in the River Stör at the gauge station Willenscharen (April 2011).

5.5.5 *Autocorrelation analysis*

Autocorrelation (AC) plots of PCP, Q, TSS, TP, PP, PO₄-P, TN, NO₃-N and NH₄-N are shown in Fig. 5.22. First it is necessary to analyze the time series of PCP and the time series of Q. The time series of PCP shows a very sharp decline in the autocorrelation curve indicating a very unpredictable behavior. On the other side, the autocorrelation curve of the time series of Q is quite high, being statistically significant up to 45 days. This indicates that discharge is not much influenced by rainfall but by groundwater flow, which is characteristic of lowland catchments. Bieger et al. (2012a) studying a mountainous catchment in China observed a significant autocorrelation of Q of 10 days.

The AC of TSS can be divided into two stages. One has a very steep decline up to four days, showing a similar trend as PCP. The other stage has a slower decrease, similar to the time series of Q. Therefore it indicates that TSS is related to the effects of precipitation, as a result of the surface runoff process. AC of TP, PP and PO₄-P follow the same trend as the AC of TSS. This fact was expected because of the high correlation between these parameters (Fig. 5.20).

Normally hilly catchments have higher P losses and soil erosion (Sileika et al., 2005, Hu et al., 2013). However, the high correlation of PP and TP with TSS (Fig. 5.20, $r=0.81$ for both) and the sharp initial curve of the AC of PP and TP (Fig. 5.22) confirm the influence of surface processes such as runoff and soil erosion on the P pollution for this lowland catchment. Even in rivers with a "good status" (EC, 2000) of $\text{PO}_4\text{-P}$ throughout the year (Fig. 5.4 and Fig. 5.5), TSS can stay high for a long time (Walling and Amos, 1999, Kerr et al., 2011) and plays an important role as source of $\text{PO}_4\text{-P}$ in water bodies (Pereira et al., 2009). According to Bieger et al. (2012b), the combination of increasing inputs of sediment with P and reduced flow velocities induce prolonged residence times of water inducing a higher risk of eutrophication.

The AC of $\text{NH}_4\text{-N}$ follows a similar trend as the one of TSS, with an initially stronger decline and subsequently a slower decrease. AC of TN and $\text{NO}_3\text{-N}$ are higher and longer than the AC of Q, being statistically significant up to 78 and 74 days respectively. The high AC of $\text{NO}_3\text{-N}$ (Fig. 5.22) suggests that there is a constant transport of $\text{NO}_3\text{-N}$ concentration via leaching, which may be explained by the following: (i) a large amount of N stored in the soil has a slow but continuous mineralization rate of the organic matter (Grimvall et al., 2000; Stålnacke et al., 2004; Sileika et al., 2006) and (ii) it is due to the catchment buffering potential (Cherry et al., 2008). Alewell et al. (2004) found a strong AC of NO_3 in a semi-natural catchment with predominantly forest and pasture areas. In agricultural catchments, this behavior should be different due to peaks of NO_3 concentration after fertilizer application (Tisseuil et al., 2008). However, peaks with higher levels of $\text{NO}_3\text{-N}$ at the time of fertilizer application were not observed. In addition, the AC of $\text{NO}_3\text{-N}$ was really high. This means that $\text{NO}_3\text{-N}$ concentrations are linked to the constant groundwater flow in the studied rural lowland catchment.

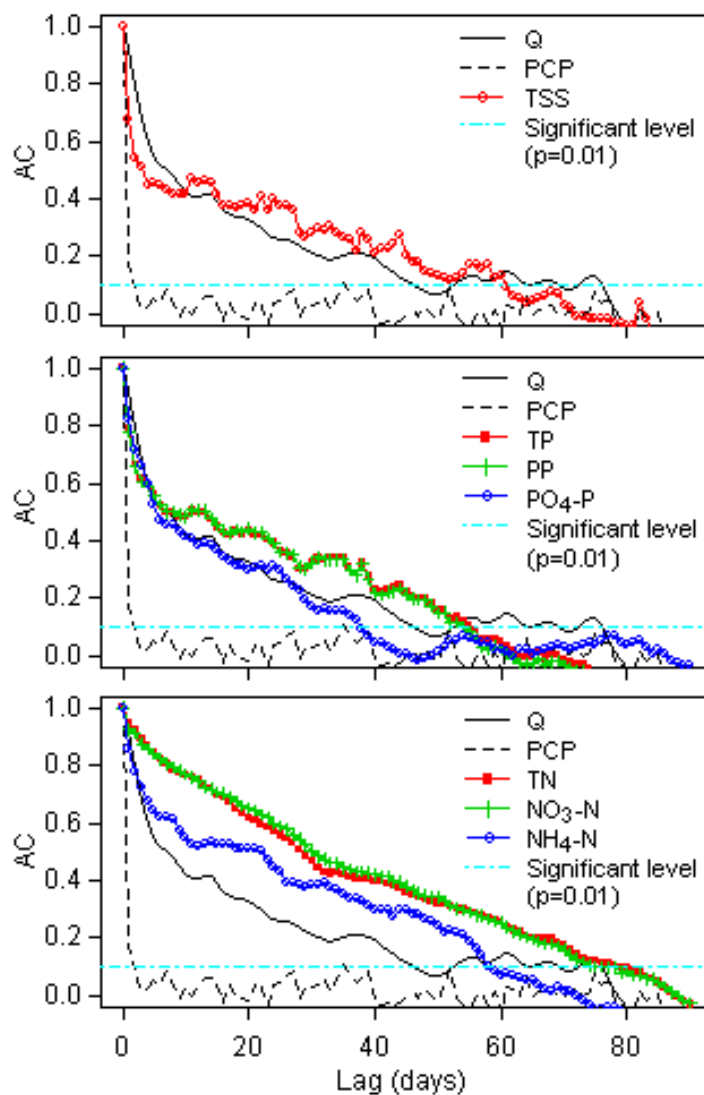


Fig. 5.22 Autocorrelation (AC) plots from PCP, Q, TSS, TP, PP, PO₄-P, TN, NO₃-N and NH₄-N concentrations of the upper river Stör at the gauge Willenscharen.

5.6 Prediction of water balance, sediment and nutrient load using the ecohydrological SWAT model

5.6.1 Modeling of hydrological processes

The calibration and validation of daily discharge were successfully achieved as can be seen graphically in Fig. 5.23 and Fig. 5.24, respectively, as well as from the performance measures shown in Table 5.5. The measured and simulated daily discharge from the calibration period (January 1st 2006 - December 31st 2011) at the discharge gauge stations Padenstedt, Sarlhusen

and Willenscharen are shown in Fig. 5.23. Daily discharge calibration showed an underestimation of simulated data at gauges Sarlhusen and Willenscharen, with lower peaks compared with the measured data set, specially in winter months. The underestimation of discharge in winter was also observed by Schmalz et al. (2007) and Lam et al. (2012) in rural lowland areas in northern Germany with SWAT modeling. Nevertheless, at the three gauge stations, the calibration period showed NSE and R^2 greater than 0.80, indicating a very good agreement between measured and simulated daily discharge (Table 5.5). Daily discharge validation (January 1st 2000 - December 31st 2005) was done for the same three discharge gauge stations, as can be seen in Fig. 5.24. An underestimation of simulated data can be observed at the three discharge gauge stations (Fig. 5.24) indicated by positive values of PBIAS (Table 5.5). Daily discharge validation was also carried out successfully, with NSE and R^2 greater than 0.79 and 0.80, respectively.

The main parameters used for discharge calibration were listed in Table 4.9. The main processes calculated by SWAT model are graphically represented in Fig. 5.25, which are predominantly influenced by groundwater (52.8%) and drainage flow (34.3%) (Table 5.6). Surface runoff and lateral flow contributed only with 5.2 and 7.7 % (Table 5.6) to the flow discharge at the outlet of the upper Stör catchment (Willenscharen).

Daily discharge simulations using the SWAT model have reached success worldwide (Pisinaras et al., 2010; Laurent and Ruelland, 2011; Andrade et al., 2013). Usually, in lowland catchments, the NSE is less than 0.80. Hesse et al. (2008) using the ecohydrological model SWIM in a lowland rural catchment in Germany achieved only NSE = 0.60 in the simulation of daily discharge during 2001 and 2005. Lam et al. (2009) using the SWAT model obtained a good agreement between simulated and measured daily discharge in the lowland Kielstau catchment in Schleswig-Holstein, Germany, with a NSE and R^2 of 0.76 and 0.88 for the calibration period and 0.75 and 0.92 for the validation period, respectively. In the same catchment, Kiesel et al. (2010) achieved a NSE of 0.78 for the daily calibration (1999-2003) and validation (2004-2009). The quality of input data is very important for obtaining success in modeling. Dobsclaff (2005) simulated discharge in the upper Stör achieved NSE = 0.76 for the daily discharge calibration, using a DEM resolution map of 50m. In this study, a DEM map with 5 m resolution was used. In a catchment with a total difference of 90 m of elevation (Fig. 3.1), a high resolution data set can influence on the final results. Thus, adequate

performance of the model is due to the quality of data used to run the model as well the good performance of the calibration. Also, using the SWAT-CUP software (Abbaspour, 2011) for the discharge calibration has assisted to define suitable parameters simultaneously for the three gauge discharge stations.

5.6.2 *Modeling of sediment load*

The sediment modeling was carried out in daily and monthly time steps simultaneously. The daily sediment calibration (August 8th 2010 - July 10th 2011) and validation (November 1st 2009 - July 7th 2010) from the outlet of the upper Stör catchment (Willenscharen) are graphically represented in Fig. 5.26. The monthly sediment calibration (August 2010 - July 2011) and validation (November 2009 - July 2010) from the outlet Willenscharen are shown in Fig. 5.27. Underestimation from the simulated sediment data was verified in the winter period and overestimation can be observed in summer (Fig. 5.26 and Fig. 5.27). The daily calibration and validation were carried out with NSE of 0.52 and 0.55, respectively (Table 5.7). Daily sediment simulation was overestimated in the calibration period (PBIAS = -16.5, Table 5.7) and underestimated in the validation period (PBIAS = 7.0, Table 5.7).

Other studies also showed low values of NSE for daily sediment simulation with SWAT model (Wu and Chen, 2012; Lam et al., 2011; Kühling, 2011; Oeurng et al., 2011). Wu and Chen (2012) simulating sediment in the East River Basin in China with the SWAT model achieved NSE of 0.54 and 0.44 for the daily time steps, respectively for the calibration (1973 - 1980) and validation (1981 - 1988) period. Oeurng et al. (2011) simulating daily sediment load in a mountainous catchment in France found R² value of 0.51 and NSE of 0.31. In the lowland Kielstau catchment, Lam et al. (2011) found NSE of 0.57 and 0.58 for daily sediment calibration and validation, respectively. Kühling (2011) also simulating daily sediment in the lowland Kielstau catchment, achieved only NSE of 0.45 and 0.27 for the calibration and validation period, respectively.

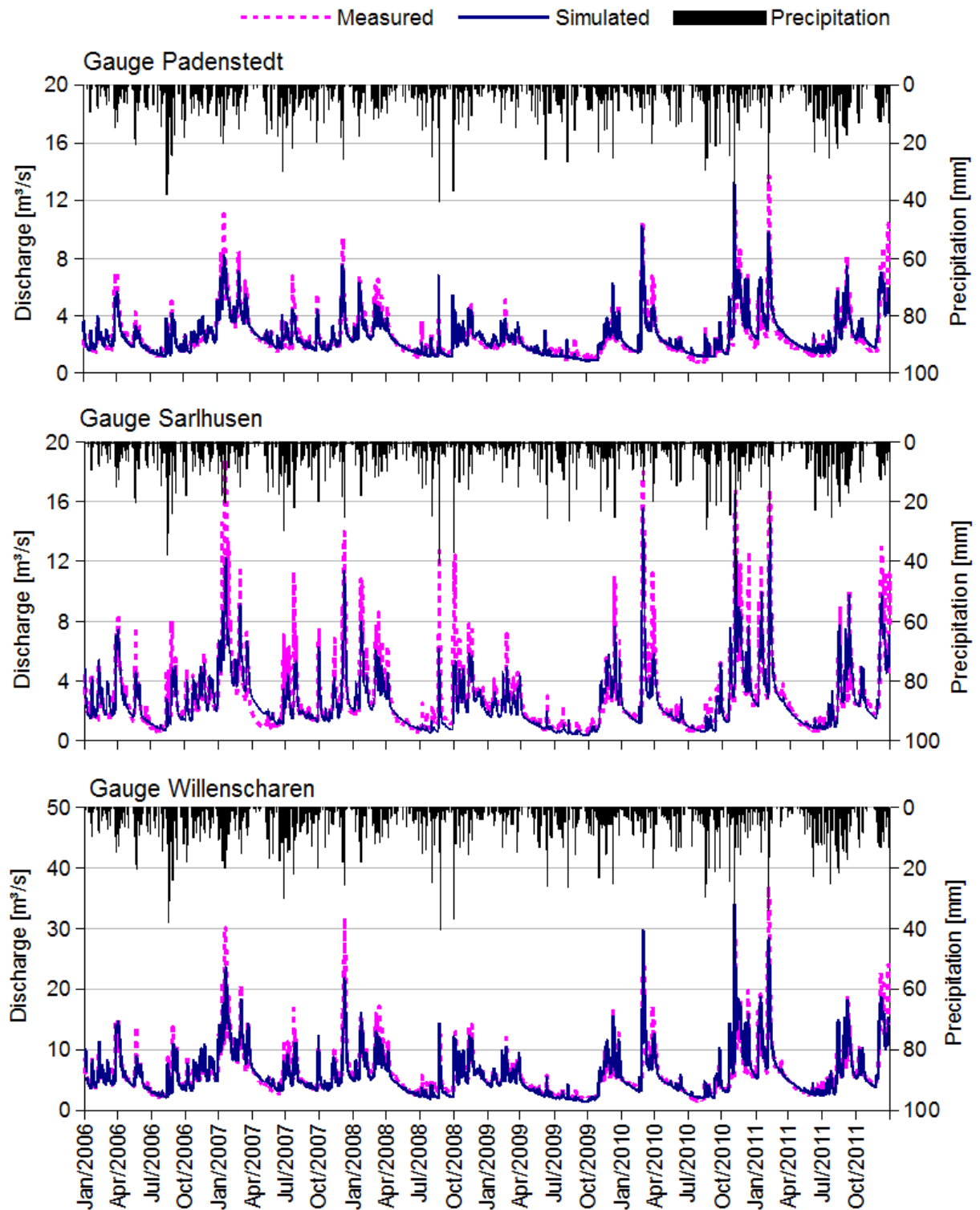


Fig. 5.23 Measured and simulated daily discharge at the gauge stations Padenstedt, Sarlhusen and Willenscharen over the calibration period (2006-2011).

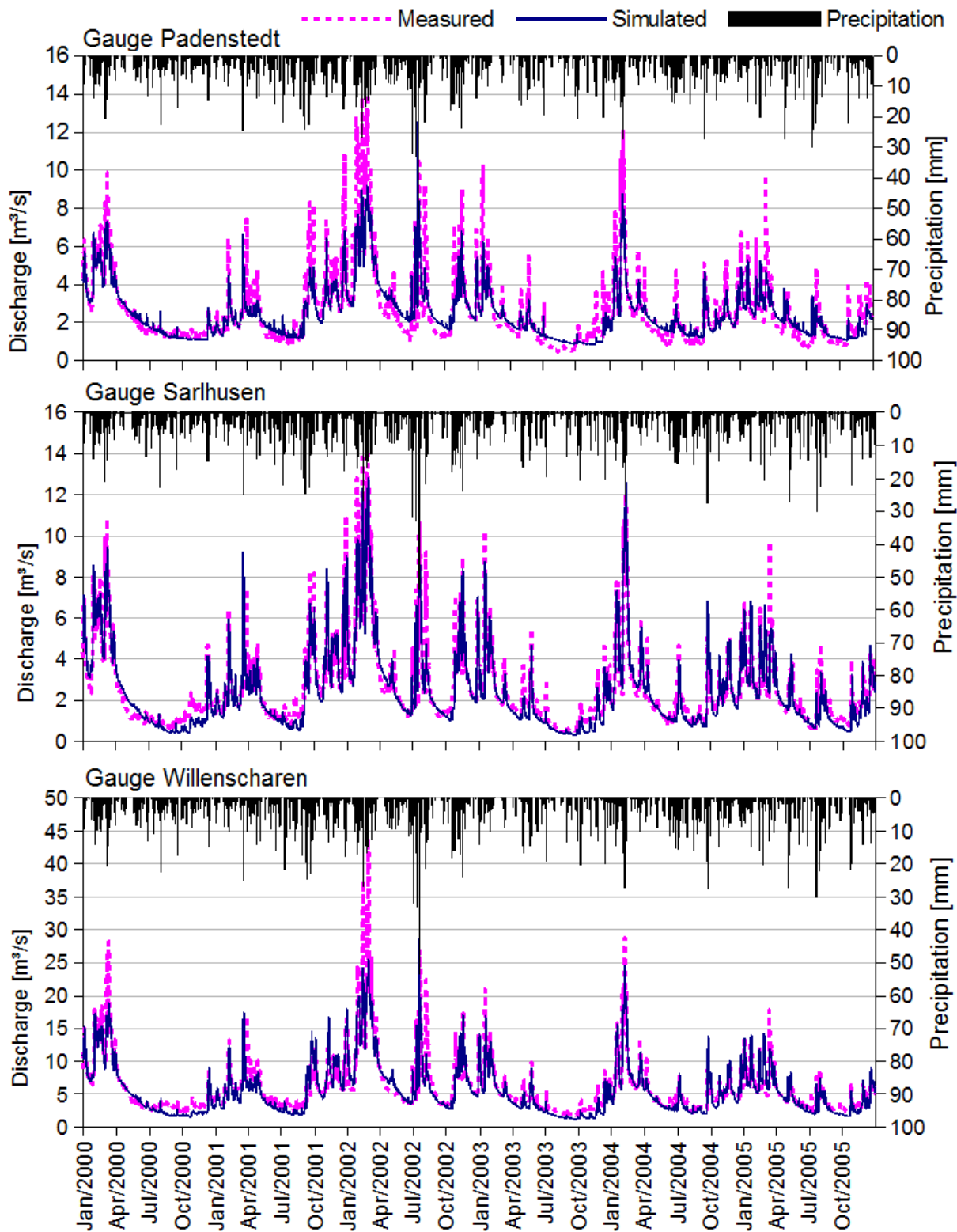
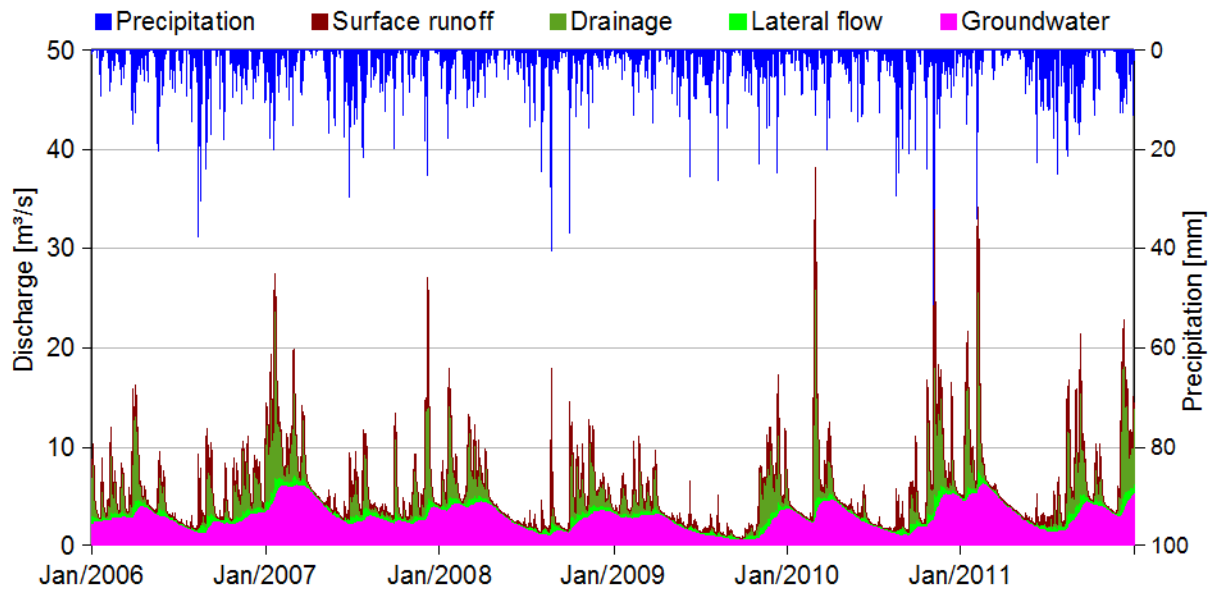


Fig. 5.24 Measured and simulated daily discharge at the gauge stations Padenstedt, Sarlhusen and Willenscharen over the validation period (2000-2005).

Table 5.5 Performance rating parameters of the daily discharge over the calibration and validation periods of the SWAT modeling.

Gauge	Q_{obs} [m^3/s]	Q_{sim} [m^3/s]	R^2	NSE	PBIAS	RSR
Calibration period (2006-2011)						
Padenstedt	2.52	2.58	0.85	0.84	-2.2	0.39
Sarlhusen	2.82	2.64	0.84	0.83	6.7	0.42
Willenscharen	5.99	5.92	0.86	0.86	1.1	0.38
Validation period (2000-2005)						
Padenstedt	2.57	2.48	0.82	0.79	3.4	0.46
Sarlhusen	2.52	2.47	0.86	0.85	2.3	0.38
Willenscharen	5.97	5.61	0.84	0.83	6.1	0.41

**Fig. 5.25** Graphic representation of discharge components calculated by SWAT model during the calibration period at the gauge station Willenscharen.**Table 5.6** Discharge components calculated by SWAT model during the calibration period at the gauge station Willenscharen.

Discharge components	Percentage [%]
Surface runoff	5.2
Lateral flow	7.7
Drainage flow	34.3
Groundwater	52.8

Nevertheless, the monthly sediment calibration showed NSE and R^2 equal to 0.90 and 0.92, respectively (Table 5.8). Monthly sediment validation presented values of 0.66 and 0.76 for NSE and R^2 respectively. According to Moriasi et al. (2007), these results indicate a very good and good performance for the sediment calibration and validation, respectively. Other studies also show higher values of NSE for monthly sediment modeling. Shen et al. (2009), modeling monthly sediment achieved NSE of 0.68 and 0.82 for the calibration and validation period at the Three Gorges Reservoir Area in China. Wu and Chen (2012) found NSE of 0.69 and 0.67 for the calibration and validation period, respectively. Panagopoulos et al. (2011) in Greece found R^2 of 0.81 and 0.83, NSE of 0.38 and 0.46 of the calibration and validation, respectively.

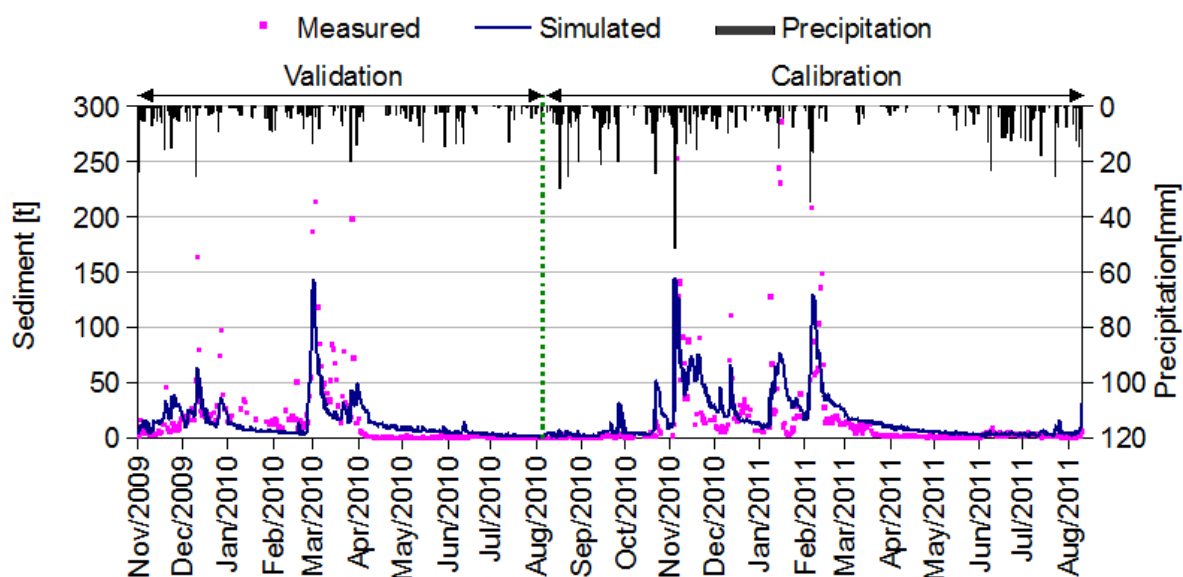


Fig. 5.26 Measured and simulated daily sediment load at the gauge station Willenscharen over the calibration and validation period.

Table 5.7 Performance rating parameters of the daily sediment load over the calibration and validation period at the gauge station Willenscharen.

Period	Sed _{obs} [t/d]	Sed _{sim} [t/d]	R^2	NSE	PBIAS	RSR
Calibration	15.0	17.5	0.54	0.52	-16.5	0.69
Validation	15.4	14.4	0.61	0.55	7.0	0.67

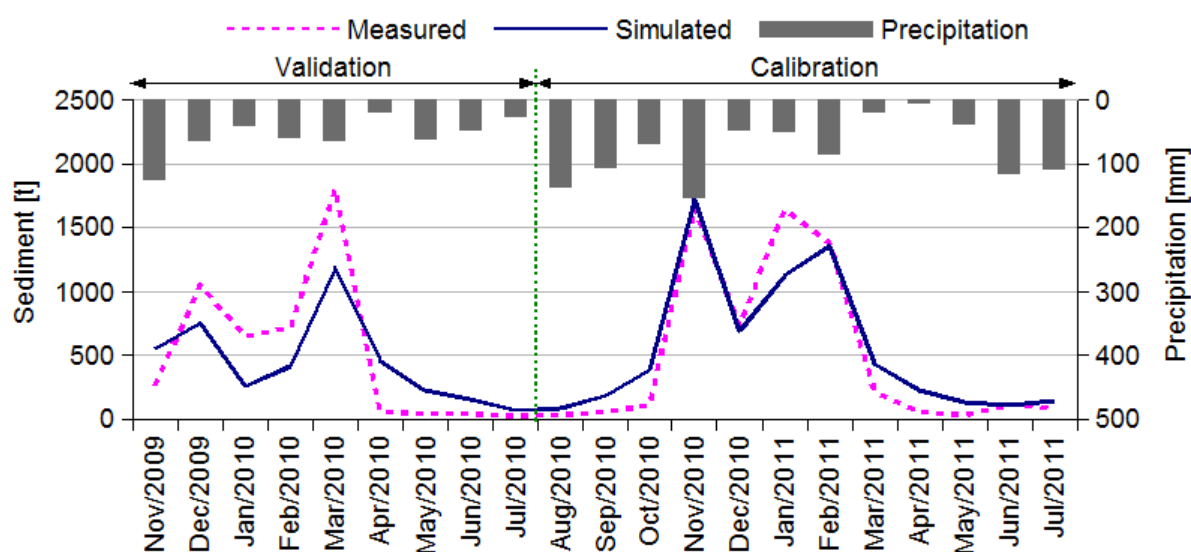


Fig. 5.27 Measured and simulated monthly sediment load at the gauge station Willenscharen over the calibration and validation period.

Table 5.8 Performance rating parameters of the monthly sediment load over the calibration and validation period at the gauge station Willenscharen.

Period	Sed _{obs} [t/month]	Sed _{sim} [t/month]	R ²	NSE	PBIAS	RSR
Calibration	506	547	0.92	0.90	-8.1	0.31
Validation	514	451	0.76	0.66	12.3	0.58

5.6.3 Modeling of nutrient load

To perform the SWAT modeling of N and P the following factors were taken into account: 1) the results of daily water quality at the gauge station Willenscharen (item 5.2.2) showed that PP represents the major part of TP (on average 77%) and NO₃-N is the dominant part of TN (on average 78%); 2) with regard to P, the SWAT model allows differentiate between organic P and mineral P (Neitsch et al., 2010, 2011); 3) in relation to N, the SWAT model is capable to simulated organic N, NO₃-N, NO₂-N and NH₄-N (Neitsch et al., 2010, 2011); 4) NO₃-N and TP represented 93.7 and 91.6% of diffuse pollution, respectively, in the upper Stör catchment during 2009-2011 (Table 5.3). Therefore in this study, TP and NO₃-N loads were simulated because these represent the most important forms of diffuse pollution in the upper Stör catchment and are possible to modeled with the SWAT model.

As the goal of the modeling is to explain the evolution of water quality with the model as well as the availability of data set of the historical water quality campaign was monthly (Ripl et al., 1996), it was decided to run daily and monthly simulation of sediment and nutrient load. The major part of papers have used monthly time steps to simulate nutrients with SWAT model (Chaplot et al., 2004; Tong and Naramngam, 2007; Lee et al., 2010; Tuppad et al., 2010). Fewer number of studies have been successful in N and P daily simulation with SWAT (Schmalz et al., 2008b; Lam et al., 2009). The studies with good performance of daily simulation of nutrient load with the SWAT model usually occur in small catchments, which have a consistent hydrologic data set and a represented data set of land use and management operations.

5.6.3.1 Modeling of NO₃-N load

Fig. 5.28 shows the daily calibration (August 8th 2010 - August 10th 2011) and validation period (August 8th 2009 - August 7th 2010) of NO₃-N load from the gauge stations Padenstedt, Sarlhusen and Willenscharen. The results of daily NO₃-N load simulation showed R² between 0.63 - 0.95 for the calibration and 0.60 - 0.87 for the validation, NSE between 0.62 - 0.94 in calibration and 0.50 - 0.78 in validation period (Table 5.9). Fig. 5.29 shows the monthly calibration (August 2010 - July 2011) and validation period (August 2009 - July 2010) of NO₃-N load from gauge stations Padenstedt, Sarlhusen and Willenscharen.

Jamshidi et al. (2010) simulating daily NO₃-N load in a mountainous catchment in Iran achieved NSE of 0.55 and 0.36 for the calibration and validation period, respectively. For monthly simulation, these authors found better NSE, 0.82 and 0.57 for calibration and validation, respectively. Lam et al. (2009) studying daily NO₃-N load at the lowland Kielstau, found NSE of 0.64 and 0.50 for the calibration and validation, respectively. Pisinaras et al. (2010) simulating daily NO₃-N load with SWAT using monthly measured data obtained very good calibration, with NSE varying between 0.86 to 0.90 for four gauging stations in a mountainous catchment in Greece. The results of performance of daily NO₃-N simulation of the gauge stations Padenstedt and Sarlhusen (Table 5.9), where monthly measurement data for the calibration and validation of the model was used, also showed very good performance (Moriassi et al., 2007). However, for the daily calibration with daily measured data, the SWAT modeling does not achieve such a good performance, as can be seen at the results of daily

NO₃-N simulation of the gauge Willenscharen (Fig. 5.28 and Table 5.9).

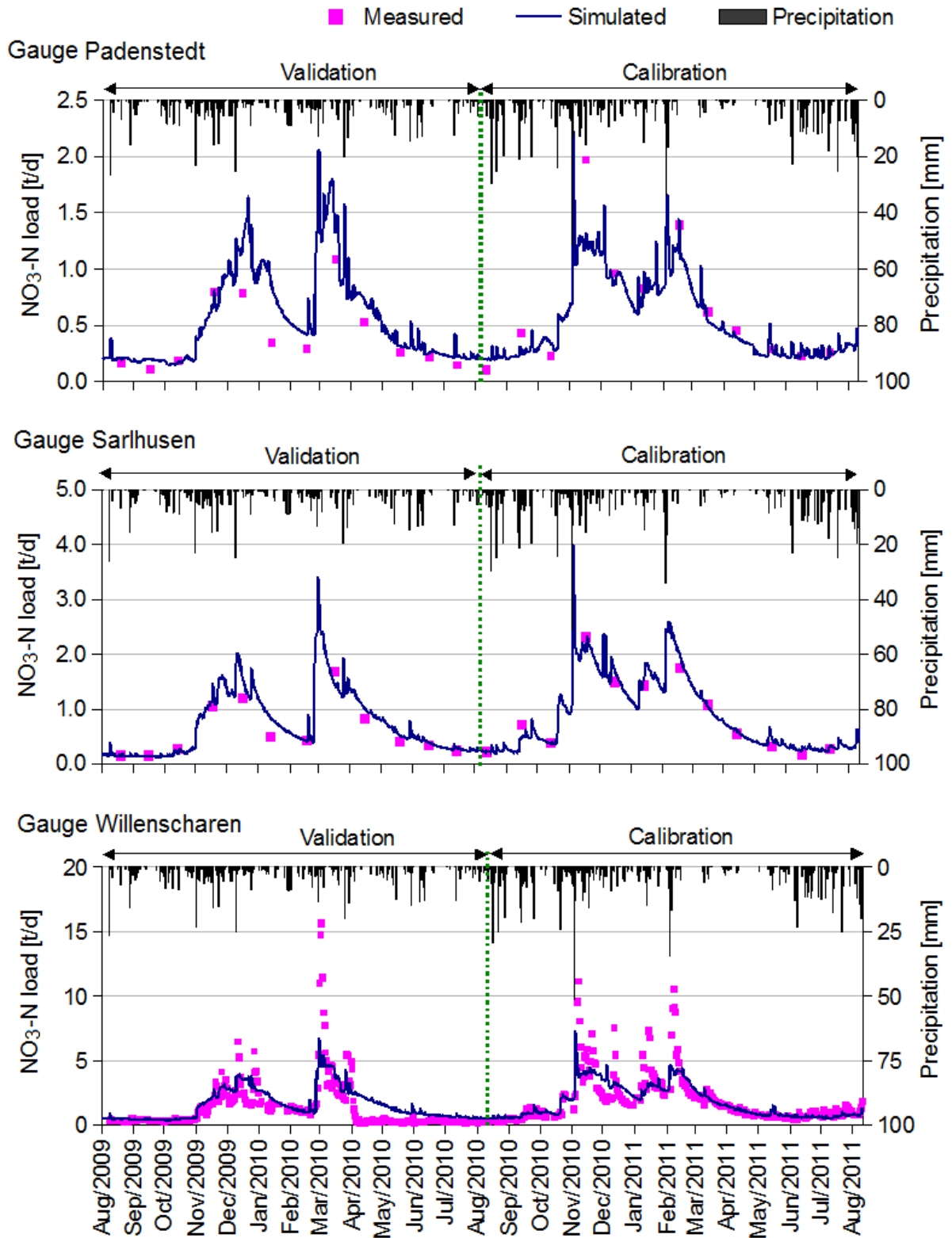


Fig. 5.28 Measured and simulated daily NO₃-N load at the gauges Willenscharen over the calibration and validation period.

The daily NO₃-N load simulation of the gauge station Willenscharen showed underestimation of various peaks in the calibration and validation periods, however at the calibration period, PBIAS = 0.2, indicates a slight overestimation of NO₃-N load in the simulated data. The monthly NO₃-N load modeling showed underestimation in winter months in the calibration, represented by PBIAS values 19.4, 7.7 and 0.2, respectively for gauges Padenstedt, Sarlhusen and Willenscharen (Table 5.10). The validation of NO₃-N load showed different behavior, with overestimation in winter months. The results of monthly NO₃-N load simulation achieved R² between 0.86 - 0.96 for the calibration and 0.84 - 0.94 for the validation, NSE was between 0.69 - 0.92 in calibration and 0.77 - 0.86 in validation period (Table 5.10). According to Moriasi et al. (2007), these results indicated a performance ranging from good to very good for NO₃-N modeling with the SWAT model.

Table 5.9 Performance rating parameters of the daily NO₃-N load at the gauges Padenstedt, Sarlhusen and Willenscharen over the calibration and validation period.

Gauge station	NO ₃ -N _{obs} [t/d]	NO ₃ -N _{sim} [t/d]	R ²	NSE	PBIAS	RSR
Calibration period						
Padenstedt	0.64	0.57	0.86	0.79	11.8	0.46
Sarlhusen	0.88	0.91	0.95	0.94	-3.3	0.23
Willenscharen	1.82	1.73	0.63	0.62	5.0	0.61
Validation period						
Padenstedt	0.41	0.55	0.86	0.50	-36.1	0.71
Sarlhusen	0.59	0.69	0.87	0.78	-17.4	0.47
Willenscharen	1.23	1.53	0.60	0.56	-24.3	0.66

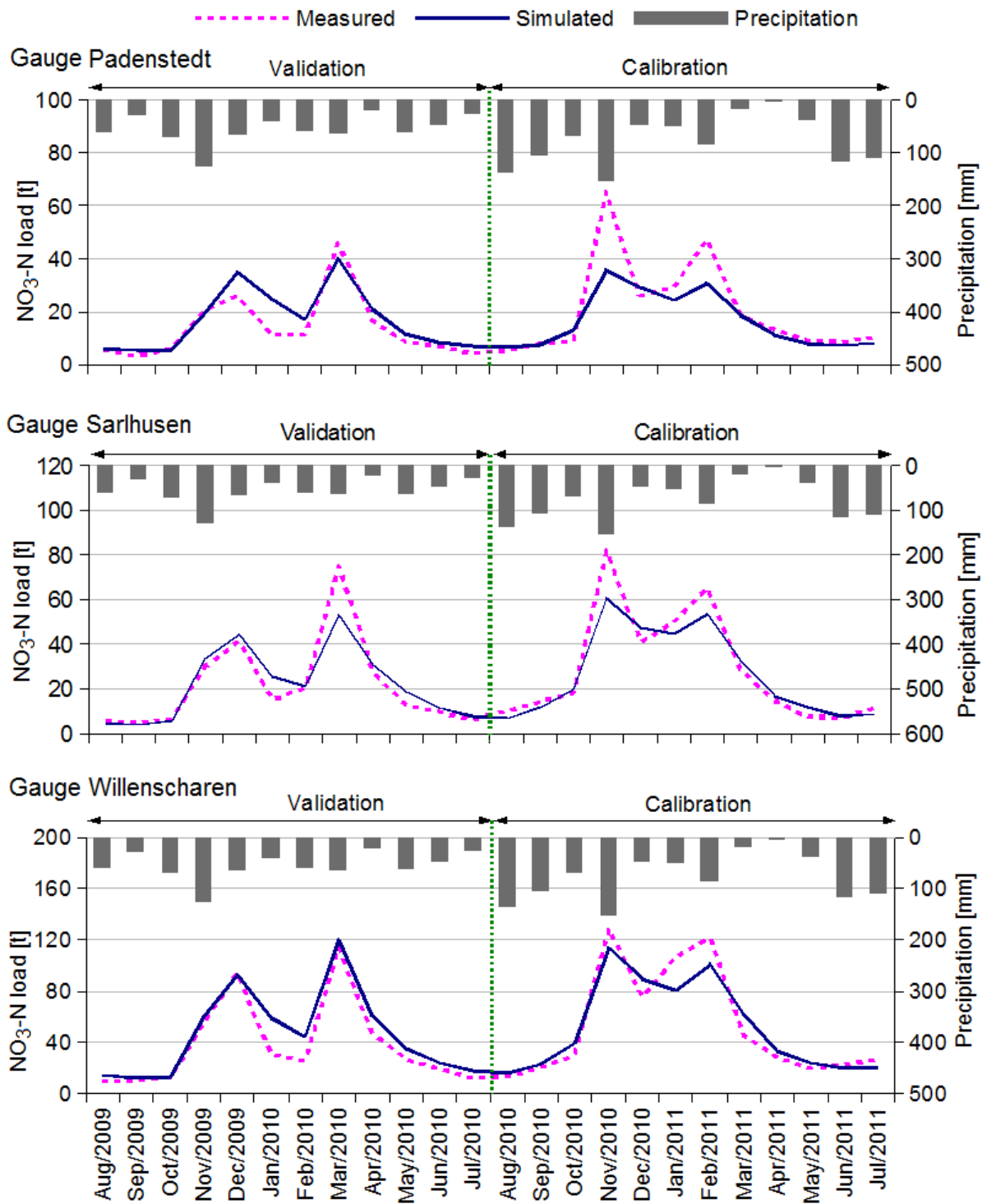


Fig. 5.29 Measured and simulated monthly NO₃-N load at the gauges Padenstedt, Sarlhusen and Willenscharen over the calibration and validation period.

Table 5.10 Performance rating parameters of the monthly NO₃-N load at the gauges Padenstedt, Sarlhusen and Willenscharen over the calibration and validation period.

Gauge station	NO ₃ -N _{obs} [t/month]	NO ₃ -N _{sim} [t/month]	R ²	NSE	PBIAS	RSR
Calibration period						
Padenstedt	20.8	16.8	0.86	0.69	19.4	0.56
Sarlhusen	29.2	27.0	0.93	0.90	7.7	0.32
Willenscharen	53.2	53.1	0.92	0.92	0.2	0.29
Validation period						
Padenstedt	13.9	16.8	0.84	0.77	-20.9	0.45
Sarlhusen	21.4	21.8	0.88	0.86	-2.2	0.37
Willenscharen	38.2	47.3	0.94	0.86	-24.0	0.37

5.6.3.2 Modeling of TP load

Fig. 5.30 shows the daily calibration (August 8th 2010 - August 10th 2011) and validation period (August 8th 2009 - August 7th 2010) of TP load from gauge stations Padenstedt, Sarlhusen and Willenscharen. The performance rating of daily TP load simulation (Table 5.11) show worse values than daily NO₃-N simulation (Table 5.9), with R² between 0.30 - 0.62 for the calibration and 0.29 - 0.74 for the validation, NSE between 0.24 - 0.55 in calibration and 0.19 - 0.72 in validation period (Table 5.11). For all gauge stations, simulated daily TP load was underestimated, as can be observed with positive PBIAS values at Table 5.11. The gauge station Willenscharen, which had daily measured data, the SWAT model showed underestimation in some peaks of TP load. In the other hand, for the gauge stations Padenstedt and Sarlhusen, various simulated peaks of TP were not intercepted by the measured data because these gauges had only monthly measured data from water quality.

The monthly TP load of the calibrated (August 2010 - July 2011) and validated period (August 2009 - July 2010) from gauge stations Padenstedt, Sarlhusen and Willenscharen are shown in Fig. 5.31. The peaks of TP load were underestimated in the three gauging during the calibrated time, but during the validated time, TP load was overestimated at all gauge stations. In general, the monthly simulation of TP (Table 5.11) had a better performance than the daily simulation (Table 5.12). Considering the index parameters presented in Table 5.12 and the

performance values recommended by Moriasi et al. (2007) (Table 4.2), monthly TP load modeling with SWAT can be ranked, at least, as satisfactory.

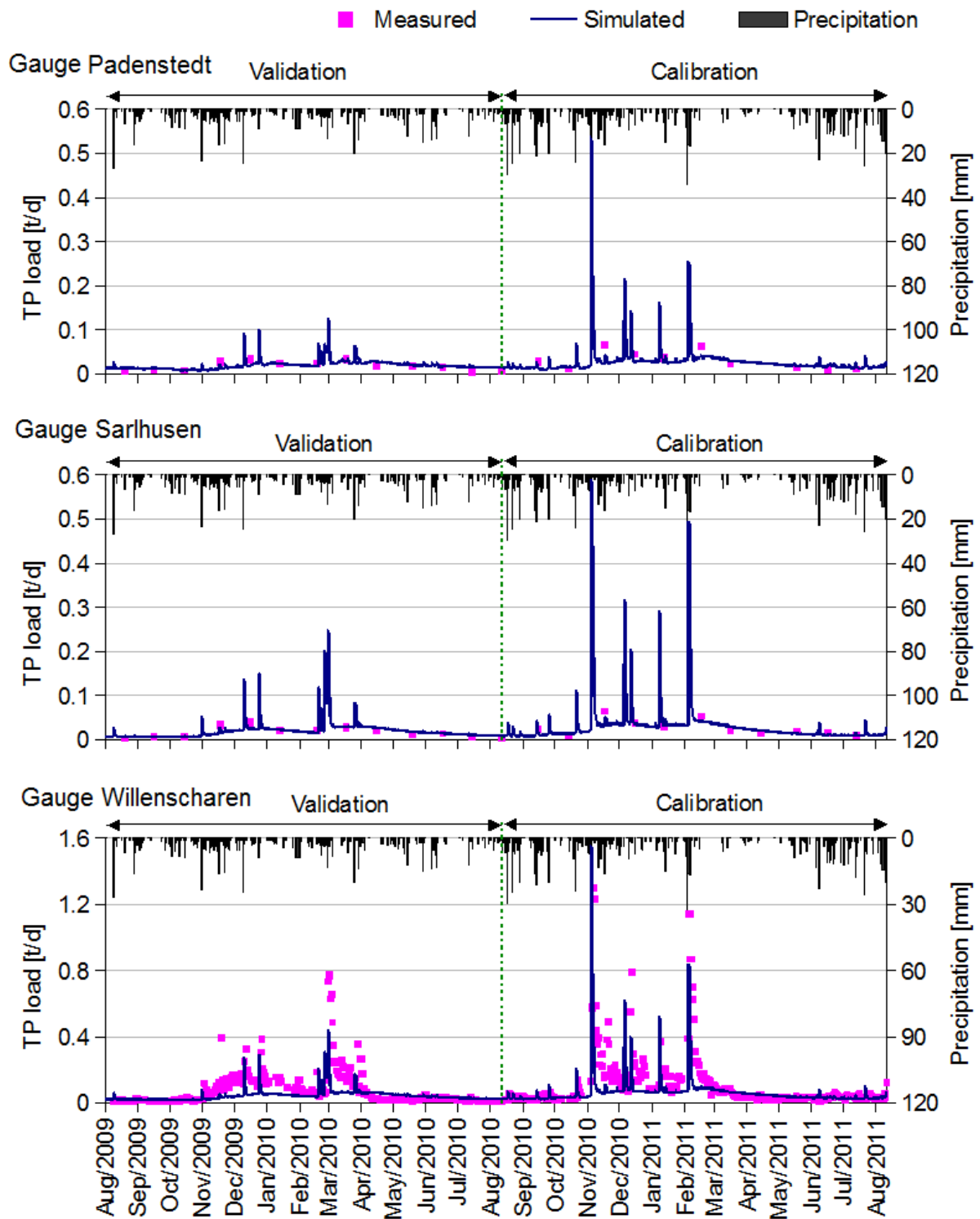


Fig. 5.30 Measured and simulated daily TP load at the gauges Padenstedt, Sarlhusen and Willenscharen over the calibration and validation period.

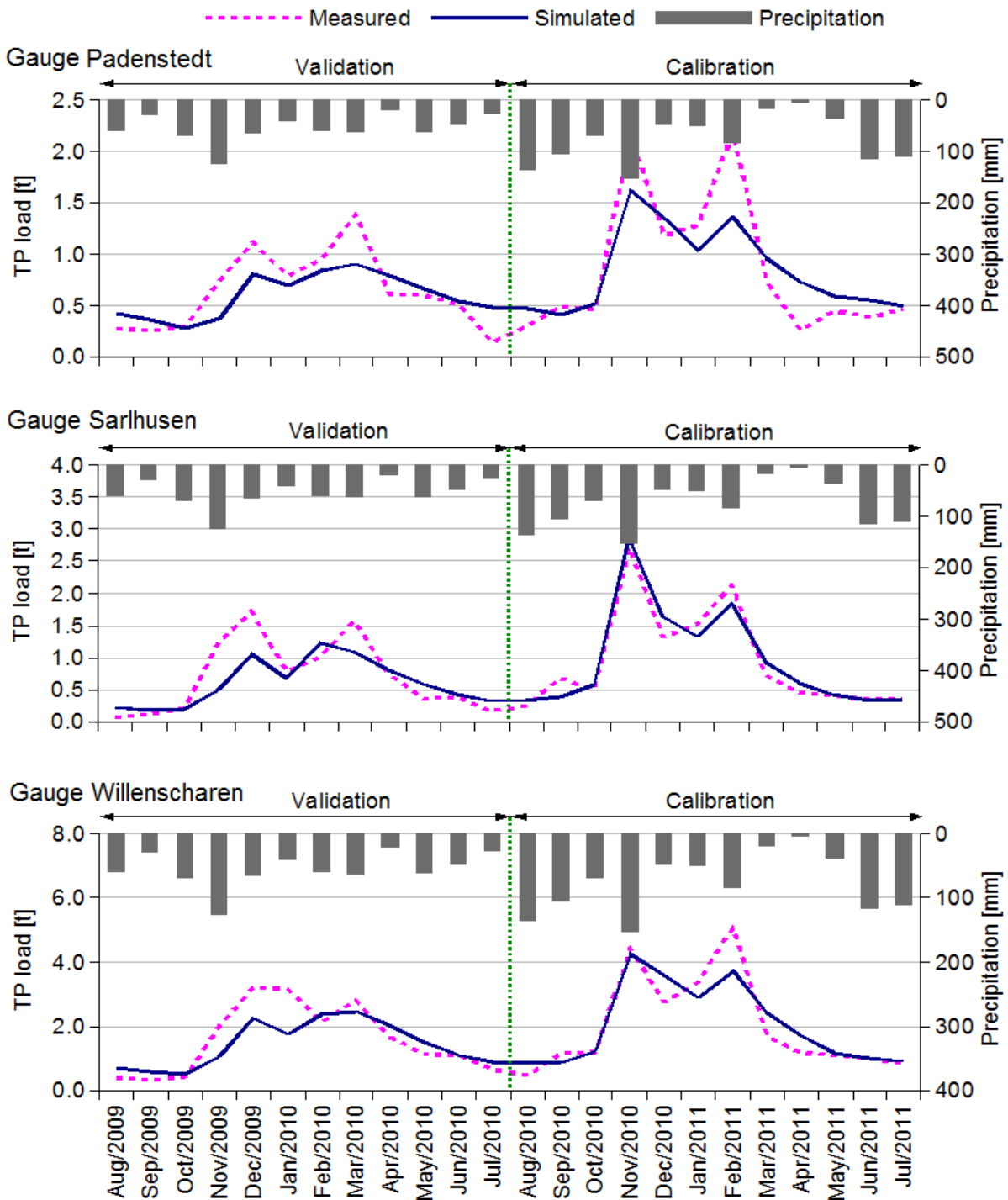


Fig. 5.31 Measured and simulated monthly TP load at the gauges Padenstedt, Sarlhusen and Willenscharen over the calibration and validation period.

In general, the performance of the TP was worse than $\text{NO}_3\text{-N}$ modeling. Results of literature also show low efficiency of TP modeling with the SWAT model. Tuppard et al. (2010) using the SWAT model achieved R^2 of 0.75 and 0.96 for the calibration and validation period, but only 0.01 and 0.35 of NSE for the calibration and validation, respectively, in the Bosque River

Watershed in the USA. Kühling (2011) modeling daily TP at time steps in the lowland Kielstau in Germany found NSE of 0.24 and 0.26 for the calibration and validation, respectively.

Table 5.11 Performance rating parameters of the daily TP load at the gauges Padenstedt, Sarlhusen and Willenscharen over the calibration and validation period.

Gauge station	TP _{obs} [t/d]	TP _{sim} [t/d]	R ²	NSE	PBIAS	RSR
Calibration period						
Padenstedt	0.027	0.023	0.41	0.29	14.9	0.50
Sarlhusen	0.025	0.022	0.62	0.55	13.0	0.66
Willenscharen	0.099	0.051	0.30	0.24	39.2	0.87
Validation period						
Padenstedt	0.019	0.018	0.44	0.44	2.2	0.74
Sarlhusen	0.018	0.017	0.74	0.72	5.8	0.52
Willenscharen	0.070	0.043	0.29	0.19	39.0	0.89

Table 5.12 Performance rating parameters of the monthly TP load at the gauges Padenstedt, Sarlhusen and Willenscharen over the calibration and validation period.

Gauge station	TP _{obs} [t/month]	TP _{sim} [t/month]	R ²	NSE	PBIAS	RSR
Calibration period						
Padenstedt	0.86	0.84	0.83	0.73	2.5	0.52
Sarlhusen	0.94	0.96	0.94	0.94	-1.8	0.23
Willenscharen	2.01	2.05	0.86	0.85	-1.7	0.22
Validation period						
Padenstedt	0.64	0.60	0.65	0.58	6.5	0.64
Sarlhusen	0.69	0.61	0.69	0.63	12.6	0.61
Willenscharen	1.58	1.44	0.70	0.65	9.2	0.59

5.7 Simulation of the historic scenario of 1990s

The historical scenario represents in this study the period of 1991 until 1999. After the calibration and validation of discharge, sediment and nutrient load with the SWAT model, the modeling of the historical scenario was carried out. All parameters used in discharge (Table 4.9), sediment (Table 4.10) and nutrients (Table 4.11) calibration and validation were also used for the historical scenario. Only the land use map (Ripl et al., 1996) and the management

operations were modified, aiming to use the SWAT model to understand why the improvement of TP and NO₃-N occurred over the last 20 years, observed in Fig. 5.4. The explanations of why occurred changes in N and P concentrations reported in item 5.2.1 are subjective. However, if the ecohydrological SWAT model can simulate hydrology processes and nutrients cycles, this means that it could also help to explain long-term changes in water quality.

The results of the daily discharge modeling of the historical scenario (January 1st 1991 - December 31st 1999) from the gauge stations Padenstedt, Sarlhusen and Willenscharen are shown in Fig. 5.32. The SWAT model showed lower peaks of discharge, especially in winter, following the same trend of the discharge in the calibration and validation periods. According to the results of performance of the discharge simulation (Table 5.13), confronted with the index parameters of Moriasi et al. (2007) (Table 4.2), the historical scenario modeling was successfully carried out.

The results of monthly NO₃-N and TP load of the historical scenario are graphically represented in Fig. 5.33 and Fig. 5.34, respectively. To run the simulation of nutrient load of the historical scenario, modifications on the management operations were necessary to achieve a minimal performance of the model. The main management operations that were modified for the simulation of the historical scenario are described in Table 4.12. The results of the performance of the simulated historical scenario are summarized in Table 5.14. The average annual load of NO₃-N of the historical scenario was overestimated (Table 5.14). Graphically, it is possible to see a delay in the measured data when compared to the simulated, especially in winter months (Fig. 5.33). As can be seen in Table 4.12, the fertilizer periods were anticipated, considering the explicit possibilities of field management, compared to the actual management practices.

TP load of the historical scenario showed better performance than NO₃-N load (Table 5.14), however, the average annual simulated TP load was 15% higher (PBIAS=-15%) than the average annual measured TP load. The performance of NO₃-N and TP load based on NSE (Moriasi et al., 2007) were ranked as satisfactory and good, respectively.

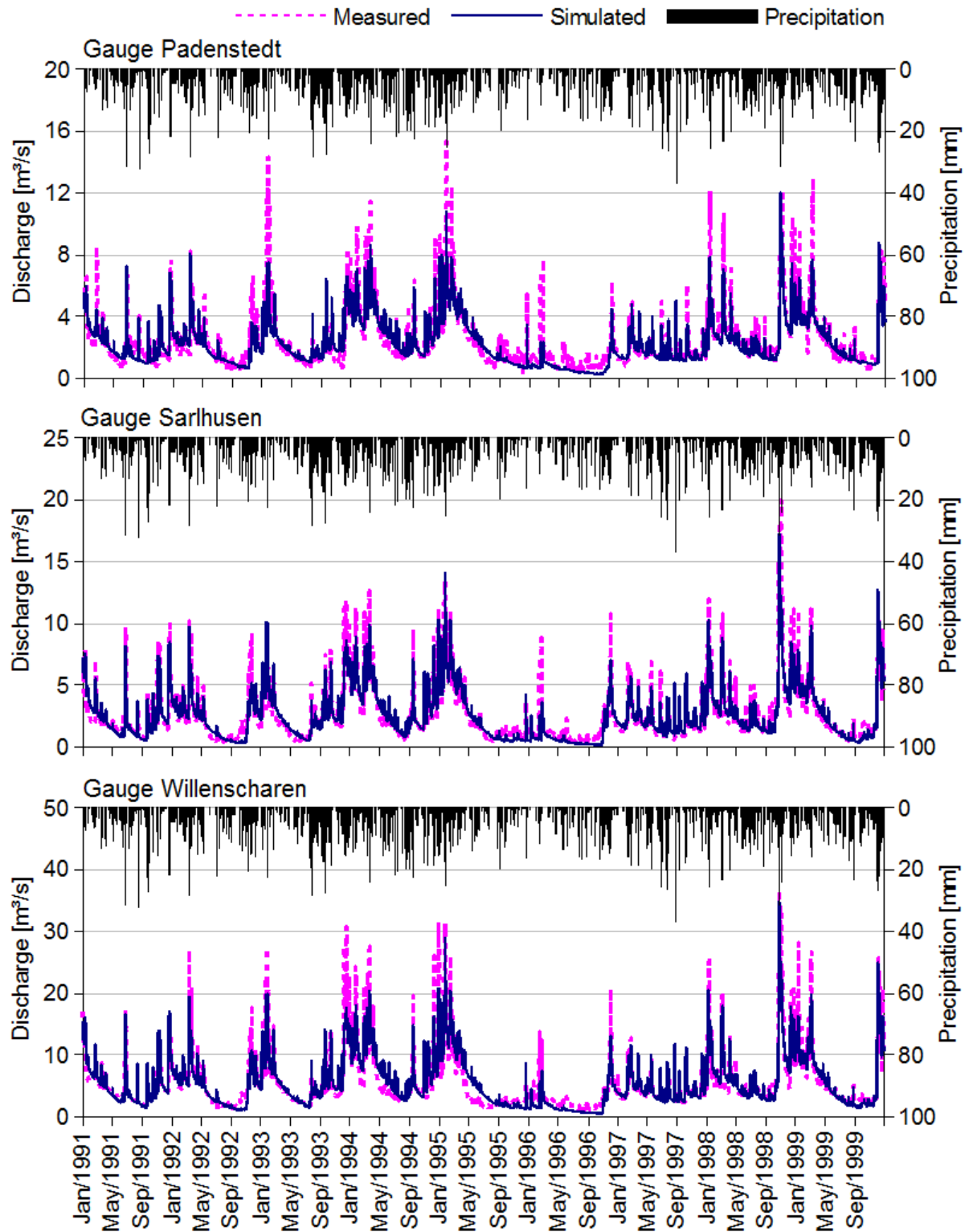


Fig. 5.32 Measured and simulated daily discharge at the gauges Padenstedt, Sarlhusen and Willenscharen over the historical scenario (1991-1999).

Table 5.13 Performance rating parameters of the daily discharge over the historical scenario (1991-1999).

Gauge station	Q_{obs} [m ³ /s]	Q_{sim} [m ³ /s]	R ²	NSE	PBIAS	RSR
Padenstedt	2.45	2.26	0.79	0.77	7.6	0.47
Sarlhusen	2.58	2.61	0.85	0.85	-0.8	0.38
Willenscharen	5.47	5.59	0.82	0.82	-2.2	0.43

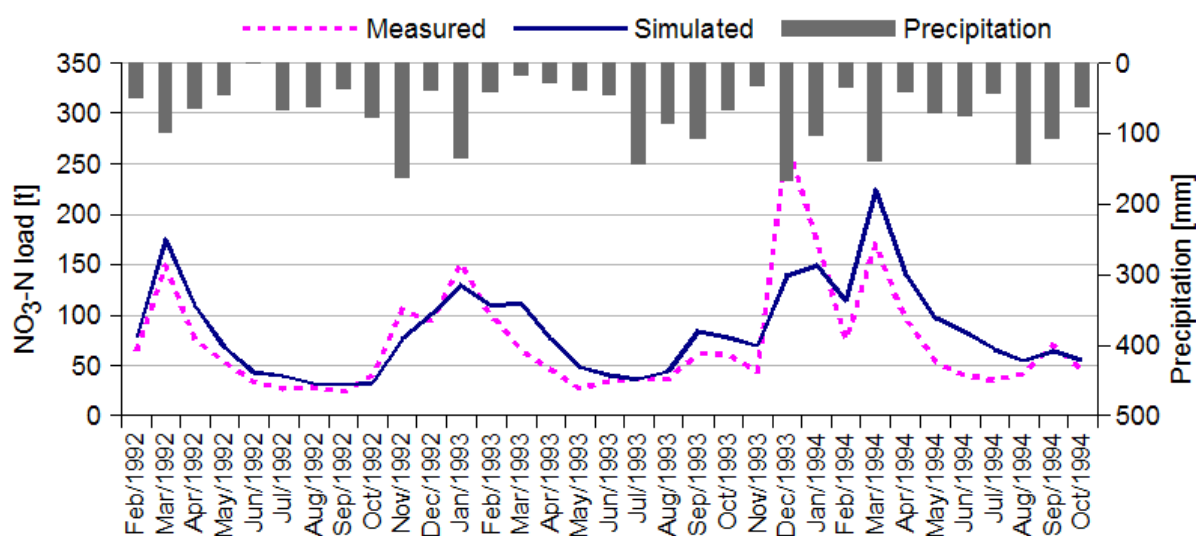
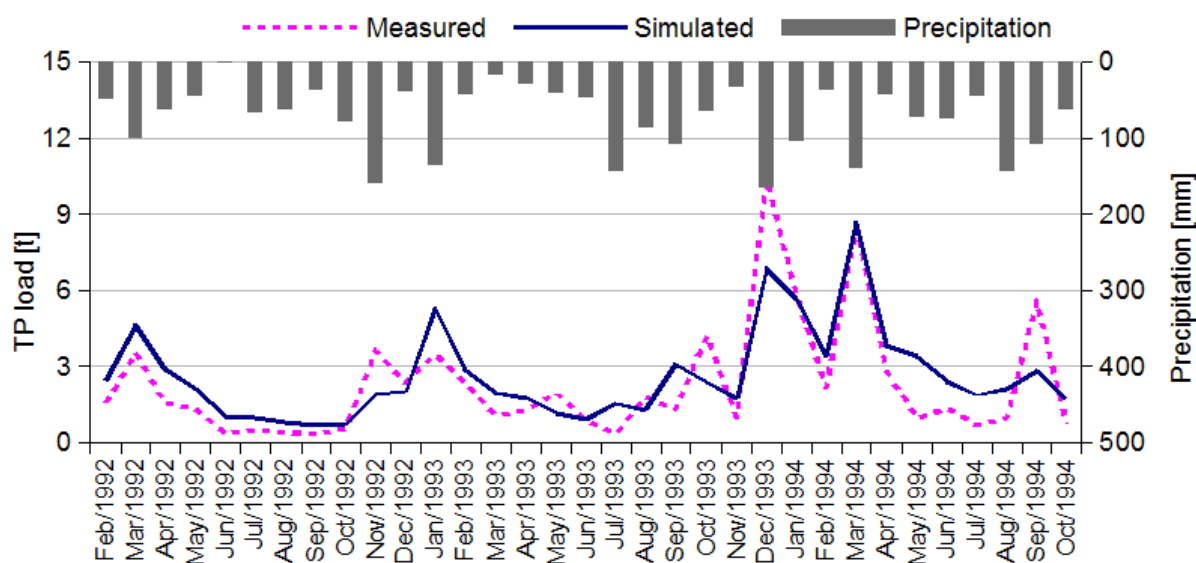

Fig. 5.33 Measured and simulated monthly NO₃-N load at the gauge Willenscharen over the historical scenario (February 1991 - October 1994).

Fig. 5.34 Measured and simulated monthly TP load at the gauge Willenscharen over the historical scenario (February 1991 - October 1994).

Table 5.14 Performance rating parameters of monthly NO₃-N and TP load at the gauge Willenscharen over the historical scenario (February 1991 - October 1994).

Simulation	Nutrient _{obs} [t/month]	Nutrient _{sim} [t/month]	R ²	NSE	PBIAS	RSR
NO ₃ -N load	73.95	85.10	0.64	0.60	-15.0	0.63
TP load	2.27	2.61	0.71	0.68	-15.0	0.56

The current monthly simulation of nutrients, NO₃-N and TP load, had a good performance for calibration and validation in the three gauge stations (Table 5.10 and Table 5.12), indicating that the management operations, the fertilization schedule and the applied rates of mineral and organic fertilizers were adequate for the current period. Usually, after a good calibration and validation of nutrient load, the major part of researchers proposes new alternative scenarios aiming to minimize the N and P pollution (Hesse et al., 2008; Ouyang et al., 2008; Lee et al., 2010; Tuppad et al., 2010; Lam et al., 2011; Laurent and Ruelland, 2011). In this study, the purpose was to simulate the historical scenario to check whether it is possible to explain the long-term changes. The same parameters used in calibration and validation were used in the SWAT model to simulate the historical scenario, only being modified the land use map (Ripl et al., 1996), the fertilization schedule and the applied rates of mineral and organic fertilizers. To achieve a satisfactory performance of NO₃-N and TP load simulation of the historical scenario (Table 5.14), several attempts were carried out. It was always considered the realistic recommendations of fertilizer amounts for this period, considering information of KTBL (1995) and LWK (1991, 1998). After several simulations, the best NO₃-N and TP modeling of the historical scenario was found, which is shown in Fig. 5.33 and Fig. 5.34, respectively. To achieve the best simulation of the historical scenario, modification in the fertilization schedule was necessary. Even so, same peaks of NO₃-N and TP load occurred beforehand in the simulated data, indicating an earlier fertilizer application. Even indicating a shift in peaks of simulated curve of NO₃-N and TP load, the periods and doses of fertilizer application of the 1990s were respected (KTBL, 1995; LWK, 1991, 1998).

An important perception which was observed using the SWAT model in the historical scenario simulation was the change on the fertilization schedule application. Currently, the German law of fertilizer application in agricultural and pasture areas is regulated by DÜV (2006) and DÜNGG (2009), which prohibits the use of N fertilizer during November 1st to January 31st

on farmland and during November 15th to January 31st on pasture areas. These guidelines were observed to simulate the current scenario, but organic manure applications were considering in December and January (Table 4.12) in the historical scenario simulation, indicating that the policy regulation had positive influence on the improvement of water quality after the implementation of the environment directives.

A reduction of mineral N and P fertilizer use in Germany over the last 20 years is observed in Fig. 5.3. This trend was observed with the modeled data, calculated by SWAT model (Table 5.15), which reduces from 64.7 to 58.1 kg/ha the input of mineral P fertilizer from the historical scenario to the current period. However, this trend does not occur with the input of mineral N fertilizer (Table 5.15). Furthermore, the calculated input of organic N and P fertilizer increased from the historical to the current period, resulting in an increase of input of total N and total P in the upper Stör over the last 20 years (Table 5.15). Despite the reduced use of mineral and organic fertilizer from the historical scenario (Table 4.12) to the current scenario (Table 4.5), the total input of N and P fertilizer was increased, because an increase of silage corn and pasture areas occurred in the upper Stör catchment, both using the organic manure as source of fertilizer.

Table 5.15 Mean annual input of N and P fertilizer calculated by SWAT model in the current (calibration and validation) and in the historical scenario period.

Use of fertilizer	historical scenario	Current period (Calibration and validation)
	----- kg/ha -----	
Mineral N	127.9	138.2
Organic N	47.1	76.5
Total N	175.0	214.7
Mineral P	64.7	58.1
Organic P	23.6	38.2
Total P	88.3	96.3

5.8 Modeling of best management practices

With the SWAT model calibrated and validated, it was possible to create alternative scenarios aiming to reduce N and P pollution in the upper Stör catchment. The main BMPs tested in this

study considered: i) reduction on fertilizer application and ii) implementation of field filter strip. Detailed description of all alternative BMPs scenarios can be seen in Table 4.13.

The results of reduction of $\text{NO}_3\text{-N}$ and TP load with the SWAT model are shown in Fig. 5.35. The BMPs linked with reduction of fertilizer application (DMA50, DMA20, DFA20) were efficient to minimize $\text{NO}_3\text{-N}$ and TP load. In general, the reduction of $\text{NO}_3\text{-N}$ load was more effective than TP load reduction in this lowland catchment. The CSC scenario, which changed the USLE_P factor, considering agriculture area with more than 2% slope with contour practices, influenced only the TP load because in SWAT, the USLE_P factor modifies the sediment transport and consequently the P transport, but not the $\text{NO}_3\text{-N}$.

BMPs related with implementation of field filter strip were also effective to reduce $\text{NO}_3\text{-N}$ and TP load. WFS30 had a greater reduction on $\text{NO}_3\text{-N}$ and TP than WFS10. Finally, the combination of various BMPs showed more reduction of N and P pollution (Fig. 5.35). In this study, two combinations (CMB1 and CMB2) were tested. Both contribute similarly $\text{NO}_3\text{-N}$ and TP reduction of pollution. CMB1 is a combination of DMA20, DFA20 and WFS30 scenarios. CMB2 is a combination of the scenarios DMA50, DFA20 and WFS10. The CMB1 reduces 20% the mineral fertilizer and organic manure and introduces the 30 m width of field filter strip. CMB2 works with a smaller filter strip (10m) but reduces the application of organic manure to 50%. It is clear that intensive BMPs are necessary to minimize the N and P pollution in rivers coming from diffuse sources. In this case, a reduction on fertilizer application (organic or mineral) and/or an increase in protection areas (areas without use of fertilizer) are important to reduce the $\text{NO}_3\text{-N}$ and TP load into the rivers.

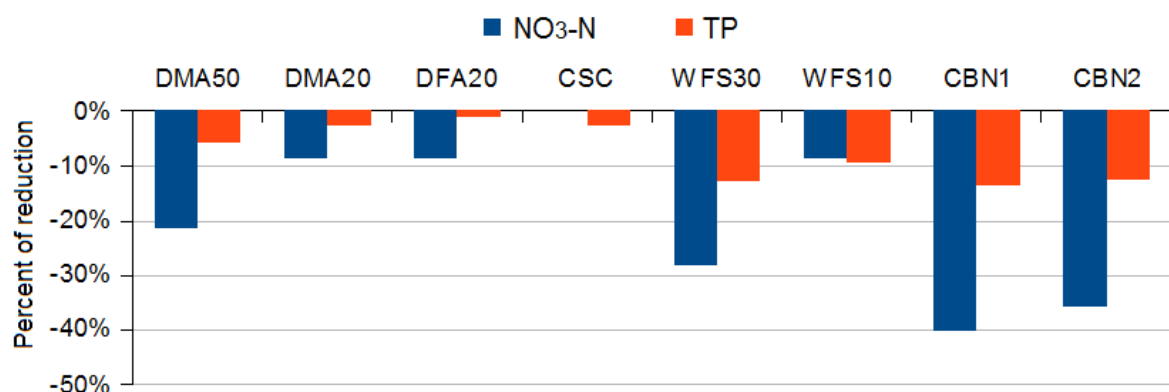


Fig. 5.35 Average annual reduction in $\text{NO}_3\text{-N}$ and TP load at the gauge Willenscharen by implementing new BMPs scenarios.

The choice of alternative BMP scenarios were considered after several attempts to match a satisfactory simulation of the historical scenario. The adjustment of $\text{NO}_3\text{-N}$ and TP load simulation of the historical scenario helped to understand some processes involved in the output of N and P of the watershed. Changes in the period of fertilizer application, type of fertilizer and the amount of fertilizer applications are some examples of practices that can modify the dynamic of N and P pollution at the catchment. In this sense, the successful practices found to reduce N and P pollution are related to the reduction of amount of fertilizer and increase of conservation areas that do not use fertilization practices (Fig. 5.35). Laurent and Ruelland (2011) testing several alternative scenarios in a French catchment, verified that the fertilizer reduction was the most effective practice to reduce $\text{NO}_3\text{-N}$ pollution. Other studies about SWAT modeling in lowland catchments aiming to determine new scenarios, also verified efficient reduction of $\text{NO}_3\text{-N}$ pollution when the reduction of N fertilizer was simulated (Chaplot et al., 2004; Hesse et al., 2008; Lam et al., 2011). Hesse et al. (2008) reducing the N and P fertilizer in agriculture areas obtained a decrease of 13 and 2 % of TN and TP load. At the lowland Kielstau catchment, Lam et al. (2011) achieved reduction of 10% and 1% of $\text{NO}_3\text{-N}$ and TP load with an alternative scenario called Nutrient Management Plan, which consisted in a reduction of 20% of N and P fertilizer.

One reason for the success of $\text{NO}_3\text{-N}$ load reduction by use of decreasing of N fertilizer can be attributed to the strong influence of hydrologic components linked to drainage and groundwater, as can be seen in Fig. 5.25. Kennedy et al. (2012) also evidenced the influence of tile drainage on $\text{NO}_3\text{-N}$ load in different tile drainage densities. Table 4.11 describes the main parameters that were sensitive to $\text{NO}_3\text{-N}$ load calibration. In this sense, there are important parameters that can influence the subsurface movement of NO_3 , such as the denitrification threshold of water content (SDNCO), NO_3 percolation coefficient (NPERCO), fraction of porosity from which anions are excluded (ANION_EXCL) and half-life of NO_3 in the shallow aquifer (HLIFE_NGW).

Regarding P, the most important part of P loss is linked to sediment, due to P adsorption at soil particles. This was very well observed in Fig. 5.20 which showed the high correlation between TP and TSS. Also, the autocorrelation of TSS and TP (Fig. 5.22) put forward a similar trend with the autocorrelation of precipitation, indicating an influence of surface processes, such as erosion. Despite the TP load simulation with the SWAT model achieving a

satisfactory performance (Fig. 5.31 and Table 5.12), parameters that link P to the sediment, especially in erosive processes, as in the river channel are still lacking in the model. GWSOLP parameter was crucial to achieve a good performance of the TP load calibration, but it represented a constant value of P concentration in groundwater. Groundwater represents 52.8% (Table 5.6) of the discharge components. In this sense, it is comprehensible that GWSOLP is an important parameter in the TP load simulation. However, this parameter may be negatively influencing the low response in TP load when alternative scenarios are modeled.

The reduction of fertilizer application was more effective for NO₃-N compared to TP (Fig. 5.35). The lower efficiency to reduce P pollution in lowland catchment was also verified by Lam et al. (2011). If the goal of modeling with SWAT model is to find alternative scenarios to minimize sedimentation in the river, practices such as reforestation and mulching are quite efficient (Phomcha et al., 2012; Wu and Chen, 2012). Best responses in reducing P pollution are achieved in mountainous basins where runoff component plays an important role in the hydrologic processes, as observed by Liu et al. (2013) with SWAT modeling in a mountainous catchment. Ferrant et al. (2013) tested long-term simulation of NO₃-N mitigation using the TNT2 model (Beaujouan et al., 2002) in a pilot study catchment in France. They stated that a global reduction of fertilization by 10% would decreased NO₃-N fluxes in stream by 13.8%. O'Shea and Wade (2009) examined a variety of policies targeted to reduce fertilizer use and changing the way in which farm land is managed. They suggested that a tax on nitrogen emerges as the best policy both in terms of cost and environmental effectiveness.

6 CONCLUSION AND OUTLOOK

In this study, monitoring, assessment and modeling of N and P pollution in a lowland catchment were carried out. The monitoring consisted of monthly and daily campaigns to assess the water quality during August 2009 until August 2011. Also, data set of monthly WWTPs campaign from December 2009 until August 2010 (Redeker, 2011; Honsel, 2011), and a historical data set of monthly water quality campaign, from March 1991 until March 1995 of the upper Stör catchment (Ripl et al., 1996), were used to compare the development of N and P pollution over the past 20 years. The main conclusions of this study are following:

Regarding P pollution, TP concentrations in the upper Stör catchment in Northern Germany decreased during the last 20 years. There are seasonal influences in P pollution. Winter and summer values of TP, PP and PO₄-P are significantly different. In general, P pollution in winter is higher than in summer. Specific problems in summer occur only in regions with peaty soils. In general the level of PO₄-P pollution is as low as required by the WFD (EC, 2000). However, there are subbasins with higher PO₄-P pollution, especially those subbasins with a substantial fraction of peaty soils. Pollution of TP is not yet at a level required by the WFD (EC, 2000). TP problems are related to high concentrations of PP, originated from erosion of agricultural land and pasture areas, as well as river bank erosion caused by high water flow and sediment transport. The critical pollution problems at the upper Stör catchment can be separated divided into two mechanisms: The first is the PP pollution from agricultural areas and mobilization from the river bed. The second is the PO₄-P pollution originated by pasture areas, peaty soils and WWTPs.

With regard to N pollution, TN and NO₃-N pollution decreased significantly over the past 20 years, but NH₄-N concentration remained at the same level in the upper Stör catchment. Despite the improvement of TN and NO₃-N concentrations, the environmental goals set by the WFD were not reached. In winter, N pollution is higher than in summer, caused by lower

uptake of N by plants and lower microbiological activity of the WWTPs. In general, $\text{NO}_3\text{-N}$ problems are linked to farming areas and $\text{NH}_4\text{-N}$ problems to WWTPs.

Daily time series data set were useful to show the temporal variability of water quality parameters. $\text{NO}_3\text{-N}$ and PP are the major forms of N and P in the upper river Stör. Discharge and water quality parameters show a distinct seasonal pattern, with more water pollution problems in winter. The higher DIN/DIP ratio indicates a P limitation in this lowland catchment. Autocorrelations of N and P parameters with the daily data set of the gauge station Willenscharen help to understand the dynamic of both nutrients. A quite strong autocorrelation of $\text{NO}_3\text{-N}$ and TN show a stable and constant influence of groundwater flow on $\text{NO}_3\text{-N}$ pollution. The high correlation between TSS and PP as well as the initially strong decrease in autocorrelation of these parameters indicate an influence of surface erosion processes. Autocorrelation function were efficient to characterize the N and P pollution, which can assist to plan and to manage water quality monitoring in other lowland catchments.

Daily discharge was successfully calibrated and validated in the three gauging stations in the upper Stör catchment with the ecohydrological SWAT model. It stressed the importance of drainage (34.3%) and groundwater flow (52.8%) compared to other flow components. Lateral flow (7.7%) and surface runoff (5.2%) are the hydrological components that less affect the river discharge less in this lowland catchment.

In general, monthly time steps predict sediment and nutrient load with better performance rating than daily simulations. The modeling of daily sediment load and $\text{NO}_3\text{-N}$ load were satisfactory. However, the daily simulation of TP load resulted in low performance measures of the SWAT model, especially because overestimation occurs in summer and underestimation of simulated TP in winter. The overestimation is related to the parameter related to concentration of soluble P in groundwater (GWSOLP), which is constant over the year in the SWAT model. Underestimation of TP in winter is possibly linked to river bed and river bank erosion, which are still difficult to simulate with SWAT. Also, the definition of the time of management practices (tillage operation, time of planting, fertilizer application, harvest) often vary from one year to another due to climate conditions, causing consequently a lower performance of the model. The monthly simulation of sediment and nutrients was successfully calibrated and validated for the three gauge discharge stations (Padenstedt, Sarlhusen and

Willenscharen).

Based on the calibrated and validated nutrient load model (NO₃-N and TP), a historical monthly scenario for nutrient load was also simulated to analyze the changes in N and P pollution over the past 20 years. The historical scenario model was parametrized based on the land use map from 1987 (Ripl et al., 1996), management schedule and amount of fertilization were changed based on bibliographic information (KTBL, 1995; LWK, 1991, 1998) aiming to achieve a good performance of the model. In this sense, a satisfactory NO₃-N and TP load modeling was achieved. Fertilizer application during the winter, especially organic manure application in December and January was a common practice in the historical scenario. Currently, this practice is prohibited by the German Department of Agriculture (DÜV, 2006; DÜNGG, 2009) aiming to achieve the goals of water quality directives (EEC, 1991a; EC, 2000). Furthermore, higher mineral fertilizer doses were used in the historical scenario of the 1990s. However, with the recent increase of silage corn and pasture areas, greater amounts of organic manure were estimated in the upper Stör catchment.

Based on the development of the current and of the historical scenario, BMPs scenarios were proposed aiming to reduce the N and P pollution in the upper Stör catchment. Most effective BMPs obtained to minimize N and P pollution were linked to the reduction of N and P fertilizer application and the increasing of conservation areas that without the use of any fertilizer, such as field filter strips.

The long-term monitoring of water quality is necessary to verify the development of N and P pollution. Also, a consistent data set of monitoring is essential to achieve a good calibration and validation using an ecohydrological model, such as the SWAT model. Hydrological processes that affect the N and P processes are complex and the ecohydrological modeling can assist to understand the changes that occur in a long-term, as well as changes that may occur to obtain improvement of water quality in the future. Also, the SWAT model represents a very useful tool to support catchment managers to improve water quality using BMPs. The results obtained in this study can serve as an example for other rural lowland catchments with similar characteristics. Also, it can be used to identify sources of N and P pollution and to understand the mitigation of N and P load on a long-term.

In the future, some studies could be carried out to improve the knowledge about monitoring

and modeling of sediment and nutrient loads in lowland catchments. About modeling, improvement in P processes in drainage and river systems should be investigated. Moreover, the impact of the wetland areas in the P pollution was not possible to be simulated. Another research topic in lowland areas that deserves more attention is the influence of the bioenergy production, especially the production of biogas from corn silage and its impact on water quality. In the case of point pollution, a high resolution temporal monitoring programs should be considered to obtain more information about the dynamic of N and P originated from the WWTPs. Last but not least research, how to decrease the impact of N and P during the winter period. In winter, plants and macrophytes decrease the absorption of this nutrients, which are transported out of the watershed, and accumulate in the ocean, which can cause eutrophication in this ecosystem in the future.

For many constituents (e.g., sediment and phosphorus) in situ sensor technology is rare and still expensive. It can be useful in the future, as describe Horsburgh et al. (2010), which proposed monitoring water quality measures such as turbidity or specific conductance, which can be measured in situ with high frequency, and can be used as surrogates for other water quality constituents that cannot economically be measured with high frequency.

The decrease of fertilizer application is one alternative to reduce N and P pollution in water systems. However, the need to maximize the productivity of crops for food and bioenergy must also be considered. In this sense, investigation about soil management and more efficient fertilizers should also be investigate in future monitoring and modeling research of water quality.

Finally, the monthly (Table 9.2) and daily (Table 9.3) measured database about water quality from the upper Stör catchment during August 2009 and August 2011 can be useful as baseline of new studies of assessment, monitoring and modeling of N and P pollution in the future.

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This dissertation is result of 105 field trips with about 13,000 km traveled in the State of Schleswig-Holstein, Germany. Over 1,200 water samples were collected in the upper Stör catchment and over 7,000 laboratory analyzes were carried out. Finally over 100,000 simulations were run with the SWAT-CUP to calibrate discharge, sediment and nutrients. The achievement of all these activities was a great challenge, and a lot of people and institutions have contributed to overall success.

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Fig. 7.1 Canoeing on the river Stör at Willenscharen, Germany.

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9 ANNEX

Table 9.1 Suitability of soil types in the upper Stör catchment.

German classification (Finnern, 1997)	%	International Classification System	%
Gyttja	0.03	Histosol	12.87
Typisches Hochmoor	3.38		
Moor-Podsol	2.17		
Typisches Niedermoor	5.48		
Geringmächtiges Niedermoor	1.81		
Typischer Pseudogley	9.14	Planosol	12.19
Braunerde-Pseudogley	0.99		
Gley-Pseudogley	0.23		
Podsolierter Pseudogley	1.83		
Typische Parabraunerde	6.93	Luvisol	8.22
Pseudogley Parabraunerde	0.18		
Podsolierte Parabraunerde	0.52		
Podsolierte Pseudogley-Parabraunerde	0.59		
Abgrabungen	0.02	Gley-Podsol	19.16
Gley-Podsol	19.14		
Pseudogley-Podsol	1.94	Podsol	30.99
Eisenhumuspodsol	25.09		
Vergleyter Podsol	3.96		
Pseudogley-Braunerde	1.89	Cambisol	4.02
Podsolierte Braunerde	2.13		
Podsol-Gley	0.32	Gley	12.55
Typischer Anmorgley	4.18		
Podsolierte Gley	8.05		

Table 9.2 Monthly water quality parameters in the 21 sampling points in the upper Stör catchment.

Date	Sampling point	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]
Aug/19/2009	1	0.062	0.11	0.67	0.15	1.80
Sep/16/2009	1	0.053	0.13	0.69	0.07	1.60
Oct/14/2009	1	0.095	0.17	0.78	0.27	2.00
Nov/18/2009	1	0.081	0.17	3.25	0.28	5.00
Dec/16/2009	1	0.107	0.18	3.00	0.28	4.30
Jan/13/2010	1	0.098	0.18	2.37	0.61	3.10
Feb/17/2010	1	0.120	0.16	1.55	0.79	2.80
Mar/17/2010	1	0.093	0.15	2.78	0.31	4.00
Apr/14/2010	1	0.072	0.14	2.12	0.14	3.30
May/19/2010	1	0.070	0.17	1.20	0.07	2.80
Jun/16/2010	1	0.108	0.20	1.13	0.18	2.70
Jul/14/2010	1	0.123	0.22	1.01	0.08	1.90
Aug/11/2010	1	0.082	0.13	0.70	0.07	1.20
Sep/15/2010	1	0.183	0.35	1.81	0.41	4.30
Oct/13/2010	1	0.107	0.22	1.17	0.33	2.90
Nov/17/2010	1	0.123	0.20	2.98	0.21	4.20
Dec/15/2010	1	0.108	0.19	2.78	0.40	4.20
Jan/12/2011	1	0.099	0.16	2.84	0.44	4.20
Feb/16/2011	1	0.080	0.125	2.96	0.28	3.70
Mar/16/2011	1	0.070	0.122	2.54	0.22	3.60
Apr/13/2011	1	0.053	0.107	2.61	0.199	3.20
May/18/2011	1	0.099	0.192	1.96	0.721	3.20
Jun/15/2011	1	0.121	0.20	2.27	0.159	2.70
Jul/13/2011	1	0.126	0.19	1.30	0.09	2.00
Aug/19/2009	2	0.015	0.03	0.93	0.04	2.00
Sep/16/2009	2	0.018	0.05	1.23	0.03	2.20
Oct/14/2009	2	0.016	0.06	1.57	0.04	2.10
Nov/18/2009	2	0.047	0.17	8.49	0.10	9.90
Dec/16/2009	2	0.041	0.19	6.34	0.26	8.10
Jan/13/2010	2	0.017	0.14	1.58	0.18	3.30
Feb/17/2010	2	0.015	0.19	2.08	0.27	3.40
Mar/17/2010	2	0.033	0.10	6.11	0.15	7.10
Apr/14/2010	2	0.014	0.07	3.28	0.03	3.80
May/19/2010	2	0.017	0.10	1.86	0.18	2.90
Jun/16/2010	2	0.019	0.08	1.76	0.11	2.70
Jul/14/2010	2	0.020	0.04	1.91	0.06	2.20
Aug/11/2010	2	0.025	0.07	1.62	0.05	2.10
Sep/15/2010	2	0.045	0.22	1.45	0.09	2.40
Oct/13/2010	2	0.022	0.09	1.98	0.05	2.90
Nov/17/2010	2	0.074	0.18	7.63	0.15	9.20
Dec/15/2010	2	0.043	0.15	5.92	0.20	7.10
Jan/12/2011	2	0.056	0.14	5.34	0.24	7.20
Feb/16/2011	2	0.025	0.131	4.66	0.16	5.30
Mar/16/2011	2	0.021	0.086	4.31	0.12	5.10
Apr/13/2011	2	0.012	0.067	2.94	0.085	3.40
May/18/2011	2	0.015	0.116	2.33	0.234	3.10
Jun/15/2011	2	0.016	0.08	2.33	0.063	2.80
Jul/13/2011	2	0.034	0.12	2.17	0.045	3.10

... continuation of Table 9.2.

Date	Sampling point	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]
Aug/19/2009	3	0.033	0.09	3.08	0.05	5.00
Sep/16/2009	3	0.024	0.07	2.41	0.03	4.40
Oct/14/2009	3	0.069	0.12	1.72	0.09	2.50
Nov/18/2009	3	0.087	0.18	3.28	0.19	5.40
Dec/16/2009	3	0.089	0.18	3.60	0.22	5.00
Jan/13/2010	3	0.069	0.20	3.69	0.30	4.00
Feb/17/2010	3	0.059	0.18	2.98	0.34	3.80
Mar/17/2010	3	0.080	0.12	3.41	0.25	4.70
Apr/14/2010	3	0.053	0.10	3.91	0.07	4.90
May/19/2010	3	0.055	0.13	2.97	0.04	4.10
Jun/16/2010	3	0.069	0.13	2.93	0.08	4.30
Jul/14/2010	3	0.043	0.05	3.56	0.07	4.30
Aug/11/2010	3	0.028	0.07	2.61	0.04	4.10
Sep/15/2010	3	0.100	0.20	1.58	0.43	3.00
Oct/13/2010	3	0.072	0.12	3.07	0.09	4.30
Nov/17/2010	3	0.107	0.19	3.24	0.18	4.50
Dec/15/2010	3	0.082	0.19	4.05	0.29	5.00
Jan/12/2011	3	0.077	0.15	3.70	0.41	5.30
Feb/16/2011	3	0.067	0.128	4.18	0.24	5.10
Mar/16/2011	3	0.052	0.106	4.32	0.17	5.10
Apr/13/2011	3	0.035	0.085	4.69	0.082	5.50
May/18/2011	3	0.025	0.109	3.78	0.084	4.70
Jun/15/2011	3	0.028	0.08	3.67	0.091	4.70
Jul/13/2011	3	0.064	0.13	3.19	0.083	3.90
Aug/19/2009	4	0.008	0.08	1.01	0.06	2.20
Sep/16/2009	4	0.014	0.11	1.44	0.06	2.30
Oct/14/2009	4	0.018	0.153	1.90	0.07	2.10
Nov/18/2009	4	0.077	0.19	9.65	0.16	10.90
Dec/16/2009	4	0.062	0.21	7.96	0.46	10.30
Jan/13/2010	4	0.025	0.13	3.64	0.24	4.20
Feb/17/2010	4	0.027	0.15	3.79	0.39	4.30
Mar/17/2010	4	0.052	0.11	6.88	0.19	8.10
Apr/14/2010	4	0.017	0.07	4.27	0.04	4.30
May/19/2010	4	0.030	0.10	2.45	0.12	2.60
Jun/16/2010	4	0.024	0.09	2.34	0.11	3.10
Jul/14/2010	4	0.022	0.03	2.46	0.19	3.20
Aug/11/2010	4	0.016	0.08	1.83	0.07	2.50
Sep/15/2010	4	0.021	0.53	2.80	0.21	4.60
Oct/13/2010	4	0.040	0.13	2.70	0.06	3.90
Nov/17/2010	4	0.092	0.19	8.40	0.12	9.90
Dec/15/2010	4	0.055	0.15	6.94	0.19	8.30
Jan/12/2011	4	0.070	0.13	5.92	0.25	8.10
Feb/16/2011	4	0.043	0.143	5.53	0.17	6.20
Mar/16/2011	4	0.033	0.096	4.95	0.15	6.20
Apr/13/2011	4	0.018	0.041	4.03	0.11	4.30
May/18/2011	4	0.025	0.151	3.46	0.241	4.00
Jun/15/2011	4	0.019	0.09	3.20	0.05	3.80
Jul/13/2011	4	0.054	0.11	2.87	0.035	3.80

... continuation of Table 9.2.

Date	Sampling point	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]
Aug/19/2009	5	0.014	0.04	1.27	0.04	2.20
Sep/16/2009	5	0.016	0.12	1.34	0.05	2.60
Oct/14/2009	5	0.018	0.12	2.44	0.08	3.00
Nov/18/2009	5	0.023	0.20	4.06	0.19	5.20
Dec/16/2009	5	0.086	0.32	7.26	1.27	8.53
Jan/13/2010	5	0.026	0.16	3.58	0.20	3.80
Feb/17/2010	5	0.011	0.17	3.51	0.31	4.30
Mar/17/2010	5	0.033	0.10	5.79	0.12	7.10
Apr/14/2010	5	0.011	0.06	4.04	0.02	4.80
May/19/2010	5	0.020	0.09	3.18	0.15	4.60
Jun/16/2010	5	0.016	0.07	3.19	0.09	4.30
Jul/14/2010	5	0.031	0.18	2.91	0.43	3.50
Aug/11/2010	5	0.019	0.08	2.08	0.03	3.30
Sep/15/2010	5	0.082	0.22	2.26	0.74	4.60
Oct/13/2010	5	0.008	0.06	2.86	0.04	4.00
Nov/17/2010	5	0.055	0.21	6.67	0.11	8.10
Dec/15/2010	5	0.033	0.18	5.30	0.19	6.40
Jan/12/2011	5	0.051	0.15	5.49	0.24	7.00
Feb/16/2011	5	0.036	0.158	5.80	0.19	6.60
Mar/16/2011	5	0.014	0.094	5.20	0.05	6.00
Apr/13/2011	5	0.011	0.035	4.62	0.04	5.30
May/18/2011	5	0.028	0.207	3.87	0.274	5.10
Jun/15/2011	5	0.023	0.08	4.24	0.039	5.00
Jul/13/2011	5	0.034	0.11	3.71	0.025	5.20
Aug/19/2009	6	0.023	0.03	0.94	0.09	1.80
Sep/16/2009	6	0.028	0.08	0.84	0.09	1.80
Oct/14/2009	6	0.021	0.08	1.22	0.11	1.50
Nov/18/2009	6	0.032	0.08	1.62	0.17	2.10
Dec/16/2009	6	0.030	0.11	2.21	0.24	2.60
Jan/13/2010	6	0.033	0.10	2.46	0.24	2.70
Feb/17/2010	6	0.025	0.12	1.61	0.24	2.20
Mar/17/2010	6	0.024	0.07	2.24	0.22	2.90
Apr/14/2010	6	0.020	0.06	2.08	0.11	2.70
May/19/2010	6	0.023	0.09	1.59	0.12	2.40
Jun/16/2010	6	0.026	0.07	1.53	0.10	2.00
Jul/14/2010	6	0.031	0.05	1.24	0.08	1.60
Aug/11/2010	6	0.027	0.07	1.23	0.06	1.60
Sep/15/2010	6	0.031	0.13	1.09	0.09	2.00
Oct/13/2010	6	0.022	0.05	1.41	0.08	2.10
Nov/17/2010	6	0.030	0.12	2.42	0.38	3.10
Dec/15/2010	6	0.029	0.13	2.48	0.61	3.30
Jan/12/2011	6	0.025	0.10	2.24	0.42	3.20
Feb/16/2011	6	0.031	0.124	2.53	0.67	3.20
Mar/16/2011	6	0.021	0.092	2.22	0.25	3.20
Apr/13/2011	6	0.020	0.101	1.95	0.149	2.50
May/18/2011	6	0.025	0.134	1.97	0.178	2.50
Jun/15/2011	6	0.025	0.09	1.97	0.105	2.20
Jul/13/2011	6	0.027	0.11	1.81	0.107	2.20

... continuation of Table 9.2.

Date	Sampling point	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]
Aug/19/2009	7	0.029	0.06	1.13	0.03	2.30
Sep/16/2009	7	0.031	0.08	1.31	0.04	2.10
Oct/14/2009	7	0.028	0.14	1.48	0.06	1.90
Nov/18/2009	7	0.033	0.14	1.71	0.11	2.30
Dec/16/2009	7	0.034	0.22	1.83	0.17	2.70
Jan/13/2010	7	0.032	0.18	1.97	0.19	2.80
Feb/17/2010	7	0.023	0.18	1.58	0.23	2.50
Mar/17/2010	7	0.028	0.11	2.41	0.19	2.90
Apr/14/2010	7	0.033	0.09	2.01	0.16	2.50
May/19/2010	7	0.038	0.14	1.69	0.14	2.60
Jun/16/2010	7	0.035	0.10	1.61	0.10	2.30
Jul/14/2010	7	0.036	0.05	1.75	0.05	2.00
Aug/11/2010	7	0.035	0.07	1.26	0.04	1.80
Sep/15/2010	7	0.052	0.12	1.26	0.17	2.40
Oct/13/2010	7	0.029	0.09	1.64	0.08	2.50
Nov/17/2010	7	0.049	0.12	2.67	0.48	3.30
Dec/15/2010	7	0.037	0.15	2.51	0.56	3.40
Jan/12/2011	7	0.042	0.14	2.38	0.48	3.40
Feb/16/2011	7	0.036	0.150	2.39	0.38	3.30
Mar/16/2011	7	0.031	0.106	2.37	0.30	3.10
Apr/13/2011	7	0.026	0.055	2.50	0.155	2.70
May/18/2011	7	0.040	0.140	2.02	0.19	2.70
Jun/15/2011	7	0.033	0.10	2.15	0.095	2.40
Jul/13/2011	7	0.036	0.10	2.19	0.075	2.40
Aug/19/2009	8	0.005	0.05	1.17	0.09	2.50
Sep/16/2009	8	0.030	0.04	1.45	0.04	2.30
Oct/14/2009	8	0.004	0.04	1.21	0.12	1.60
Nov/18/2009	8	0.010	0.09	0.58	0.15	1.50
Dec/16/2009	8	0.015	0.11	0.90	0.28	1.50
Jan/13/2010	8	0.007	0.10	0.71	0.30	1.40
Feb/17/2010	8	0.010	0.10	0.99	0.30	1.40
Mar/17/2010	8	0.014	0.07	0.71	0.24	1.60
Apr/14/2010	8	0.006	0.06	0.68	0.13	1.50
May/19/2010	8	0.005	0.06	0.64	0.10	1.40
Jun/16/2010	8	0.007	0.07	0.61	0.12	1.40
Jul/14/2010	8	0.004	0.02	1.10	0.12	1.70
Aug/11/2010	8	0.010	0.04	1.15	0.10	1.80
Sep/15/2010	8	0.052	0.09	0.76	0.11	1.50
Oct/13/2010	8	0.003	0.08	0.62	0.15	1.50
Nov/17/2010	8	0.011	0.08	0.66	0.25	1.60
Dec/15/2010	8	0.019	0.08	0.67	0.37	1.50
Jan/12/2011	8	0.023	0.08	0.70	0.36	1.70
Feb/16/2011	8	0.020	0.087	0.82	0.34	1.60
Mar/16/2011	8	0.014	0.077	0.76	0.26	1.40
Apr/13/2011	8	0.009	0.036	1.27	0.151	1.50
May/18/2011	8	0.008	0.053	1.05	0.162	1.50
Jun/15/2011	8	0.003	0.04	1.35	0.168	1.60
Jul/13/2011	8	0.008	0.05	1.05	0.134	1.50

... continuation of Table 9.2.

Date	Sampling point	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]
Aug/19/2009	9	0.034	0.08	1.64	0.06	2.70
Sep/16/2009	9	0.005	0.08	1.05	0.10	2.80
Oct/14/2009	9	0.035	0.09	1.93	0.10	2.30
Nov/18/2009	9	0.037	0.13	3.71	0.15	4.10
Dec/16/2009	9	0.033	0.15	3.43	0.257	4.10
Jan/13/2010	9	0.025	0.16	2.26	0.30	3.30
Feb/17/2010	9	0.022	0.19	2.16	0.41	3.40
Mar/17/2010	9	0.034	0.10	3.43	0.28	4.50
Apr/14/2010	9	0.019	0.08	2.32	0.13	3.00
May/19/2010	9	0.030	0.12	1.75	0.18	2.50
Jun/16/2010	9	0.043	0.12	1.59	0.19	2.10
Jul/14/2010	9	0.022	0.05	1.56	0.09	2.20
Aug/11/2010	9	0.038	0.10	1.72	0.09	2.30
Sep/15/2010	9	0.061	0.12	1.89	0.15	2.60
Oct/13/2010	9	0.021	0.10	1.87	0.10	2.90
Nov/17/2010	9	0.054	0.14	4.28	0.22	4.80
Dec/15/2010	9	0.037	0.15	3.33	0.31	4.60
Jan/12/2011	9	0.043	0.14	3.25	0.37	4.60
Feb/16/2011	9	0.041	0.162	3.54	0.26	4.10
Mar/16/2011	9	0.032	0.111	2.82	0.28	4.10
Apr/13/2011	9	0.021	0.054	2.79	0.139	3.10
May/18/2011	9	0.032	0.108	2.19	0.246	2.90
Jun/15/2011	9	0.023	0.10	2.15	0.103	2.60
Jul/13/2011	9	0.039	0.10	2.27	0.109	2.60
Aug/19/2009	10	0.013	0.04	2.03	0.05	2.80
Sep/16/2009	10	0.015	0.05	1.66	0.03	2.28
Oct/14/2009	10	0.012	0.05	1.96	0.05	2.20
Nov/18/2009	10	0.011	0.07	1.59	0.13	2.10
Dec/16/2009	10	0.013	0.11	1.89	0.18	2.40
Jan/13/2010	10	0.007	0.10	1.23	0.18	2.40
Feb/17/2010	10	0.007	0.09	1.21	0.21	2.30
Mar/17/2010	10	0.015	0.05	1.98	0.19	2.90
Apr/14/2010	10	0.007	0.04	1.69	0.09	1.90
May/19/2010	10	0.012	0.05	1.49	0.04	2.20
Jun/16/2010	10	0.011	0.05	1.25	0.07	2.20
Jul/14/2010	10	0.014	0.02	2.21	0.05	2.26
Aug/11/2010	10	0.012	0.05	2.41	0.06	3.20
Sep/15/2010	10	0.017	0.17	0.84	0.07	1.50
Oct/13/2010	10	0.004	0.05	1.73	0.08	2.40
Nov/17/2010	10	0.007	0.08	2.19	0.25	2.90
Dec/15/2010	10	0.011	0.10	2.02	0.32	2.70
Jan/12/2011	10	0.017	0.08	1.78	0.32	2.70
Feb/16/2011	10	0.014	0.105	1.73	0.25	2.50
Mar/16/2011	10	0.013	0.059	1.82	0.21	2.50
Apr/13/2011	10	0.007	0.032	2.04	0.097	2.30
May/18/2011	10	0.015	0.048	0.78	0.05	2.30
Jun/15/2011	10	0.008	0.05	2.31	0.048	2.60
Jul/13/2011	10	0.013	0.06	1.72	0.091	2.20

... continuation of Table 9.2.

Date	Sampling point	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]
Aug/19/2009	11	0.005	0.02	0.31	0.02	1.00
Sep/16/2009	11	0.006	0.03	0.38	0.03	1.20
Oct/14/2009	11	0.005	0.03	0.45	0.05	0.85
Nov/18/2009	11	0.011	0.07	1.27	0.19	2.10
Dec/16/2009	11	0.017	0.12	1.98	0.24	3.10
Jan/13/2010	11	0.008	0.11	1.40	0.20	2.10
Feb/17/2010	11	0.006	0.13	0.87	0.27	1.80
Mar/17/2010	11	0.028	0.06	2.31	0.23	3.40
Apr/14/2010	11	0.008	0.05	1.44	0.14	2.40
May/19/2010	11	0.007	0.06	0.59	0.05	1.40
Jun/16/2010	11	0.006	0.10	0.55	0.13	1.50
Jul/14/2010	11	0.008	0.07	0.54	0.06	1.10
Aug/11/2010	11	0.007	0.05	0.47	0.04	0.90
Sep/15/2010	11	0.019	0.12	0.63	0.11	1.60
Oct/13/2010	11	0.000	0.03	0.57	0.14	1.40
Nov/17/2010	11	0.014	0.08	2.71	0.25	3.50
Dec/15/2010	11	0.022	0.08	2.09	0.34	3.00
Jan/12/2011	11	0.038	0.09	2.07	0.33	3.10
Feb/16/2011	11	0.027	0.091	1.90	0.29	2.60
Mar/16/2011	11	0.020	0.067	1.61	0.26	2.40
Apr/13/2011	11	0.005	0.031	1.38	0.103	1.50
May/18/2011	11	0.011	0.092	0.66	0.186	1.10
Jun/15/2011	11	0.002	0.06	0.69	0.109	0.96
Jul/13/2011	11	0.011	0.05	1.00	0.058	1.40
Aug/19/2009	12	0.009	0.04	2.28	0.03	4.20
Sep/16/2009	12	0.020	0.04	2.78	0.02	4.30
Oct/14/2009	12	0.014	0.06	2.54	0.03	3.30
Nov/18/2009	12	0.044	0.12	4.39	0.08	5.10
Dec/16/2009	12	0.052	0.13	4.94	0.27	5.80
Jan/13/2010	12	0.023	0.14	4.04	0.20	5.30
Feb/17/2010	12	0.019	0.13	4.24	0.18	4.80
Mar/17/2010	12	0.049	0.09	5.07	0.26	5.90
Apr/14/2010	12	0.025	0.08	4.27	0.101	5.60
May/19/2010	12	0.021	0.09	2.79	0.03	4.70
Jun/16/2010	12	0.033	0.10	3.42	0.13	4.80
Jul/14/2010	12	0.014	0.03	3.29	0.03	4.00
Aug/11/2010	12	0.048	0.10	3.09	0.66	4.60
Sep/15/2010	12	0.017	0.13	2.01	0.05	3.30
Oct/13/2010	12	0.027	0.06	3.35	0.05	4.90
Nov/17/2010	12	0.055	0.13	4.90	0.16	5.90
Dec/15/2010	12	0.047	0.13	5.10	0.24	5.50
Jan/12/2011	12	0.058	0.11	4.32	0.25	5.70
Feb/16/2011	12	0.044	0.124	4.42	0.24	5.30
Mar/16/2011	12	0.045	0.092	4.39	0.21	5.30
Apr/13/2011	12	0.028	0.103	3.59	0.076	4.70
May/18/2011	12	0.015	0.077	3.33	0.041	4.00
Jun/15/2011	12	0.010	0.10	2.97	0.045	3.80
Jul/13/2011	12	0.050	0.11	3.45	0.049	4.20

... continuation of Table 9.2.

Date	Sampling point	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]
Aug/19/2009	13	0.006	0.02	0.21	0.03	1.10
Sep/16/2009	13	0.005	0.05	0.19	0.05	0.97
Oct/14/2009	13	0.006	0.05	0.65	0.04	1.20
Nov/18/2009	13	0.023	0.08	1.89	0.11	2.80
Dec/16/2009	13	0.023	0.11	2.79	0.20	3.40
Jan/13/2010	13	0.009	0.14	1.52	0.22	2.50
Feb/17/2010	13	0.007	0.09	1.27	0.20	2.10
Mar/17/2010	13	0.026	0.08	2.48	0.19	3.70
Apr/14/2010	13	0.028	0.07	2.06	0.18	3.20
May/19/2010	13	0.008	0.06	1.29	0.08	2.20
Jun/16/2010	13	0.007	0.07	1.19	0.09	2.00
Jul/14/2010	13	0.008	0.02	0.79	0.06	1.40
Aug/11/2010	13	0.005	0.06	0.22	0.03	0.54
Sep/15/2010	13	0.012	0.10	0.86	0.07	1.80
Oct/13/2010	13	0.001	0.04	1.43	0.05	2.50
Nov/17/2010	13	0.030	0.11	3.08	0.20	3.90
Dec/15/2010	13	0.032	0.12	2.27	0.26	3.10
Jan/12/2011	13	0.036	0.09	2.38	0.27	3.40
Feb/16/2011	13	0.033	0.113	2.25	0.24	3.00
Mar/16/2011	13	0.032	0.069	2.14	0.25	3.00
Apr/13/2011	13	0.008	0.040	1.50	0.106	2.20
May/18/2011	13	0.012	0.059	1.43	0.09	1.60
Jun/15/2011	13	0.003	0.05	1.05	0.099	1.20
Jul/13/2011	13	0.022	0.08	1.56	0.088	2.10
Aug/19/2009	14	0.030	0.06	3.27	0.04	5.60
Sep/16/2009	14	0.028	0.07	4.37	0.03	7.40
Oct/14/2009	14	0.056	0.11	4.26	0.12	4.50
Nov/18/2009	14	0.112	0.17	4.69	0.17	6.40
Dec/16/2009	14	0.087	0.16	5.42	0.45	6.80
Jan/13/2010	14	0.076	0.17	5.86	0.38	6.40
Feb/17/2010	14	0.057	0.14	5.87	0.50	6.40
Mar/17/2010	14	0.097	0.14	5.36	0.44	6.70
Apr/14/2010	14	0.082	0.12	5.95	0.22	6.17
May/19/2010	14	0.068	0.11	4.26	0.14	6.30
Jun/16/2010	14	0.064	0.16	4.10	0.21	5.60
Jul/14/2010	14	0.066	0.09	4.76	0.09	5.50
Aug/11/2010	14	0.038	0.09	5.38	0.04	6.60
Sep/15/2010	14	0.087	0.27	1.94	0.33	3.80
Oct/13/2010	14	0.074	0.11	4.57	0.12	6.60
Nov/17/2010	14	0.125	0.19	5.15	0.19	6.00
Dec/15/2010	14	0.103	0.17	4.84	0.34	6.30
Jan/12/2011	14	0.108	0.18	4.58	0.39	6.20
Feb/16/2011	14	0.098	0.153	4.99	0.38	5.80
Mar/16/2011	14	0.101	0.150	4.99	0.37	6.50
Apr/13/2011	14	0.061	0.097	4.74	0.242	6.30
May/18/2011	14	0.040	0.137	4.56	0.179	6.20
Jun/15/2011	14	0.038	0.15	4.15	0.176	5.80
Jul/13/2011	14	0.105	0.18	5.01	0.167	5.80

... continuation of Table 9.2.

Date	Sampling point	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]
Aug/19/2009	15	0.013	0.06	0.50	0.02	0.87
Sep/16/2009	15	0.011	0.05	0.48	0.02	0.94
Oct/14/2009	15	0.012	0.05	0.48	0.02	0.63
Nov/18/2009	15	0.009	0.03	3.75	0.06	4.60
Dec/16/2009	15	0.013	0.04	2.57	0.04	2.90
Jan/13/2010	15	0.009	0.03	0.72	0.05	0.78
Feb/17/2010	15	0.008	0.03	0.80	0.04	0.87
Mar/17/2010	15	0.015	0.04	3.10	0.05	7.70
Apr/14/2010	15	0.014	0.04	0.62	0.05	0.97
May/19/2010	15	0.015	0.05	0.44	0.03	0.91
Jun/16/2010	15	0.014	0.06	0.48	0.03	0.79
Jul/14/2010	15	0.018	0.03	0.60	0.02	0.76
Aug/11/2010	15	0.017	0.06	0.53	0.02	0.65
Sep/15/2010	15	0.016	0.10	4.85	0.02	7.00
Oct/13/2010	15	0.011	0.01	0.48	0.01	0.68
Nov/17/2010	15	0.017	0.04	4.57	0.02	5.40
Dec/15/2010	15	0.016	0.03	2.45	0.03	3.10
Jan/12/2011	15	0.016	0.03	2.57	0.06	3.50
Feb/16/2011	15	0.016	0.033	2.06	0.04	2.50
Mar/16/2011	15	0.015	0.046	1.99	0.03	2.70
Apr/13/2011	15	0.009	0.035	0.93	0.022	0.95
May/18/2011	15	0.014	0.050	1.05	0.011	1.06
Jun/15/2011	15	0.007	0.06	1.03	0.029	1.06
Jul/13/2011	15	0.018	0.07	0.93	0.028	0.96
Aug/19/2009	16	0.017	0.04	7.42	0.09	8.10
Sep/16/2009	16	0.029	0.08	7.83	0.10	10.40
Oct/14/2009	16	0.039	0.10	5.15	0.42	6.80
Nov/18/2009	16	0.111	0.28	6.24	0.52	8.30
Dec/16/2009	16	0.084	0.19	5.47	0.52	8.10
Jan/13/2010	16	0.053	0.22	4.56	0.59	7.20
Feb/17/2010	16	0.095	0.23	6.96	0.70	8.10
Mar/17/2010	16	0.179	0.30	6.29	1.12	8.50
Apr/14/2010	16	0.065	0.14	6.82	0.37	8.30
May/19/2010	16	0.042	0.15	6.96	0.21	7.90
Jun/16/2010	16	0.055	0.16	6.74	0.27	8.40
Jul/14/2010	16	0.056	0.07	8.81	0.09	9.70
Aug/11/2010	16	0.035	0.07	7.40	0.02	10.90
Sep/15/2010	16	0.379	0.64	4.51	0.76	7.80
Oct/13/2010	16	0.028	0.08	6.42	0.24	9.10
Nov/17/2010	16	0.084	0.17	6.13	0.46	7.70
Dec/15/2010	16	0.086	0.14	6.44	0.64	8.50
Jan/12/2011	16	0.100	0.16	5.69	0.72	7.80
Feb/16/2011	16	0.085	0.180	6.67	0.58	8.10
Mar/16/2011	16	0.084	0.125	4.51	0.54	7.90
Apr/13/2011	16	0.044	0.165	7.21	0.237	8.80
May/18/2011	16	0.068	0.170	6.36	0.338	8.50
Jun/15/2011	16	0.047	0.12	7.48	0.165	9.60
Jul/13/2011	16	0.039	0.07	6.56	0.044	9.10

... continuation of Table 9.2.

Date	Sampling point	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]
Aug/19/2009	17	0.038	0.05	3.00	0.03	4.80
Sep/16/2009	17	0.034	0.09	2.84	0.03	4.70
Oct/14/2009	17	0.046	0.11	2.18	0.17	2.60
Nov/18/2009	17	0.045	0.20	3.48	0.27	4.70
Dec/16/2009	17	0.039	0.22	3.88	0.32	4.90
Jan/13/2010	17	0.021	0.19	3.32	0.44	4.60
Feb/17/2010	17	0.031	0.14	3.95	0.58	4.70
Mar/17/2010	17	0.040	0.08	3.83	0.35	5.20
Apr/14/2010	17	0.020	0.07	3.65	0.15	4.70
May/19/2010	17	0.019	0.08	3.14	0.13	3.70
Jun/16/2010	17	0.037	0.10	3.26	0.13	4.30
Jul/14/2010	17	0.066	0.10	4.53	0.09	5.40
Aug/11/2010	17	0.053	0.09	3.28	0.04	4.10
Sep/15/2010	17	0.150	0.43	2.97	0.54	5.80
Oct/13/2010	17	0.018	0.11	2.56	0.11	4.40
Nov/17/2010	17	0.043	0.13	3.67	0.25	5.10
Dec/15/2010	17	0.044	0.11	3.59	0.42	5.00
Jan/12/2011	17	0.049	0.11	3.75	0.49	5.20
Feb/16/2011	17	0.040	0.122	4.05	0.43	5.30
Mar/16/2011	17	0.040	0.082	3.98	0.42	5.00
Apr/13/2011	17	0.009	0.046	3.96	0.046	5.00
May/18/2011	17	0.065	0.172	2.80	0.484	4.00
Jun/15/2011	17	0.009	0.15	3.65	0.027	5.20
Jul/13/2011	17	0.047	0.07	2.76	0.034	3.90
Aug/19/2009	18	0.063	0.09	7.77	0.06	11.90
Sep/16/2009	18	0.057	0.12	6.73	0.07	9.20
Oct/14/2009	18	0.064	0.11	6.21	0.13	7.60
Nov/18/2009	18	0.079	0.16	6.89	0.16	8.10
Dec/16/2009	18	0.054	0.13	7.97	0.30	9.50
Jan/13/2010	18	0.049	0.26	6.00	0.47	9.70
Feb/17/2010	18	0.073	0.13	6.15	0.64	9.90
Mar/17/2010	18	0.058	0.09	7.05	0.31	8.20
Apr/14/2010	18	0.031	0.09	8.52	0.21	10.40
May/19/2010	18	0.042	0.12	7.62	0.13	9.40
Jun/16/2010	18	0.046	0.14	8.76	0.12	9.50
Jul/14/2010	18	0.076	0.12	9.68	0.12	11.10
Aug/11/2010	18	0.117	0.24	9.15	0.04	11.00
Sep/15/2010	18	0.247	0.40	5.61	0.46	9.40
Oct/13/2010	18	0.226	0.48	6.66	0.23	11.60
Nov/17/2010	18	0.064	0.15	5.70	0.25	7.40
Dec/15/2010	18	0.047	0.16	7.64	0.39	8.20
Jan/12/2011	18	0.060	0.10	7.18	0.43	9.60
Feb/16/2011	18	0.049	0.104	7.38	0.37	8.00
Mar/16/2011	18	0.059	0.102	6.54	0.43	8.90
Apr/13/2011	18	0.040	0.078	7.79	0.241	9.30
May/18/2011	18	0.073	0.196	6.25	0.432	9.00
Jun/15/2011	18	0.123	0.32	8.56	0.305	10.10
Jul/13/2011	18	0.081	0.14	6.44	0.241	8.40

... continuation of Table 9.2.

Date	Sampling point	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]
Aug/19/2009	19	0.006	0.02	0.80	0.02	1.60
Sep/16/2009	19	0.008	0.03	0.83	0.02	1.70
Oct/14/2009	19	0.009	0.03	0.86	0.10	1.30
Nov/18/2009	19	0.012	0.08	1.06	0.20	1.80
Dec/16/2009	19	0.020	0.11	1.94	0.38	2.70
Jan/13/2010	19	0.011	0.09	1.40	0.45	2.40
Feb/17/2010	19	0.011	0.12	1.04	0.42	2.00
Mar/17/2010	19	0.024	0.07	2.53	0.43	3.00
Apr/14/2010	19	0.006	0.06	1.87	0.19	2.50
May/19/2010	19	0.006	0.05	0.94	0.10	1.90
Jun/16/2010	19	0.009	0.09	1.01	0.26	1.90
Jul/14/2010	19	0.009	0.04	1.06	0.06	1.60
Aug/11/2010	19	0.007	0.03	0.88	0.02	1.10
Sep/15/2010	19	0.048	0.057	0.41	0.06	1.20
Oct/13/2010	19	0.005	0.03	0.87	0.11	1.70
Nov/17/2010	19	0.016	0.08	2.55	0.17	3.10
Dec/15/2010	19	0.037	0.09	1.83	0.61	2.70
Jan/12/2011	19	0.036	0.09	1.84	0.55	3.00
Feb/16/2011	19	0.040	0.103	2.04	0.54	3.00
Mar/16/2011	19	0.034	0.078	1.66	0.50	2.60
Apr/13/2011	19	0.011	0.031	1.32	0.382	1.90
May/18/2011	19	0.010	0.071	1.00	0.304	1.40
Jun/15/2011	19	0.001	0.05	0.97	0.186	1.20
Jul/13/2011	19	0.007	0.03	1.02	0.143	1.30
Aug/19/2009	20	0.024	0.03	3.07	0.02	4.70
Sep/16/2009	20	0.026	0.07	2.89	0.03	4.70
Oct/14/2009	20	0.031	0.08	2.54	0.11	3.20
Nov/18/2009	20	0.053	0.15	3.80	0.22	5.10
Dec/16/2009	20	0.045	0.17	4.11	0.35	5.30
Jan/13/2010	20	0.030	0.15	2.91	0.35	4.50
Feb/17/2010	20	0.022	0.16	3.17	0.46	4.60
Mar/17/2010	20	0.050	0.09	4.19	0.29	5.30
Apr/14/2010	20	0.025	0.10	3.56	0.15	3.90
May/19/2010	20	0.023	0.08	2.86	0.10	4.30
Jun/16/2010	20	0.033	0.11	2.76	0.10	4.30
Jul/14/2010	20	0.032	0.09	3.32	0.05	4.10
Aug/11/2010	20	0.026	0.07	2.71	0.03	3.50
Sep/15/2010	20	0.084	0.11	2.30	0.36	4.90
Oct/13/2010	20	0.023	0.08	2.82	0.07	4.30
Nov/17/2010	20	0.075	0.14	4.24	0.23	5.40
Dec/15/2010	20	0.046	0.13	4.06	0.38	5.10
Jan/12/2011	20	0.053	0.12	3.80	0.39	5.40
Feb/16/2011	20	0.029	0.135	4.15	0.36	5.20
Mar/16/2011	20	0.042	0.093	3.73	0.30	4.90
Apr/13/2011	20	0.029	0.100	3.26	0.131	4.80
May/18/2011	20	0.041	0.152	2.89	0.264	3.90
Jun/15/2011	20	0.030	0.15	2.97	0.071	4.30
Jul/13/2011	20	0.041	0.09	2.99	0.064	3.70

... continuation of Table 9.2.

Date	Sampling point	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]
Aug/19/2009	21	0.027	0.07	1.64	0.02	3.30
Sep/16/2009	21	0.031	0.06	1.99	0.02	3.70
Oct/14/2009	21	0.032	0.08	2.21	0.07	2.80
Nov/18/2009	21	0.050	0.15	3.61	0.19	4.70
Dec/16/2009	21	0.040	0.16	4.72	0.28	5.10
Jan/13/2010	21	0.018	0.26	2.52	0.32	4.00
Feb/17/2010	21	0.020	0.18	2.11	0.37	4.00
Mar/17/2010	21	0.039	0.1	3.62	0.29	4.60
Apr/14/2010	21	0.020	0.10	2.81	0.11	4.10
May/19/2010	21	0.028	0.10	2.34	0.10	3.60
Jun/16/2010	21	0.034	0.12	2.20	0.12	3.50
Jul/14/2010	21	0.030	0.08	2.35	0.06	2.80
Aug/11/2010	21	0.025	0.071	2.07	0.01	3.00
Sep/15/2010	21	0.094	0.120	2.12	0.23	3.60
Oct/13/2010	21	0.016	0.10	2.49	0.04	3.90
Nov/17/2010	21	0.059	0.13	3.81	0.23	4.80
Dec/15/2010	21	0.042	0.14	3.83	0.32	4.90
Jan/12/2011	21	0.044	0.13	3.99	0.37	5.00
Feb/16/2011	21	0.039	0.150	3.59	0.30	4.50
Mar/16/2011	21	0.029	0.101	2.72	0.27	4.50
Apr/13/2011	21	0.016	0.115	2.80	0.114	3.90
May/18/2011	21	0.036	0.142	2.58	0.261	3.60
Jun/15/2011	21	0.023	0.13	3.08	0.077	3.40
Jul/13/2011	21	0.032	0.08	2.38	0.038	3.10

Table 9.3 Daily water quality parameters from the automatic water sampler at Willenscharen.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Aug/08/2009	0.04	0.04	1.85	0.07	2.9	
Aug/09/2009	0.02	0.04	1.93	0.05	2.6	
Aug/10/2009	0.04	0.07	1.62	0.14	2.5	
Aug/11/2009	0.03	0.05	1.69	0.05	2.8	
Aug/12/2009	0.03	0.05	1.74	0.04	2.6	
Aug/13/2009	0.03	0.05	1.69	0.03	2.7	
Aug/14/2009	0.02	0.08	1.91	0.02	2.3	
Aug/15/2009	0.02	0.08	1.71	0.01	2.5	
Aug/16/2009	0.02	0.09	1.88	0.01	2.3	
Aug/17/2009	0.03	0.10	1.87	0.02	2.4	
Aug/18/2009	0.02	0.08	1.86	0.04	2.5	
Aug/19/2009	0.02	0.06	1.79	0.04	2.5	
Aug/20/2009	0.02	0.08	2.04	0.05	2.5	
Aug/21/2009	0.02	0.09	1.70	0.05	2.3	
Aug/22/2009	0.02	0.08	1.96	0.04	2.7	
Aug/23/2009	0.02	0.07	1.45	0.03	2.5	
Aug/24/2009	0.03	0.08	1.73	0.02	2.6	
Aug/25/2009	0.02	0.07	1.53	0.02	2.5	
Aug/26/2009	0.02	0.08	1.96	0.02	2.4	
Aug/27/2009	0.02	0.07	1.54	0.03	2.6	
Aug/28/2009	0.03	0.07	1.96	0.05	2.4	
Aug/29/2009	0.03	0.09	2.27	0.07	2.7	
Aug/30/2009	0.03	0.12	2.17	0.09	2.6	
Aug/31/2009	0.04	0.11	2.16	0.16	2.7	
Sep/01/2009	0.05	0.12	2.00	0.14	2.7	
Sep/02/2009	0.03	0.10	1.98	0.06	2.8	
Sep/03/2009	0.03	0.09	2.07	0.03	2.6	
Sep/04/2009	0.02	0.09	1.96	0.02	2.6	
Sep/05/2009	0.03	0.09	2.02	0.02	2.6	
Sep/06/2009	0.02	0.09	2.00	0.02	2.8	
Sep/07/2009	0.03	0.10	2.00	0.03	2.8	
Sep/08/2009	0.04	0.08	2.45	0.04	2.9	
Sep/09/2009	0.03	0.08	2.66	0.04	2.7	
Sep/10/2009	0.03	0.09	2.19	0.03	2.9	
Sep/11/2009	0.03	0.09	2.42	0.04	2.7	
Sep/12/2009	0.02	0.08	2.77	0.02	3.1	
Sep/13/2009	0.02	0.08	2.65	0.02	3.1	
Sep/14/2009	0.02	0.09	2.27	0.02	2.7	
Sep/15/2009	0.02	0.07	2.47	0.02	2.5	
Sep/16/2009	0.03	0.08	2.08	0.02	2.6	
Sep/17/2009	0.02	0.08	2.33	0.02	2.5	
Sep/18/2009	0.022	0.07	2.14	0.03	2.6	
Sep/19/2009	0.02	0.07	2.40	0.03	2.4	

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Sep/20/2009	0.02	0.07	2.40	0.03	2.7	
Sep/21/2009	0.02	0.07	2.29	0.02	2.6	
Sep/22/2009	0.02	0.07	2.34	0.02	2.8	
Sep/23/2009	0.02	0.08	2.37	0.02	2.7	
Sep/24/2009	0.02	0.08	2.15	0.02	2.7	
Sep/25/2009	0.02	0.07	2.28	0.02	2.8	
Sep/26/2009	0.03	0.08	2.40	0.02	2.8	
Sep/27/2009	0.02	0.07	2.29	0.01	2.8	
Sep/28/2009	0.02	0.07	2.05	0.01	2.7	
Sep/29/2009	0.02	0.07	2.11	0.05	2.7	
Sep/30/2009	0.02	0.09	2.09	0.04	2.6	
Oct/01/2009	0.03	0.07	1.33	0.04	2.0	
Oct/02/2009	0.02	0.06	2.46	0.04	2.7	
Oct/03/2009	0.02	0.08	1.76	0.02	1.9	
Oct/04/2009	0.03	0.09	1.83	0.04	2.4	
Oct/05/2009	0.03	0.09	1.56	0.10	2.5	
Oct/06/2009	0.03	0.09	2.16	0.08	2.4	
Oct/07/2009	0.03	0.09	1.95	0.03	2.6	
Oct/08/2009	0.03	0.10	1.67	0.03	2.8	
Oct/09/2009	0.03	0.09	2.25	0.04	3.0	
Oct/10/2009	0.03	0.08	2.22	0.04	2.4	
Oct/11/2009	0.03	0.09	2.24	0.05	2.9	
Oct/12/2009	0.03	0.13	2.43	0.06	2.5	
Oct/13/2009	0.03	0.12	2.39	0.10	3.1	
Oct/14/2009	0.03	0.10	2.36	0.06	3.2	
Oct/15/2009	0.03	0.10	2.44	0.06	3.0	
Oct/16/2009	0.03	0.13	1.99	0.05	2.3	
Oct/17/2009	0.02	0.21	2.36	0.05	2.5	
Oct/18/2009	0.02	0.13	2.36	0.05	3.0	
Oct/19/2009	0.02	0.18	2.48	0.05	2.6	
Oct/20/2009	0.023	0.13	1.82	0.01	2.1	
Oct/21/2009	0.02	0.09	2.35	0.03	2.8	
Oct/22/2009	0.02	0.08	2.10	0.04	2.3	
Oct/23/2009	0.02	0.04	2.15	0.04	2.7	
Oct/24/2009	0.02	0.08	2.43	0.05	2.6	
Oct/25/2009	0.02	0.09	2.18	0.03	2.4	
Oct/26/2009	0.02	0.08	2.18	0.04	2.4	
Oct/27/2009	0.03	0.11	2.39	0.05	2.6	
Oct/28/2009	0.03	0.11	2.07	0.06	2.4	
Oct/29/2009	0.03	0.11	2.08	0.05	2.3	
Oct/30/2009	0.03	0.11	2.48	0.03	3.3	7.70
Oct/31/2009	0.03	0.11	2.40	0.03	3.0	6.40
Nov/01/2009	0.03	0.10	2.15	0.03	2.7	5.80
Nov/02/2009	0.04	0.28	2.36	0.01	3.2	39.50
Nov/03/2009	0.07	0.27	2.55	0.18	3.0	21.50
Nov/04/2009	0.05	0.18	3.38	0.12	4.1	11.80
Nov/05/2009	0.05	0.18	3.34	0.16	4.2	11.80
Nov/06/2009	0.04	0.15	2.82	0.11	3.5	12.70
Nov/07/2009	0.04	0.14	2.58	0.11	2.7	11.30

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Nov/08/2009	0.04	0.14	3.07	0.095	4.4	9.70
Nov/09/2009	0.03	0.13	2.77	0.08	4.0	8.70
Nov/10/2009	0.04	0.12	2.22	0.11	2.8	7.40
Nov/11/2009	0.04	0.15	2.69	0.06	3.3	11.10
Nov/12/2009	0.04	0.16	3.47	0.07	3.5	8.90
Nov/13/2009	0.04	0.18	3.60	0.08	4.1	10.30
Nov/14/2009	0.04	0.20	3.24	0.09	4.5	14.60
Nov/15/2009	0.04	0.17	3.92	0.10	4.8	10.80
Nov/16/2009	0.04	0.17	3.53	0.09	4.5	14.40
Nov/17/2009	0.04	0.23	3.28	0.11	4.7	21.20
Nov/18/2009	0.05	0.23	4.34	0.02	5.3	21.80
Nov/19/2009	0.06	0.47	3.93	0.02	4.6	54.20
Nov/20/2009	0.05	0.23	4.82	0.02	6.8	14.50
Nov/21/2009	0.04	0.16	4.45	0.02	6.0	11.00
Nov/22/2009	0.04	0.17	3.68	0.04	4.6	11.00
Nov/23/2009	0.04	0.18	4.32	0.04	5.3	13.40
Nov/24/2009	0.04	0.20	3.10	0.05	3.5	17.70
Nov/25/2009	0.04	0.16	5.24	0.03	5.7	12.90
Nov/26/2009	0.04	0.14	3.57	0.03	5.6	11.50
Nov/27/2009	0.05	0.17	4.31	0.02	5.0	11.90
Nov/28/2009	0.05	0.17	4.27	0.02	5.7	13.10
Nov/29/2009	0.05	0.21	4.77	0.02	6.2	16.80
Nov/30/2009	0.05	0.27	4.64	0.02	6.3	28.00
Dec/01/2009	0.04	0.26	4.19	0.03	4.8	30.00
Dec/02/2009	0.04	0.30	3.96	0.04	5.5	40.90
Dec/03/2009	0.04	0.26	3.42	0.07	3.7	32.40
Dec/04/2009	0.04	0.25	3.50	0.11	3.7	27.00
Dec/05/2009	0.04	0.26	3.16	0.14	3.4	35.80
Dec/06/2009	0.04	0.23	3.52	0.14	3.7	29.00
Dec/07/2009	0.04	0.28	3.24	0.15	4.4	41.20
Dec/08/2009	0.05	0.25	3.50	0.03	4.8	42.50
Dec/09/2009	0.04	0.22	5.26	0.04	5.6	30.80
Dec/10/2009	0.04	0.35	3.38	0.03	4.6	73.10
Dec/11/2009	0.07	0.50	4.45	0.07	5.5	112.95
Dec/12/2009	0.06	0.30	4.72	0.15	6.5	72.20
Dec/13/2009	0.05	0.23	4.38	0.14	5.9	39.70
Dec/14/2009	0.05	0.22	4.45	0.15	5.4	34.60
Dec/15/2009	0.04	0.25	3.69	0.19	4.9	31.70
Dec/16/2009	0.04	0.23	3.97	0.20	4.9	34.50
Dec/17/2009	0.04	0.24	4.57	0.20	4.8	33.90
Dec/18/2009	0.03	0.25	3.78	0.16	4.6	34.90
Dec/19/2009	0.03	0.27	3.27	0.17	4.6	42.10
Dec/20/2009		0.22			4.7	
Dec/21/2009		0.45			4.3	
Dec/22/2009	0.03	0.29	3.44	0.22	4.2	49.00
Dec/23/2009	0.03	0.23	3.49	0.22	4.3	33.50
Dec/24/2009	0.03	0.27	3.39	0.24	4.1	66.29
Dec/25/2009	0.02	0.25	3.54	0.23	4.1	38.80
Dec/26/2009	0.03	0.36	3.26	0.31	4.7	86.70

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Dec/27/2009	0.05	0.36	5.22	0.26	6.0	89.40
Dec/28/2009	0.05	0.25	4.67	0.21	6.1	44.80
Dec/29/2009	0.04	0.26	5.88	0.21	6.1	37.70
Dec/30/2009	0.03	0.26	5.45	0.14	5.6	44.10
Dec/31/2009	0.03	0.19	4.40	0.14	4.9	25.40
Jan/01/2010	0.04	0.23	3.03	0.18	4.6	33.90
Jan/02/2010	0.03	0.24	3.29	0.20	4.2	36.10
Jan/03/2010	0.03	0.28	3.83	0.23	4.2	43.20
Jan/09/2010	0.03	0.39	3.06	0.15	3.7	
Jan/10/2010	0.02	0.43	4.00	0.13	4.2	73.20
Jan/11/2010	0.03	0.39	3.89	0.16	4.1	
Jan/12/2010	0.02	0.31	2.93	0.22	4.1	88.64
Jan/13/2010	0.02	0.40	4.43	0.14	4.6	85.20
Jan/14/2010	0.02	0.33	3.41	0.13	4.1	58.90
Jan/20/2010	0.02	0.24	3.96	0.30	4.3	42.20
Jan/27/2010		0.22			2.9	
Jan/28/2010	0.02	0.21	3.31	0.21	3.6	39.70
Jan/29/2010	0.02	0.24	2.97	0.25	4.0	34.80
Jan/31/2010	0.03	0.40	3.47	0.07	3.9	47.60
Feb/01/2010	0.02	0.22	4.10	0.08	4.2	34.70
Feb/02/2010	0.03	0.23	3.43	0.11	3.6	49.38
Feb/03/2010	0.02	0.21	3.62	0.13	3.9	43.60
Feb/04/2010	0.02	0.20	3.94	0.16	4.1	30.00
Feb/05/2010	0.02	0.18	3.47	0.17	3.8	28.60
Feb/06/2010	0.03	0.18	3.68	0.23	3.9	26.40
Feb/07/2010	0.02	0.21	3.29	0.31	3.8	26.92
Feb/09/2010	0.02	0.24	3.68	0.06	4.1	76.00
Feb/10/2010		0.27			4.2	
Feb/11/2010		0.27			4.0	
Feb/12/2010	0.02	0.23	3.45	0.10	3.6	54.00
Feb/13/2010		0.24			3.9	
Feb/14/2010	0.02	0.19	3.30	0.10	3.7	66.50
Feb/15/2010	0.02	0.21	3.39	0.12	4.0	51.33
Feb/16/2010	0.02	0.20	3.41	0.12	3.7	56.60
Feb/17/2010	0.02	0.63	3.91	0.03	4.1	168.29
Feb/18/2010	0.02	0.22	3.40	0.14	3.6	27.62
Feb/19/2010	0.003	0.13	2.66	0.004	3.0	41.10
Feb/20/2010	0.03	0.19	3.38	0.11	3.8	45.40
Feb/21/2010	0.03	0.17	3.54	0.13	3.9	32.10
Feb/22/2010	0.02	0.17	3.75	0.15	3.9	36.10
Feb/23/2010	0.03	0.20	3.49	0.17	3.7	27.80
Feb/24/2010	0.03	0.15	3.71	0.18	3.9	53.80
Feb/25/2010	0.02	0.16	3.65	0.17	3.8	31.20
Feb/26/2010	0.01	0.17	3.63	0.04	3.7	47.20
Feb/27/2010	0.03	0.19	4.22	0.13	4.6	42.50
Feb/28/2010	0.05	0.41	6.04	0.36	6.5	102.90
Mar/01/2010	0.05	0.35	6.68	0.25	6.9	
Mar/02/2010	0.06	0.27	6.63	0.30	7.1	90.70
Mar/03/2010	0.08	0.33	5.83	0.38	6.7	

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Mar/04/2010	0.06	0.33	5.92	0.32	6.7	80.10
Mar/05/2010	0.05	0.31	6.77	0.29	6.5	75.00
Mar/06/2010	0.04	0.26	5.79	0.29	6.1	66.60
Mar/07/2010	0.04	0.30	6.10	0.29	5.6	55.20
Mar/08/2010	0.04	0.26	4.02	0.26	5.3	65.40
Mar/09/2010	0.04	0.25	5.74	0.23	5.2	54.90
Mar/10/2010	0.03	0.24	4.61	0.17	4.9	48.80
Mar/11/2010	0.03	0.22	6.79	0.21	5.1	49.10
Mar/12/2010	0.03	0.21	3.61	0.23	4.9	66.20
Mar/13/2010	0.04	0.26	4.63	0.27	5.6	86.10
Mar/14/2010	0.04	0.23	3.73	0.20	5.6	81.70
Mar/15/2010	0.05	0.23	3.69	0.23	5.3	70.70
Mar/16/2010	0.04	0.19	3.92	0.23	5.2	62.80
Mar/17/2010	0.04	0.17	3.39	0.17	5.1	39.60
Mar/18/2010	0.04	0.19	3.37	0.20	4.9	24.80
Mar/19/2010	0.03	0.20	3.28	0.18	4.8	20.10
Mar/20/2010	0.03	0.22	3.25	0.22	4.7	48.20
Mar/21/2010	0.04	0.23	3.42	0.21	5.0	86.30
Mar/22/2010	0.04	0.19	3.49	0.18	5.1	41.70
Mar/23/2010	0.04	0.18	3.00	0.09	5.1	40.90
Mar/24/2010	0.04	0.16	3.00	0.11	4.6	40.20
Mar/25/2010	0.03	0.19	3.18	0.12	4.5	34.50
Mar/26/2010	0.03	0.24	3.11	0.13	4.5	30.90
Mar/27/2010	0.09	0.63	3.64	0.59	6.5	133.00
Mar/28/2010	0.07	0.30	4.48	0.27	7.1	59.90
Mar/29/2010	0.04	0.07	3.58	0.09	5.3	35.30
Mar/30/2010	0.04	0.12	3.72	0.01	4.6	15.70
Mar/31/2010	0.05	0.20	3.75	0.04	5.0	28.50
Apr/01/2010	0.04	0.15	3.71	0.03	5.1	14.70
Apr/02/2010	0.03	0.09	1.91	0.05	2.8	6.70
Apr/03/2010	0.01	0.07	1.43	0.03	2.3	6.20
Apr/04/2010	0.02	0.07	0.88	0.14	1.7	5.30
Apr/05/2010	0.02	0.08	0.34	0.27	1.3	4.40
Apr/06/2010	0.02	0.07	0.30	0.29	1.1	3.20
Apr/07/2010	0.02	0.07	0.30	0.27	1.2	2.80
Apr/08/2010	0.03	0.08	0.63	0.41	1.4	2.00
Apr/09/2010	0.02	0.06	0.19	0.27	1.0	2.40
Apr/10/2010	0.02	0.05	0.28	0.25	1.0	2.30
Apr/11/2010	0.02	0.05	0.34	0.33	1.2	1.10
Apr/12/2010	0.02	0.05	0.53	0.31	1.3	0.30
Apr/13/2010	0.02	0.05	0.42	0.27	1.2	1.50
Apr/14/2010	0.016	0.05	0.33	0.32	1.1	0.70
Apr/15/2010	0.02	0.05	0.73	0.27	1.5	0.80
Apr/16/2010	0.02	0.05	0.65	0.28	1.5	1.10
Apr/17/2010	0.02	0.05	0.64	0.27	1.5	1.10
Apr/18/2010	0.02	0.04	0.42	0.31	1.1	1.50
Apr/19/2010	0.02	0.04	0.54	0.32	1.2	1.20
Apr/20/2010	0.02	0.04	0.53	0.33	1.3	1.00
Apr/21/2010	0.02	0.05	0.87	0.30	1.7	1.60

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Apr/22/2010	0.02	0.05	0.68	0.39	1.4	0.70
Apr/23/2010	0.02	0.04	0.72	0.34	1.6	1.50
Apr/24/2010	0.02	0.05	0.75	0.28	1.5	1.30
Apr/25/2010	0.02	0.05	0.52	0.30	1.3	0.60
Apr/26/2010	0.017	0.06	0.51	0.30	1.1	0.60
Apr/27/2010	0.02	0.06	0.48	0.30	1.2	0.50
Apr/28/2010	0.02	0.06	0.61	0.26	1.3	1.30
Apr/29/2010	0.02	0.06	0.47	0.26	1.1	1.60
Apr/30/2010	0.03	0.06	0.51	0.24	1.1	1.40
May/01/2010	0.017	0.06	1.02	0.21	1.6	2.30
May/02/2010	0.02	0.07	1.44	0.15	2.0	2.10
May/03/2010	0.02	0.06	1.10	0.15	1.7	4.90
May/04/2010	0.02	0.06	1.08	0.19	1.7	0.70
May/05/2010	0.02	0.05	1.01	0.18	1.6	1.00
May/06/2010	0.017	0.05	1.01	0.17	1.6	2.30
May/07/2010	0.02	0.05	0.88	0.20	1.5	0.70
May/08/2010	0.02	0.05	0.86	0.17	1.4	0.90
May/09/2010	0.02	0.04	0.52	0.21	1.1	0.80
May/10/2010	0.018	0.05	0.57	0.24	1.2	0.70
May/11/2010	0.016	0.05	0.65	0.23	1.3	1.50
May/12/2010	0.02	0.05	0.65	0.26	1.3	1.00
May/13/2010	0.02	0.06	0.61	0.27	1.3	1.20
May/14/2010	0.02	0.05	0.64	0.27	1.4	1.10
May/15/2010	0.02	0.05	0.71	0.24	1.4	2.50
May/16/2010	0.02	0.05	0.54	0.24	1.2	1.10
May/17/2010	0.02	0.06	0.45	0.28	1.1	1.30
May/18/2010	0.02	0.05	0.53	0.26	1.3	0.60
May/19/2010	0.02	0.03	0.64	0.25	1.4	1.20
May/20/2010	0.02	0.07	0.40	0.27	1.2	1.60
May/21/2010	0.02	0.05	0.56	0.25	1.2	2.40
May/22/2010	0.02	0.07	0.52	0.24	1.1	21.60
May/23/2010	0.02	0.07	0.59	0.21	1.1	3.90
May/24/2010	0.02	0.07	0.66	0.19	1.1	3.40
May/25/2010	0.02	0.06	0.77	0.19	1.2	3.20
May/26/2010	0.02	0.07	0.95	0.17	1.5	3.40
May/27/2010	0.02	0.10	1.08	0.16	1.6	3.20
May/28/2010	0.02	0.10	1.08	0.13	1.4	7.00
May/29/2010	0.02	0.09	0.99	0.14	1.5	4.60
May/30/2010	0.02	0.11	0.83	0.14	1.4	6.50
May/31/2010	0.03	0.12	1.65	0.20	2.2	8.60
Jun/01/2010	0.02	0.08	0.34	0.27	1.1	2.00
Jun/02/2010	0.02	0.08	0.62	0.22	1.2	1.10
Jun/03/2010	0.02	0.09	0.63	0.21	1.4	3.50
Jun/04/2010	0.02	0.11	0.71	0.19	1.3	1.20
Jun/05/2010	0.02	0.08	0.85	0.17	1.5	2.90
Jun/06/2010	0.02	0.10	0.80	0.15	1.4	3.00
Jun/07/2010	0.02	0.09	0.62	0.20	1.2	2.70
Jun/08/2010	0.02	0.10	0.61	0.21	1.3	2.10
Jun/09/2010	0.03	0.08	0.79	0.18	1.4	3.30

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Jun/10/2010	0.03	0.09	0.81	0.17	1.5	3.10
Jun/11/2010	0.02	0.08	0.71	0.19	1.3	3.30
Jun/12/2010	0.03	0.08	0.61	0.21	1.2	3.40
Jun/13//2010	0.03	0.08	0.81	0.19	1.4	2.30
Jun/14/2010	0.03	0.10	1.08	0.15	1.7	2.90
Jun/15/2010	0.02	0.10	1.20	0.14	1.7	5.80
Jun/16/2010	0.03	0.11	1.27	0.13	1.9	4.10
Jun/17/2010	0.02	0.10	1.25	0.12	2.0	5.00
Jun/18/2010	0.03	0.13	1.34	0.11	2.0	6.50
Jun/19/2010	0.02	0.12	1.58	0.10	2.2	5.70
Jun/20/2010	0.02	0.10	1.69	0.08	2.2	4.50
Jun/21/2010	0.03	0.11	1.71	0.11	2.2	4.20
Jun/22/2010	0.02	0.11	1.82	0.10	2.6	5.20
Jun/23/2010	0.02	0.11	1.78	0.07	2.4	4.80
Jun/24/2010	0.02	0.09	1.56	0.09	2.1	5.40
Jun/25/2010	0.03	0.12	1.46	0.09	2.0	5.00
Jun/26/2010	0.02	0.12	1.55	0.07	2.0	5.60
Jun/27/2010	0.02	0.10	1.46	0.06	2.2	5.60
Jun/28/2010	0.01	0.11	1.66	0.01	2.2	4.50
Jun/29/2010	0.02	0.12	1.29	0.05	2.1	5.00
Jun/30/2010	0.02	0.09	1.27	0.05	1.9	6.40
Jul/01/2010	0.02	0.11	1.62	0.04	2.1	5.60
Jul/02/2010	0.03	0.11	1.44	0.06	2.0	3.90
Jul/03/2010	0.02	0.09	1.30	0.05	1.8	5.40
Jul/04/2010	0.03	0.11	1.31	0.04	1.8	5.10
Jul/05/2010	0.03	0.12	1.35	0.04	1.9	4.40
Jul/06/2010	0.02	0.09	1.63	0.03	2.2	4.70
Jul/07/2010	0.02	0.11	1.81	0.03	2.4	3.10
Jul/08/2010	0.03	0.08	1.70	0.03	2.3	4.80
Jul/09/2010	0.03	0.08	1.48	0.03	1.9	5.30
Jul/10/2010	0.03	0.06	1.32	0.03	1.9	4.10
Jul/11/2010	0.03	0.09	1.16	0.03	1.7	4.60
Jul/12/2010	0.03	0.05	1.25	0.03	1.7	5.50
Jul/13/2010	0.03	0.17	0.89	0.10	1.4	4.00
Jul/14/2010	0.03	0.12	1.09	0.06	1.6	3.00
Jul/15/2010	0.03	0.09	1.18	0.06	1.7	2.50
Jul/16/2010	0.03	0.10	1.37	0.04	1.8	3.00
Jul/17/2010	0.03	0.11	1.30	0.04	1.8	1.60
Jul/18/2010	0.03	0.14	1.46	0.05	2.0	3.29
Jul/19/2010	0.03	0.10	1.27	0.03	2.0	2.40
Jul/20/2010	0.03	0.07	1.15	0.02	1.7	2.50
Jul/21/2010	0.03	0.08	1.13	0.03	1.5	2.60
Jul/22/2010	0.03	0.08	1.31	0.03	1.8	2.50
Jul/23/2010	0.03	0.09	1.46	0.03	1.9	3.20
Jul/24/2010	0.03	0.09	1.64	0.03	2.0	3.20
Jul/25/2010	0.03	0.09	1.71	0.02	2.1	2.70
Jul/26/2010	0.03	0.07	1.62	0.02	2.1	2.40
Jul/27/2010	0.03	0.07	1.55	0.03	2.0	4.20
Jul/28/2010	0.03	0.08	1.79	0.03	2.2	2.90

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Jul/29/2010	0.03	0.09	1.72	0.03	2.2	2.70
Jul/30/2010	0.03	0.09	1.74	0.02	2.3	3.20
Jul/31/2010	0.04	0.08	2.00	0.02	2.4	2.40
Aug/01/2010	0.03	0.09	1.09	0.02	2.0	3.70
Aug/02/2010	0.04	0.09	1.47	0.02	2.1	3.50
Aug/03/2010	0.04	0.09	1.78	0.03	2.2	3.00
Aug/04/2010	0.01	0.09	1.88	0.03	2.	2.60
Aug/05/2010	0.03	0.10	1.84	0.03	2.3	3.30
Aug/06/2010	0.03	0.09	1.89	0.03	2.3	3.20
Aug/07/2010	0.04	0.09	1.94	0.03	2.3	3.50
Aug/08/2010	0.03	0.07	1.72	0.02	2.2	4.10
Aug/09/2010	0.03	0.11	1.84	0.05	2.3	3.50
Aug/10/2010	0.03	0.10	1.98	0.03	2.5	3.70
Aug/11/2010	0.03	0.09	1.88	0.02	2.3	3.50
Aug/12/2010	0.03	0.09	1.90	0.03	2.4	4.30
Aug/13/2010	0.03	0.10	1.950	0.04	2.5	3.80
Aug/14/2010	0.04	0.12	1.990	0.03	2.6	4.40
Aug/15/2010	0.04	0.11	1.920	0.03	2.4	4.10
Aug/16/2010	0.03	0.10	1.610	0.05	2.3	6.00
Aug/17/2010	0.04	0.10	1.910	0.03	2.5	3.90
Aug/18/2010	0.04	0.16	1.260	0.04	2.2	9.90
Aug/19/2010	0.04	0.16	1.200	0.04	2.0	7.90
Aug/20/2010	0.04	0.14	1.140	0.03	2.0	6.50
Aug/21/2010	0.05	0.14	1.490	0.03	2.2	5.50
Aug/22/2010	0.04	0.15	1.770	0.02	2.2	7.40
Aug/23/2010	0.04	0.15	1.300	0.02	1.7	9.50
Aug/24/2010	0.04	0.13	1.120	0.04	2.0	3.80
Aug/25/2010	0.04	0.09	0.800	0.03	1.6	0.80
Aug/26/2010	0.03	0.08	0.960	0.03	1.6	9.40
Aug/27/2010	0.04	0.10	1.420	0.02	2.0	1.20
Aug/28/2010	0.04	0.11	1.690	0.03	2.3	0.90
Aug/29/2010	0.03	0.09	1.660	0.03	2.3	3.60
Aug/30/2010	0.03	0.09	1.340	0.02	2.1	1.00
Aug/31/2010	0.04	0.12	1.680	0.03	2.3	2.60
Sep/01/2010	0.04	0.14	1.500	0.03	2.5	2.90
Sep/02/2010	0.04	0.13	1.740	0.03	2.6	1.60
Sep/03/2010	0.04	0.13	1.920	0.04	3.0	2.90
Sep/04/2010	0.03	0.14	1.880	0.02	2.8	4.60
Sep/05/2010	0.03	0.12	2.580	0.03	2.7	6.00
Sep/07/2010	0.03	0.11	2.100	0.02	2.8	4.40
Sep/08/2010	0.03	0.10	1.840	0.03	2.9	3.20
Sep/09/2010	0.03	0.14	2.130	0.02	2.7	6.10
Sep/10/2010	0.02	0.10	1.980	0.02	2.6	5.40
Sep/11/2010	0.03	0.14	2.100	0.02	2.8	5.60
Sep/12/2010	0.03	0.12	2.120	0.02	2.7	4.70
Sep/13/2010	0.03	0.10	2.120	0.01	2.8	5.20
Sep/14/2010	0.03	0.10	2.460	0.04	2.9	4.20
Sep/15/2010	0.03	0.12	1.480	0.05	2.3	9.60
Sep/16/2010	0.03	0.13	1.370	0.02	3.1	9.00

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Sep/17/2010	0.04	0.11	2.010	0.02	3.2	3.90
Sep/18/2010	0.04	0.11	2.650	0.02	3.5	5.40
Sep/19/2010	0.04	0.11	2.610	0.02	3.5	4.20
Sep/20/2010	0.04	0.10	2.720	0.01	3.5	5.50
Sep/21/2010	0.04	0.13	2.880	0.02	3.5	6.40
Sep/22/2010	0.03	0.09	2.400	0.02	3.4	6.40
Sep/23/2010	0.03	0.08	2.190	0.02	3.2	4.20
Sep/24/2010	0.04	0.09	2.300	0.04	3.4	3.10
Sep/25/2010	0.03	0.09	1.870	0.03	2.7	5.00
Sep/26/2010	0.03	0.07	2.610	0.01	3.1	7.40
Sep/27/2010	0.03	0.11	1.500	0.03	2.9	5.90
Sep/28/2010	0.03	0.08	1.460	0.01	2.8	5.70
Sep/29/2010	0.03	0.08	2.170	0.01	3.3	9.20
Sep/30/2010	0.03	0.09	2.540	0.01	3.4	6.40
Oct/01/2010	0.03	0.05	2.770	0.01	3.4	1.50
Oct/02/2010	0.03	0.06	3.190	0.01	3.4	2.22
Oct/03/2010	0.03	0.05	2.170	0.01	3.0	1.90
Oct/04/2010	0.03	0.07	1.870	0.02	2.8	1.50
Oct/05/2010	0.03	0.09	1.990	0.01	3.1	3.30
Oct/06/2010	0.04	0.09	2.010	0.02	3.0	5.10
Oct/14/2010	0.02	0.11	2.310	0.01	2.9	9.00
Oct/15/2010	0.03	0.09	2.520	0.00	3.1	7.60
Oct/16/2010	0.03	0.10	2.450	0.01	3.1	6.20
Oct/17/2010	0.03	0.09	2.550	0.01	3.1	5.30
Oct/18/2010	0.02	0.15	2.490	0.01	3.1	18.90
Oct/19/2010	0.02	0.10	2.970	0.01	3.2	10.10
Oct/20/2010	0.02	0.09	2.620	0.03	3.4	8.60
Oct/21/2010	0.03	0.09	2.360	0.01	3.2	5.50
Oct/22/2010	0.04	0.17	2.690	0.06	3.2	16.90
Oct/23/2010	0.02	0.12	2.520	0.03	3.7	12.40
Oct/24/2010	0.02	0.10	3.620	0.01	4.6	11.00
Oct/25/2010	0.02	0.08	3.940	0.01	4.8	9.00
Nov/02/2010	0.03	0.10	2.810	0.21	4.1	5.60
Nov/03/2010	0.05	0.25	4.140	0.14	5.2	22.70
Nov/04/2010	0.04	0.19	3.330	0.02	4.3	
Nov/05/2010	0.05	0.31	3.250	0.01	4.4	136.50
Nov/06/2010	0.08	0.52	3.870	0.07	5.8	52.00
Nov/07/2010	0.09	0.52	4.710	0.08	6.7	59.30
Nov/08/2010	0.07	0.23	4.280	0.16	6.1	28.30
Nov/09/2010	0.05	0.44	4.470	0.17	5.7	67.90
Nov/10/2010	0.05	0.33	4.150	0.21	5.2	62.30
Nov/11/2010	0.05	0.45	3.780	0.20	5.1	40.20
Nov/12/2010	0.04	0.24	3.650	0.12	5.2	36.70
Nov/13/2010	0.04	0.22	4.050	0.04	5.7	67.20
Nov/14/2010	0.03	0.18	4.120	0.03	5.1	
Nov/15/2010	0.04	0.19	3.880	0.02	5.5	
Nov/16/2010	0.03	0.12	3.950	0.02	5.7	
Nov/17/2010	0.03	0.17	4.220	0.04	5.4	11.00
Nov/18/2010	0.03	0.18	4.100	0.05	5.1	23.20

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Nov/19/2010	0.04	0.29	3.770	0.02	5.0	46.10
Nov/20/2010	0.04	0.31	4.460	0.03	5.8	56.30
Nov/21/2010	0.04	0.28	4.490	0.03	5.7	18.40
Nov/22/2010	0.04	0.20	4.700	0.03	5.3	18.50
Nov/23/2010	0.03	0.17	5.050	0.01	5.2	18.00
Nov/24/2010	0.03	0.13	5.030	0.02	5.3	13.40
Nov/25/2010	0.02	0.15	3.400	0.01	5.2	
Nov/26/2010	0.02	0.28	3.710	0.01	4.9	
Nov/27/2010	0.03	0.33	3.740	0.04	5.2	
Nov/28/2010	0.03	0.25	3.990	0.04	5.2	24.70
Nov/29/2010	0.03	0.30	4.050	0.08	5.0	25.70
Nov/30/2010	0.03	0.24	4.150	0.07	5.0	26.50
Dec/01/2010	0.03	0.27	3.510	0.10	4.9	30.80
Dec/02/2010	0.03	0.18	3.750	0.08	4.8	17.70
Dec/03/2010	0.02	0.16	3.460	0.09	4.1	16.10
Dec/04/2010	0.02	0.15	3.220	0.06	4.1	15.60
Dec/05/2010	0.05	0.18	3.480	0.09	4.2	10.00
Dec/06/2010	0.03	0.19	3.470	0.10	4.2	15.30
Dec/07/2010	0.02	0.17	3.250	0.10	4.4	14.50
Dec/08/2010	0.02	0.13	3.550	0.08	4.3	9.94
Dec/09/2010	0.03	0.19	3.490	0.10	4.3	14.90
Dec/10/2010	0.02	0.32	3.900	0.10	4.2	22.10
Dec/11/2010	0.03	0.48	3.370	0.06	4.3	60.70
Dec/12/2010	0.04	0.46	4.430	0.10	5.7	65.60
Dec/13/2010	0.05	0.25	4.540	0.17	5.3	45.40
Dec/14/2010	0.03	0.25	3.860	0.15	5.0	33.50
Dec/15/2010	0.03	0.32	3.790	0.16	5.0	23.00
Dec/16/2010	0.03	0.20	3.490	0.16	4.6	31.50
Dec/17/2010	0.02	0.20	3.400	0.16	4.6	22.90
Dec/18/2010	0.02	0.20	3.610	0.15	4.5	33.60
Dec/19/2010	0.02	0.33	3.270	0.16	4.5	51.86
Dec/20/2010	0.03	0.29	3.570	0.18	4.4	42.20
Dec/21/2010	0.02	0.29	3.500	0.17	4.3	49.10
Dec/22/2010	0.02	0.34	3.210	0.14	4.3	65.10
Dec/23/2010	0.02	0.51	3.650	0.16	4.1	55.90
Dec/24/2010	0.03	0.50	3.490	0.15	4.3	44.60
Dec/25/2010	0.02	0.37	3.570	0.22	4.5	56.00
Dec/28/2010	0.03	0.18	3.240	0.34	4.3	14.90
Dec/31/2010	0.01	0.17	3.260	0.47	4.2	15.30
Jan/03/2011	0.03	0.15	3.790	0.49	4.4	11.30
Jan/07/2011	0.04	0.18	3.020	0.61	4.3	15.90
Jan/08/2011	0.03	0.49	3.590	0.39	4.5	155.20
Jan/09/2011	0.05	0.26	3.880	0.38	5.2	47.20
Jan/10/2011	0.04	0.17	4.010	0.34	5.1	19.70
Jan/11/2011	0.04	0.21	3.660	0.32	4.9	28.90
Jan/12/2011	0.03	0.20	3.790	0.36	4.8	31.70
Jan/13/2011	0.03	0.26	3.530	0.32	4.5	56.80
Jan/14/2011	0.04	0.37	3.710	0.29	5.0	209.35
Jan/15/2011	0.04	0.29	4.410	0.22	5.3	140.10

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Jan/16/2011	0.03	0.17	4.430	0.12	5.7	187.80
Jan/17/2011	0.02	0.08	3.510	0.09	4.5	8.70
Jan/18/2011	0.04	0.13	3.230	0.33	4.8	10.80
Jan/19/2011	0.01	0.06	3.390	0.02	4.0	4.70
Jan/20/2011	0.02	0.09	3.110	0.05	4.4	3.10
Jan/21/2011	0.02	0.10	3.950	0.06	4.8	4.80
Jan/22/2011	0.02	0.10	3.780	0.12	4.7	5.60
Jan/23/2011	0.02	0.11	3.650	0.16	4.7	7.50
Jan/24/2011	0.02	0.13	4.200	0.20	4.8	10.40
Jan/25/2011	0.02	0.18	3.450	0.20	4.6	19.80
Jan/26/2011	0.02	0.18	3.700	0.24	5.1	33.00
Jan/27/2011	0.02	0.18	4.080	0.24	4.9	25.70
Jan/28/2011	0.02	0.21	3.660	0.27	5.0	29.70
Jan/29/2011	0.02	0.24	3.750	0.18	4.8	65.50
Feb/04/2011	0.02	0.376	2.700	0.37	4.0	50.90
Feb/05/2011	0.04	0.447	2.750	0.62	4.6	81.90
Feb/06/2011	0.03	0.274	2.860	0.46	4.8	27.60
Feb/07/2011	0.03	0.219	3.300	0.25	4.8	18.10
Feb/08/2011	0.04	0.221	3.260	0.16	5.0	21.20
Feb/09/2011	0.05	0.232	4.020	0.17	5.1	28.70
Feb/10/2011	0.05	0.187	3.290	0.10	5.1	62.40
Feb/11/2011	0.05	0.161	3.790	0.11	5.0	88.40
Feb/12/2011	0.04	0.190	3.740	0.11	4.9	114.10
Feb/13/2011	0.04	0.201	3.650	0.13	4.8	57.70
Feb/14/2011	0.04	0.171	3.950	0.13	4.9	26.90
Feb/15/2011	0.038	0.159	3.330	0.22	4.8	14.00
Feb/16/2011	0.028	0.169	3.690	0.13	4.1	18.40
Feb/17/2011	0.028	0.158	3.900	0.13	4.2	15.60
Feb/18/2011	0.029	0.208	3.620	0.13	4.2	17.60
Feb/19/2011	0.029	0.167	3.940	0.13	4.2	16.20
Feb/20/2011	0.028	0.181	3.740	0.15	4.3	23.60
Feb/21/2011	0.027	0.204	3.600	0.15	4.2	23.60
Feb/22/2011	0.025	0.173	3.600	0.17	4.2	29.00
Feb/23/2011	0.023	0.210	3.980	0.18	4.3	30.20
Feb/24/2011	0.022	0.206	3.560	0.16	4.3	25.00
Feb/25/2011	0.027	0.085	4.170	0.30	4.5	18.80
Feb/26/2011	0.020	0.168	3.670	0.10	4.5	19.60
Feb/27/2011	0.019	0.172	3.540	0.12	4.4	18.70
Feb/28/2011	0.018	0.174	3.390	0.10	4.4	19.30
Mar/01/2011	0.020	0.169	3.520	0.10	4.3	23.20
Mar/02/2011	0.021	0.135	3.670	0.13	4.4	21.90
Mar/03/2011	0.011	0.119	3.680	0.11	4.4	21.40
Mar/04/2011	0.020	0.125	3.710	0.12	4.4	17.80
Mar/05/2011	0.024	0.129	3.390	0.12	4.4	18.90
Mar/06/2011	0.014	0.105	3.310	0.11	4.3	16.70
Mar/07/2011	0.020	0.118	4.180	0.13	4.4	16.90
Mar/08/2011	0.030	0.117	3.810	0.22	4.3	9.50
Mar/09/2011	0.023	0.114	2.74	0.082	4.4	17.20
Mar/10/2011	0.025	0.135	3.35	0.093	4.5	14.50

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Mar/11/2011	0.023	0.115	4.03	0.137	4.6	16.30
Mar/12/2011	0.025	0.123	3.52	0.082	4.6	11.30
Mar/13/2011	0.025	0.116	4.08	0.067	4.5	8.00
Mar/14/2011	0.027	0.118	3.18	0.054	4.3	14.00
Mar/15/2011	0.029	0.123	3.56	0.077	4.5	15.80
Mar/16/2011	0.033	0.131	3.55	0.086	4.3	19.90
Mar/17/2011	0.025	0.110	3.60	0.072	4.4	20.30
Mar/18/2011	0.034	0.114	3.62	0.174	4.6	13.70
Mar/19/2011	0.022	0.089	3.58	0.05	4.3	8.43
Mar/20/2011	0.021	0.080	3.45	0.03	4.3	5.97
Mar/21/2011	0.019	0.084	3.40	0.04	4.1	7.00
Mar/22/2011	0.020	0.074	3.35	0.04	4.2	6.63
Mar/23/2011	0.020	0.096	3.42	0.03	4.2	6.57
Mar/24/2011	0.020	0.081	3.17	0.04	4.2	6.20
Mar/25/2011	0.021	0.085	3.09	0.05	4.2	5.80
Mar/26/2011	0.020	0.082	3.54	0.04	4.2	5.67
Mar/27/2011	0.019	0.087	3.30	0.06	4.2	5.50
Mar/28/2011	0.016	0.079	3.38	0.04	4.4	5.90
Mar/29/2011	0.019	0.083	3.23	0.12	5.0	4.53
Mar/30/2011	0.017	0.073	3.44	0.04	3.6	7.50
Mar/31/2011	0.018	0.070	3.45	0.02	3.5	4.77
Apr/01/2011	0.019	0.073	3.40	0.02	3.6	4.33
Apr/02/2011	0.019	0.082	3.34	0.01	3.5	4.83
Apr/03/2011	0.019	0.075	3.35	0.01	3.4	6.20
Apr/04/2011	0.016	0.080	3.02	0.01	3.2	3.20
Apr/05/2011	0.020	0.080	3.16	0.02	3.3	5.03
Apr/06/2011	0.017	0.077	3.20	0.03	3.6	4.27
Apr/07/2011	0.017	0.083	3.15	0.02	3.4	4.83
Apr/08/2011	0.027	0.092	2.90	0.09	3.4	3.33
Apr/09/2011	0.023	0.040	2.98	0.02	3.4	3.41
Apr/10/2011	0.021	0.071	2.99	0.02	3.3	7.53
Apr/11/2011	0.021	0.125	2.85	0.01	3.2	6.37
Apr/12/2011	0.020	0.139	3.34	0.01	3.4	9.20
Apr/13/2011	0.022	0.143	3.60	0.02	3.5	6.13
Apr/14/2011	0.022	0.068	2.93	0.04	3.3	3.47
Apr/15/2011	0.020	0.085	3.03	0.01	3.3	6.47
Apr/16/2011	0.018	0.078	2.96	0.01	3.1	6.53
Apr/17/2011	0.017	0.066	3.44	0.00	3.4	7.37
Apr/18/2011	0.018	0.065	2.69	0.01	3.1	6.03
Apr/19/2011	0.017	0.060	2.86	0.01	3.2	6.37
Apr/20/2011	0.006	0.073	2.91	0.04	3.1	6.00
Apr/21/2011	0.006	0.067	2.82	0.02	3.1	5.87
Apr/22/2011	0.008	0.058	2.77	0.03	3.0	5.60
Apr/23/2011	0.005	0.066	2.82	0.03	2.9	5.40
Apr/24/2011	0.006	0.064	2.72	0.02	2.8	5.80
Apr/25/2011	0.007	0.066	2.70	0.02	2.9	6.03
Apr/26/2011	0.008	0.060	2.67	0.03	3.0	3.37
Apr/27/2011	0.006	0.060	2.71	0.03	2.9	7.27
Apr/28/2011	0.003	0.053	3.18	0.02	3.2	5.30

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Apr/29/2011	0.003	0.062	2.85	0.01	3.0	4.73
Apr/30/2011	0.002	0.052	3.06	0.01	3.1	3.90
May/01/2011	0.007	0.119	2.89	0.02	3.1	4.60
May/02/2011	0.007	0.136	2.92	0.02	3.1	3.97
May/03/2011	0.007	0.119	3.13	0.02	3.2	2.57
May/04/2011	0.005	0.121	2.97	0.02	3.1	4.20
May/05/2011	0.003	0.100	2.92	0.02	3.1	2.70
May/06/2011	0.004	0.131	2.85	0.02	3.0	3.63
May/07/2011	0.003	0.122	2.87	0.01	3.0	4.60
May/08/2011	0.002	0.150	3.00	0.01	3.0	3.57
May/09/2011	0.003	0.124	2.53	0.02	3.0	4.53
May/10/2011	0.004	0.095	2.65	0.03	3.0	3.00
May/11/2011	0.008	0.103	2.72	0.06	3.2	3.93
May/12/2011	0.008	0.111	3.32	0.04	3.4	3.60
May/13/2011	0.008	0.101	2.80	0.03	3.3	3.73
May/14/2011	0.009	0.127	2.78	0.04	3.2	2.93
May/15/2011	0.009	0.107	2.92	0.03	3.3	3.87
May/16/2011	0.010	0.118	2.54	0.03	3.5	2.67
May/17/2011	0.012	0.140	2.90	0.04	3.4	4.40
May/18/2011	0.016	0.145	2.94	0.08	3.2	3.47
May/19/2011	0.016	0.149	2.71	0.05	3.1	2.23
May/20/2011	0.017	0.128	2.88	0.08	3.3	2.67
May/21/2011	0.016	0.128	2.72	0.05	3.2	3.30
May/22/2011	0.015	0.118	2.81	0.04	3.3	3.03
May/23/2011	0.015	0.139	2.80	0.03	3.1	4.03
May/24/2011	0.017	0.137	2.76	0.04	3.3	3.80
May/25/2011	0.017	0.135	2.84	0.04	3.3	3.87
May/26/2011	0.017	0.143	2.64	0.03	3.1	4.13
May/27/2011	0.013	0.155	2.54	0.04	3.1	3.57
May/28/2011	0.015	0.152	2.93	0.03	3.3	4.20
May/29/2011	0.013	0.144	2.99	0.03	3.1	4.13
May/30/2011	0.016	0.148	3.08	0.06	3.4	3.50
May/31/2011	0.019	0.144	2.82	0.07	3.3	3.10
Jun/01/2011	0.017	0.142	2.60	0.06	3.1	4.37
Jun/02/2011	0.016	0.158	2.70	0.03	3.2	5.27
Jun/03/2011	0.018	0.104	2.37	0.04	3.2	6.63
Jun/04/2011	0.014	0.153	2.44	0.05	3.0	25.40
Jun/05/2011	0.016	0.147	2.36	0.04	3.1	25.20
Jun/06/2011	0.016	0.141	2.46	0.04	2.8	32.30
Jun/07/2011	0.010	0.117	2.43	0.04	3.2	18.90
Jun/08/2011	0.009	0.057	2.68	0.02	3.2	28.00
Jun/09/2011	0.009	0.090	2.73	0.07	3.1	23.00
Jun/10/2011	0.019	0.144	3.18	0.09	3.5	21.50
Jun/11/2011	0.014	0.131	2.95	0.05	3.3	14.00
Jun/12/2011	0.011	0.081	2.85	0.03	3.1	8.70
Jun/13/2011	0.012	0.108	2.97	0.03	3.2	17.00
Jun/14/2011	0.008	0.137	2.91	0.03	3.0	25.20
Jun/15/2011	0.012	0.137	2.72	0.03	3.3	19.70
Jun/16/2011	0.009	0.142	2.61	0.04	2.70	12.10

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Jun/17/2011	0.018	0.162	2.50	0.03	2.60	13.10
Jun/18/2011	0.021	0.137	2.87	0.03	2.90	9.20
Jun/19/2011	0.025	0.148	2.52	0.02	2.80	10.20
Jun/20/2011	0.030	0.102	2.67	0.03	2.80	17.00
Jun/21/2011	0.056	0.178	2.93	0.11	3.20	11.30
Jun/22/2011	0.038	0.239	3.19	0.06	3.30	15.80
Jun/23/2011	0.030	0.161	2.98	0.03	3.10	12.70
Jun/24/2011	0.037	0.150	2.99	0.04	3.20	11.70
Jun/25/2011	0.040	0.142	3.24	0.04	3.30	8.70
Jun/26/2011	0.037	0.140	3.15	0.03	3.20	14.30
Jun/27/2011	0.033	0.141	3.22	0.02	3.24	11.20
Jun/28/2011	0.034	0.133	3.14	0.03	3.17	8.70
Jun/29/2011	0.033	0.163	3.07	0.02	3.09	16.50
Jun/30/2011	0.030	0.155	2.75	0.02	2.90	11.60
Jul/01/2011	0.032	0.134	2.77	0.03	2.90	11.80
Jul/02/2011	0.030	0.079	2.49	0.03	2.70	9.60
Jul/03/2011	0.032	0.102	2.66	0.02	2.90	9.70
Jul/04/2011	0.040	0.167	3.13	0.05	3.17	16.20
Jul/05/2011	0.038	0.153	2.99	0.03	3.10	13.90
Jul/06/2011	0.040	0.134	3.01	0.03	3.20	11.80
Jul/07/2011	0.034	0.125	2.92	0.02	3.10	14.40
Jul/08/2011	0.036	0.114	2.56	0.02	2.80	11.60
Jul/09/2011	0.032	0.137	2.75	0.02	2.90	12.50
Jul/10/2011	0.040	0.131	2.80	0.02	2.90	12.20
Jul/11/2011	0.035	0.125	2.71	0.01	2.80	9.20
Jul/12/2011	0.030	0.131	2.76	0.02	2.90	8.70
Jul/13/2011	0.029	0.100	2.40	0.03	2.50	6.30
Jul/14/2011	0.024	0.095	2.39	0.02	2.60	2.50
Jul/15/2011	0.030	0.117	2.73	0.04	3.00	12.10
Jul/16/2011	0.047	0.147	2.67	0.04	3.20	6.00
Jul/17/2011	0.040	0.104	2.78	0.02	3.00	4.30
Jul/18/2011	0.037	0.107	2.56	0.01	2.90	3.70
Jul/19/2011	0.034	0.096	2.55	0.02	2.80	4.50
Jul/20/2011	0.032	0.095	2.57	0.02	2.80	6.70
Jul/21/2011	0.029	0.096	2.55	0.01	2.80	6.20
Jul/22/2011	0.029	0.090	2.74	0.02	2.76	6.10
Jul/23/2011	0.025	0.061	2.41	0.04	2.50	4.43
Jul/24/2011	0.036	0.106	2.71	0.05	3.10	4.44
Jul/25/2011	0.045	0.099	2.61	0.04	3.10	4.17
Jul/26/2011	0.048	0.114	2.81	0.03	3.30	3.81
Jul/27/2011	0.040	0.096	2.98	0.03	3.30	2.56
Jul/28/2011	0.037	0.091	2.86	0.02	3.10	2.84
Jul/29/2011	0.033	0.092	2.76	0.02	2.90	2.71
Jul/30/2011	0.030	0.084	2.46	0.03	2.80	2.90
Jul/31/2011	0.022	0.072	2.78	0.02	2.80	5.00

... continuation of Table 9.3.

Date	PO ₄ -P [mg/l]	TP [mg/l]	NO ₃ -N [mg/l]	NH ₄ -N [mg/l]	TN [mg/l]	TSS [mg/l]
Aug/01/2011	0.024	0.085	2.45	0.02	2.60	2.98
Aug/02/2011	0.024	0.083	2.42	0.02	2.70	3.02
Aug/03/2011	0.029	0.101	2.44	0.03	2.80	3.60
Aug/04/2011	0.029	0.088	2.39	0.04	2.70	3.20
Aug/05/2011	0.019	0.093	2.38	0.02	2.80	3.40
Aug/06/2011	0.024	0.087	2.46	0.02	2.80	3.40
Aug/07/2011	0.020	0.081	2.35	0.02	2.80	3.60
Aug/08/2011	0.023	0.087	2.88	0.03	2.91	6.11
Aug/09/2011	0.030	0.110	2.30	0.02	2.60	2.67
Aug/10/2011	0.043	0.161	2.42	0.09	2.90	8.56

Table 9.4 Location of sampling points, tributaries and geographic coordinates.

Sampling Point	River or tributary	SWAT Subbasin	Latitude	Longitude
1	Dosenbek	3	54.11997783120	10.02166845630
2	Schwale	10	54.07927584610	10.01463080100
3	Dosenbek	7	54.08514555260	10.01271016900
4	Schwale	9	54.08059274740	10.05996376510
5	Schwale	11	54.06846420070	10.10429843320
6	Stör	17	54.04738019410	10.04229738810
7	Stör	16	54.05303106600	10.00917930270
8	Padenstedt Au	19	54.04912611600	9.91881358603
9	Stör	15	54.05103054470	9.91664074013
10	Aalbek	14	54.05137647450	9.89763092528
11	Bredenbek	13	54.06218678670	9.82185124507
12	Milbek	8	54.08324710930	9.80438195905
13	Milbek	6	54.09020632070	9.83178317265
14	Höllenu	2	54.14082803750	9.88463914340
15		1	54.14447638660	9.77122705339
16	Fuhlenau	4	54.11494294860	9.78510775935
17	Buckener Au	5	54.10140208790	9.77635536492
18	Buckener Au	12	54.06363443720	9.68128451788
19	Wischbek	18	54.04614831150	9.82107187068
20	Bünzener Au	20	54.03420911660	9.81587897119
21	Stör	21	54.00930951590	9.80684648341

Table 9.5 Curriculum Vitae of Cristiano Andre Pott

Personal Details	
Name:	Cristiano Andre Pott
Date of birth:	September 20 th 1975
Place of birth:	Panambi, Brazil
Affiliation:	Eugenio Osvaldo Pott and Neusa Dulce Pott
Academic Education	
1991 - 1994	Professional Teaching in Agricultural Technical (Technical degree) Sociedade Educacional Três de Maio, SETREM Três de Maio, Brazil
1994 - 1999	Degree in Agronomy at the University of Santa Maria (Universidade Federal de Santa Maria, UFSM) Santa Maria, Brazil
1999 - 2001	Masters in Tropical and Subtropical Agriculture at the Agronomical Institute of Campinas (Instituto Agrônômico de Campinas, IAC) Campinas, Brazil Master dissertation: Evaluation of infiltration rates with constant head permeameter, pressure infiltrometer, sprinkler infiltrometer and disk permeameter, in three soils of São Paulo State.
Professional career	
2001 - 2003	Assistant teacher at the Agronomy course at Santa Catarina State University (Universidade do Estado de Santa Catarina, UDESC) Lages, Brazil
2003 - current	Assistant teacher at the Agronomy course at the Midwest State University (Universidade Estadual do Centro-Oeste, UNICENTRO) Guarapuava, Brazil