Universität Rostock

Traditio et Innovatio

Aus der Professur für Bodenphysik
der Agrar- und Umweltwissenschaftlichen Fakultät

Phosphorus Transport Processes from Soil to Surface Waters
Case Studies from a North-Eastern German Lowland Catchment

Kumulative Dissertation

zur Erlangung des akademischen Grades
Doktor der Agrarwissenschaften (doctor agriculturae)

an der Agrar- und Umweltwissenschaftlichen Fakultät
der Universität Rostock

vorgelegt von M. Sc. Stefan Koch aus Rostock,
geboren am 27.05.1985 in Rostock

Rostock, 27.06.2017

urn:nbn:de:gbv:28-diss2018-0030-3

Gutachter der Promotion

Prof. Dr. Bernd Lennartz
Universitär Rostock,
Agrar- und Umweltwissenschaftliche Fakultät,
Professur für Bodenphysik,
Justus-von-Liebig-Weg 6
18059 Rostock

Prof. Dr. Britta Schmalz
Technische Universität Darmstadt
Fachgebiet Ingenieurhydrologie und Wasserbewirtschaftung
Franziska-Braun-Straße 7
64287 Darmstadt

Associate Prof. Dr. Goswin Hckrath
Aarhus University
Department of Agroecology
Soil Physics and Hydrogeology
Blichers Allé 20
8830 Tjele

Datum der Abgabe: 27.06.2017
Datum der Verteidigung: 26.01.2018

Preface

This dissertation thesis presents the results of my research in catchment hydrology and spatio-temporal phosphorus dynamics and transport processes at the Chair for Soil Physics at the University of Rostock under supervision of Prof. Dr. Bernd Lennartz.

As a cumulative thesis parts of it have been or are about to be presented in the following publications:

Koch, Stefan; Bauwe, A.; Lennartz, B. (2013): Application of the SWAT Model for a Tile-Drained Lowland Catchment in North-Eastern Germany on Subbasin Scale. In: *Water Resources. Management* 27 (3), S. 791–805.

Koch, Stefan; Kahle, P.; Lennartz, B.: Long-term Phosphorus Dynamics in an Agricultural Watershed in North-Eastern Germany. In: *Ambio*. Submitted in November 2016.

Koch, Stefan; Kahle, P.; Lennartz, B. (2016): Visualization of Colloid Transport Pathways Using Titanium(IV) Oxide as a Tracer. In: *Journal of Environmental Quality* 45, S. 2053–2059.

These publications are included as full-text chapters (3, 4, 6) in this thesis. A comprehensive guide on the structure of this thesis is given in the introduction.

The presented work was partly financed from the German Federal Ministry of Education and Research (BMBF) and the BonaRes research project InnoSoilPhos (No. 031A558).

Zusammenfassung

Phosphor (P) ist ein essentieller Makronährstoff im Pflanzenbau. Jedoch ist P neben Stickstoff (N) eine er Haupttriebkräfte der Eutrophierung von Oberflächengewässern im Landesinnern und der Küstengewässer in die sie entwässern. Auf Grund der geographischen Gegebenheiten – einer vergleichsweise kleinen Wasserfläche im Verhältnis zum insgesamt großen Einzugsgebiet – ist die Ostsee potentiell besonders von Eutrophierung bedroht.

Im Rahmen dieser Dissertation wurde die Hydrologie eines in die Ostsee entwässernden Tieflandeinzugsgebiets untersucht. Außerdem wurde der P-Austrag in diesem Einzugsgebiet unter besonderer Berücksichtigung der landwirtschaftlichen Entwässerung auf verschiedenen räumlichen Skalen erforscht.

Methodisch wurde ein Top-Down-Ansatz verfolgt, der vorsah, die betrachtete räumliche Skala von der Einzugsgebietsskala bis hin zur Bodenprofilskala sukzessive zu verkleinern. Dabei wurde wie folgt vorgegangen:

i. Analyse des Abflussgeschehens und seiner Abflusskomponenten mit Hilfe des ökohydrologischen Einzugsgebietsmodells SWAT (Soil Water Assessment Tool) unter besonderer Berücksichtigung der landwirtschaftlichen Entwässerung.
ii. Analyse eines langjährigen Datensatzes von gelöstem Phosphat (DRP) und Gesamtphosphor (TP).
iii. Bewertung der DRP und TP Konzentrationen einer Abflussperiode (2015/2016) am Monitoringstandort Dummerstorf unter besonderer Berücksichtigung dreier räumlicher Skalen sowie des Beitrags von Niederschlags- und Abflussereignissen.
iv. Vergleichende Färbeversuche mit Brilliant Blue (BB) und Titandioxid (TiO_2) zur Visualisierung des Präferentiellen Transports von Lösungen (BB) und Suspensionen (kolloidaler Transport, TiO_2) an drei Standorten mit steigendem Ton- und Lehmgehalt.
v. Saugplattenlysimeter-Experiment zur Abschätzung des Bromid- (Br) und P-Transportes in Form von DRP und TP nach Düngerapplikation mit Kaliumdihydrogenphosphat (KH_2PO_4).

Das SWAT-Model zeigte variable Modellgütenin der Kalbrierungsperiode Nash-Suttcliffe-Efficiencies von 0,22 bis 0,81 und in der Validierungsperiode -0,81 bis 0,66—je nach Teileinzugsgebiet im Warnow-Einzugsgebiet. Die Entfernung der unterirdischen Entwässerung aus dem Modellaufbau führte zu einer konsistenten Verschlechterung der Modellgüten und zu einem Anstieg des Grundwasserabflusses im Verhältnis zum hohen Dränabfluss mit Entwässerung. Die Berücksichtigung von Dränung in landwirtschaftlich geprägten Tieflandeinzugsgebieten ist dringend erforderlich zur akkuraten Abschätzung der Abflusskomponenten.

Ein Langzeitdatensatz (21 Jahre) von DRP- und TP-Konzentrationen für neun Messstellen des Warnoweinzugsgebietes zeigte einen signifikanten saisonbereinigten negativen Trend in allen Teileinzugsgebieten. Dies wird vor allem auf die Installation zahlreicher Kläranlagen mit P-Reinigungsstufe zurückgeführt. Einfache statistische Modelle belegen, dass DRP überwiegend dem Signal des Basisabflusses folgt, während TP mehrheitlich einer schnellen Abflusskomponente sowie Niederschlagsereignissen folgt.

Die Analyse des P-Austrags in Folge von Niederschlagsereignissen auf kleinerer räumlicher Skala (4,2 ha bis 1,550 ha) zeigte, dass 15 – 77% des DRP sowie 49 bis 68% des TP als Folge von Ereignissen ausgetragen wird. Die Gesamtfrachten von TP sind hier in der räumlichen Skala des Dränauslasses (4,2 ha) dreimal höher als die des DRP. Gleiches gilt für die Grabenskala (179 ha). Auf der Skala des Teileinzugsgebietes (1550 ha) sind DRP- und TP-Frachten nahezu identisch. Die Ergebnisse zeigen den deutlichen Beitrag der Dränung zum partikulären Transport von P aus landwirtschaftlich genutzten Flächen. Die räumlichen Muster des Doppellactat-extrahierbaren Boden-Phosphors zeigen Ähnlichkeiten im Ober- und Unterboden. Die Muster scheinen sich räumlich zu wiederholen. Der Ursprung dieser Muster kann hier nicht abschließend geklärt werden, da weitere Daten zu Eisen- und Aluminium-Gehalten des Bodens nicht vorliegen. Ein Zusammenhang zur organischen Substanz des Oberbodens konnte nicht festgestellt werden.

In den Färbeversuchen konnte das Potential des partikulären Transports durch den Boden bestätigt werden. Zwar wurde BB als Lösung auch präferentiell entlang der Bodenstruktur verlagert, doch das partikuläre TiO_2 erreichte durch präferentiellen Transport durch singuläre Makroporen (Regenwurm- und Wurzelkanäle) gleiche Tiefen innerhalb von 24 Stunden. Der Transport von TiO_2 stieg hier proportional zum Ton- und Lehmgehalt an, was vor allem durch die größere Haltbarkeit der Grobporen bei härteren Böden erklärt werden kann. TiO_2 ist ein geeigneter Tracer zur Visualisierung des kolloidalen Transportes.

Die Saugplattenversuche bestätigten die Annahme des präferentiellen Transportes von Lösungen. Das Br wurde an allen Lysimetern präferentiell verlagert. DRP und TP folgten eher erratischen Transportmustern. Wiederholte starke Niederschlagsereignisse (40 mm alle zwei Stunden) führten zu einer Mobilisierung von DRP, z. B. durch Desorption von Eisen- und Aluminiummineralen. Die TP-Frachten unterschieden sich nicht signifikant von den DRP-Frachten. Dies deutet darauf hin, dass die Lysimeter keine singulären Makroporen erfassten und die räumliche Auflösung solcher Untersuchungen erhöht werden sollte.

Die Untersuchungen im Rahmen der vorliegenden Dissertationen zeigen:

i. Die Relevanz der Dränung für die Hydrologie und den Transport von P (vor allem den partikulären P-Transport) in Tieflandeinzugsgebieten.
ii. Einen deutlichen Rückgang der P-Konzentrationen als Folge verbesserter Abwasserbehandlung.
iii. Die Relevanz von Ereignissen im Transport und der Verlagerung von P.
iv. Das Potential der Verlagerung von Kolloiden durch das Bodenprofil durch präferentiellen Transport
v. Deutlichen Forschungsbedarf in Bezug auf partikulären Transport durch das Bodenprofil sowie die Remobilisierung von Sedimenten der Gräben und Flüsse.

Dieser Forschungsbedarf beinhaltet auch die Untersuchung verschiedener P-Speicher in der Landschaft (Boden, Grundwasser, Sediment, Wasser) und deren Interaktion unter verschiedenen Szenarien der Landnutzung und des Klimas. Integrierte großskalige Modellierung sollte hierbei ein Werkzeug darstellen zur Vermittlung der Forschungsinhalte an Gesetzgeber, Verbände, Landwirte und andere Interessengruppen.

Summary

Phosphorus (P) is an essential macronutrient for crop production. However, in its soluble and particle-bound forms, P is, besides nitrate, a major contributor of freshwater eutrophication and hence of the eutrophication of coastal ecosystems. The Baltic Sea is particularly threatened by eutrophication due to its small surface area and large drainage basin.

This dissertation comprises investigations into the hydrology of the Warnow river basin, a north-eastern German watershed that drains into the Baltic Sea. Furthermore, we studied the P-export patterns on surface waters under special consideration of artificial subsurface drainage and different spatial scales.

We used a top-down approach, starting with the watershed scale and ending at the plot or pedon scale. We conducted the following studies:

i. The analysis of the hydrology of the Warnow river basin and its sub-basins using the Soil and Water Assessment Tool (SWAT), with particular consideration of subsurface drainage.
ii. The analysis of a long-term data set of dissolved reactive P (DRP) and total phosphorus (TP) concentrations in the Warnow river basin and its sub-basins.
iii. The analysis and assessment of a one-year data set from a monitoring station in the Zarnow catchment (a Warnow sub-basin) on three spatial scales with particular focus on drainage events.
iv. Dye-tracer experiments using Brilliant Blue (BB) and Titanium(IV) oxide (TiO_2) as tracers to visualize solute and particle-facilitated transport in mineral soils.
v. Suction-plate lysimeter experiments to determine the bromide (Br) and P-transport patterns, using potassium bromide and potassium dihydrogen phosphate (K_2HPO_4) as tracer.

The SWAT model showed variable model qualities in terms of Nash-Sutcliffe Efficiencies (NSEs). The NSE values ranged from 0.22 to 0.81 and -0.81 to 0.66 in the calibration and validation period respectively, depending on the sub-basin. The exclusion of the tile drainage from the model setup led to a decrease in the model quality and an increase in groundwater flow in relation to the high drainage flow with the tile drainage being included. The incorporation of tile drainage in agriculturally used watersheds is strongly recommended for a reliable reproduction of the flow constituents.

The 21-year data set of DRP and TP concentrations at nine gauge stations in the Warnow river basin showed a significant negative temporal trend. This can be attributed to improvements in wastewater treatment in the studied watershed. Simple statistical models revealed that DRP was most likely transported with the baseflow while TP followed the quickflow component and strong rainfall events.

The analysis of P export from three different spatial scales (4.2 ha to 1,550 ha) showed that 15–77% of the DRP and 49–68% of the TP were released following five single runoff events. The area-related loads of TP decreased with increasing drainage area, indicating a rapid sedimentation even under high runoff rates. The data showed a significant contribution of the tile drainage and preferential transport to the export of TP. The double lactate (DL)-extractable soil P content showed repetitive spatial patterns. The maximum spatial range for autocorrelation was 220 m and 150 m for the topsoil and the subsoil respectively. We could not address the origin

of the observed spatial patterns since additional data is missing. We could not find a clear relationship with the soil organic matter content in the topsoil either.

The dye-tracer experiments revealed a large potential of preferential transport through singular macropores for colloids. Although we could show preferential transport for BB too (through singular macropores, ped interfaces, and soil cracks), TiO_2 was exclusively transported through singular macropores (e.g. earthworm channels) and was transported to similar depths as BB in the same period. The dyed area of TiO_2 increased with increasing clay and silt content, indicates a more stable structure of the soil with increasing clay or silt content. TiO_2 is a suitable tracer to visualize colloidal transport through the soil.

The suction-plate experiments endorse the idea of preferential transport through loamy soils. The bromide was preferentially transported in all the observed lysimeters. The DRP and TP patterns were erratic but revealed a mobilization with increasing rainfall. The repetitive application of rainfall (40 mm every two hours) mobilized considerable amounts of DRP. The TP loads did not differ significantly from the DRP loads. This indicates that the lysimeter area did not cover any singular macropores that could be responsible for the preferential transport of colloid-bound P. Furthermore, the spatial resolution of this gridded lysimeter approach should be extended.

The investigations of this dissertation thesis showed:

i. The relevance of artificial subsurface drainage for catchment hydrology and the transport of P (i.e. particulate P transport) in lowland river basins.
ii. A significant decrease of riverine P concentrations over the last two decades as a consequence of improved wastewater treatment.
iii. The potential of preferential transport for colloid transport in loamy soils.
iv. The relevance of runoff and rainfall events for the transport of P. There is a need for research regarding the vertical transport of (colloid-bound) P through the soil profile and the re-mobilization of bed sediments of ditches and rivers.

This research likewise includes the interaction between different P pools in the landscape and their interaction with the scenarios of land use and climate change. The integrated eco-hydrological modeling on a large spatial scale should be a valuable tool to communicate scientific knowledge to stakeholders (water and soil associations, lawmakers, or farmers).

Table of contents

List of Figures

List of Tables

List of abbreviations and chemical symbols

Al	Aluminium
Br	Bromide
CLC	Corine Land Cover
DRP	Dissolved reactive Phosphorus
DRP	Dissolve Reactive Phosphorus
DL	Double Lactate
Fe	Iron
KBK	Konzeptbodenkarte
KBr	Potassium Bromide
KH_2PO_4	Potassium Dihydrogen Phosphate
LUNG	Landesamt für Umwelt, Naturschutz und Geologie Mecklenburg-Vorpommern (State Office for Environment, Nature Conservation and Geology of Mecklenburg-West Pomerania)
NO_3^-	Nitrate
P	Phosphorus
PO_4^{3-}	Phosphate
SWAT	Soil and Water Assessment Tool
TP	Total Phosphorus
VD-Lufa	Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten

1 Introduction

1.1 Motivation

Phosphorus (P), with its soluble compounds, is an essential nutrient for crop production and primary productivity of agro-ecosystems (George et al. 2016). The alleviation of world hunger demands a worldwide increase of P fertilizer inputs (Roberts 2009).

However, P is also a major cause for eutrophication in surface waters, resulting in algae blooms and excess aquatic plant growth. This is often seen as a consequence of an increased application of P fertilizers for either crop production for food supply or the production of energy (Correll 1998, Ekholm 1998). It has been shown that even after long periods of declining anthropogenic P inputs as fertilizers, there might be long periods of mobilization of accumulated P in soils and river sediments (Powers et al. 2016).

Since the point source inputs (e.g., wastewater treatment plants) have decreased markedly over the last two decades in Europe (Kronvang et al. 2007), the effect of non-point (diffuse) sources comes under the spotlight of environmental sciences. The emission of diffuse nutrient inputs—those which cannot be attributed to a discrete source—is a major threat to the Baltic Sea (Behrendt & Bachor 1998, Stålnacke et al. 1998, Stålnacke et al. 2015). Moreover, the Baltic Sea is, in particular, threatened by eutrophication by its geographical properties. The total area of the Baltic Sea drainage basin is about 1,745,000 km^2, which is about four times larger than the Baltic Sea itself (Stålnacke et al. 2015). In addition, the water exchange between the Baltic Sea and the North Sea is low, and the ecological status of the Baltic Sea strongly depends on water renewal events (Mohrholz et al. 2015).

However, the pathways of P leaching from agriculturally used soils to surface waters are not yet fully understood. For a long time, the surface runoff from soils has been named as the most influential pathway of P transport (Sharpley & Syers 1979, Daniel et al. 1994). But recently, there has been increasing evidence that particle-facilitated transport of P and the accelerated leaching of dissolved and total P through the soil, and hence, through tile drains, is a considerable pathway for P export to surface waters (Macrae et al. 2007, King et al. 2015a, Christianson et al. 2016, Qi & Qi 2016).

The overall P export from Germany to the Baltic Sea is high. The inputs of P originating from Germany are remarkable, with roughly 600 $t\ a^{-1}$ (LUNG MV 2016, personal communication). This thesis addresses the hydrology and the transport pathways of the dissolved reactive P (DRP) and the total P (TP) in an agricultural lowland river basin in north-eastern Germany with a considerable proportion of the agricultural land being drained by subsurface drainage.

1.2 Objective and how to read this thesis

Understanding phosphorus (P) dynamics, from inland sources to the sea, is essential for developing strategies to reduce P loads. In the light of these reduction targets, the aim of this thesis is the investigation of water and P fluxes from soil to surface waters on different spatial and temporal scales. Moreover, the relation of P transport to hydrologic properties and, in particular, to artificial subsurface drainage should be evaluated to close gaps in the knowledge of event-driven transport of different P fractions on a multi-scale level.

To this end, I have used a systematic top-down approach, beginning at the watershed scale (~ 3000 km²). Once the nutrient dynamics of dissolved reactive phosphorus (DRP) and total phosphorus (TP) on a large spatial scale are understood, one can attend to spatio-temporal patterns and processes at the sub-basin and field scale (4.2 ha – 15.5 km²). At the final step the colloid transport processes and P transport pathways on the pedon and soil profile scale were evaluated. The observed temporal scales were a bi- to four-weekly sampling scheme over a two-decade-long sampling period, one discharge period with multiple samples every week and short-term sampling with sampling pore water every two hours. To clarify this spatial top-down approach and the temporal resolution this doctoral thesis is subdivided into eight chapters.

Chapter 1 provides an overview of the background and the motivation of the study.

Chapter 2 comprises an elaborate description of the investigated Warnow River basin and all spatial sub-scales. The methods are briefly described because they are comprehensively elucidated in the following chapters.

Chapter 3 is a published manuscript that focuses on the understanding of hydrological processes in the lowland Warnow River basin using the Soil and Water Assessment Tool (SWAT model) as an eco-hydrological model. The aim was to study the tile drainage flow and the stream flow constitution as a basis for identifying major flow sources of nutrients (e. g. phosphorus and nitrogen) and to validate the performance of the SWAT model with and without tile drainages in the model set up.

Watershed scale.

Chapter 4 (a submitted manuscript) supplies some evidence for the contribution of the quickflow component (e.g. tile drainage discharge) to the release of TP from agriculturally-used soils into the receiving waters. The aim of this study was to statistically analyze an existing 21-year data set of DRP, TP and discharge for long-term trends and their origin in the Warnow River basin and its sub-basins. Another task of this chapter was the assessment of temporal and spatial variations of P concentrations and loads and the particular consideration of drainage path by implementing a deviation of streamflow in a base flow and a fast flow component.

Watershed scale.

Chapter 5 comprises data from the Dummerstorf field site maintained by the Soil Physics working group at Rostock University over the discharge period from 2015 to 2016. This chapter focuses on the contribution of drainage events to the overall release of P to surface waters at three different spatial scales. The aim of this study was to determine the contribution of DRP and TP loads to particular discharge events to the total runoff period loads on the spatial scales of a tile drainage field (4.2 ha), a drainage ditch with 19 contributing collector drains (179 ha) and the catchment (15.5 km²).

Sub-basin scale/Field scale.

Chapter 6 is a published manuscript on the topic of a new and innovative method of dye tracing to visualize colloid transport in mineral soils. The aim of this study was to validate the capability of Titanium dioxide (TiO_2) to visualize colloid transport pathways in mineral soils with a clay content gradient. The field experiment, using Brilliant Blue (BB) as a solute dye tracer and TiO2 as a colloidal dye tracer, based on the idea that both tracers follow preferential pathways. TiO2, which simulates a part of the TP fraction (particulate P), exclusively follows singular macropores like root and earthworm channels.

Plot/Soil profile scale.

Chapter 7 is a non-published/non-submitted presentation of the results from a suction-plate lysimeter experiment at the field site Dummerstorf on a loamy soil. The aim of this experiment was to find numerical evidence for the results of the dye tracing study of chapter 6. We aimed on the differentiation of pathways of DRP and TP during severe rainfall events following fertilizer application on the soil profile scale to find evidence for a quick release of P to tile drains and groundwater. Another aim was to assess the spatial variability of DRP and TP transport through the soil. This chapter has to be understood as preliminary study and delivers some suggestions for further attempts.

Plot/soil profile scale.

Chapter 8 synthesized the findings of all our modelling and field studies during the duration of my Ph. D. studies. A particular focus lies on the effects of tile drainage and discharge events on the release of DRP and TP on the varying spatial scales and future research needs.

Watershed to pedon scale

The presented dissertation thesis provides fundamental research in the field of nutrient (e.g. phosphorus) transport from soil to tile drainage and surface waters and to receiving oceans. We used modelling techniques (Soil Water Assessment Tool), the statistical analysis of existing long-term data and simple statistical models, dye tracing studies for the visualization of nutrient and solute transport, and a sophisticated in-situ micro-lysimeter set-up to assess the spatial variability of DRP and TP transport.

A future target, based on the findings of this theses and following studies, is to fully understand and model the P circle and the P balances in the Warnow River Basin using eco-hydrological models. In particular, the large-scale modelling of P fluxes in lowland ecosystems, especially under large extent of artificial drainage, is still lacking quality and needs new implementations.

1.3 Background

1.3.1 The origin of phosphorus in agricultural landscapes

P is essential for almost all life forms on earth. Most importantly, it is a key structural component of DNA and RNA. P is likewise critical to ATP (adenosine-5'-triphosphate) and to phospholipids, and thus, to cell membranes (Childers et al. 2011).

Natural and anthropogenic sources of P can be found in all ecosystems. Natural sources of P are plants, animal feces, or chemical weathering of minerals like apatites, wavellites, or vivianites.

The key sources of anthropogenic origin in soils are mineral and manure fertilizers, and atmospheric deposition. In surface waters, inputs are derived from non-point sources (surface runoff from agricultural fields, tile drainage discharge, and groundwater discharge to rivers and streams), as well as direct inputs to surface waters by sewage treatment works or animal farms. The loads of P transferred to surface waters by sewage works are strongly correlated to the size of the facility and the implementation of P reduction programs (Foy et al. 1995).

In a study from Denmark, the authors found marked surpluses of soil P from 1987 to 1998 to soil depths of 0.75 m, which indicates a too intensive fertilization with P (Rabæk et al. 2013). The recommendations of P fertilization rates in Germany are based on a standardized soil-testing procedure that can be interpreted as the availability of P from the soil to the plant (Kuchenbuch & Buczko 2011). The authors evaluated a data set of 9,000 experimental harvests in Germany and Austria and recorded mean annual P fertilizer application rates of 45.5 kg P ha a^{-1}. However, generally, higher soil P contents require lower P fertilizer application rates. In contrast, the P application rates in Sub-Saharan Africa are extremely low, and the nutrient-deficient soils need high fertilizer inputs to maintain crop yields (Neset & Cordell 2012). The worldwide requirements of P fertilization tend to increase by around 3–4% annually (Food and Agriculture Organization of the United Nations 2008).

Compared to the rates of the fertilizer applied to agriculturally used soils, the atmospheric deposition of P is low. However, it has been reported that P deposition may change lakes from a state of P limitation to one of nitrogen limitation (Ellis et al. 2015), and can severely influence oligotrophic lakes, tropical forests, and ombrotrophic peatlands (Tipping et al. 2014). An elaborate literature review shows that the rates of atmospheric P deposition are spatially highly variable. However, the worldwide geometric mean atmospheric P deposition rate is 0.027 g m^{-2} total P and 0.014 g m^{-2} orthophosphate-P (ibidem).

1.3.2 The phosphorus cycle

The anthropogenic and environmental P cycle is complex (Figure 1-1). However, to put it simply, P generally exists in two forms:

i. Dissolved P (dissolved organic P and dissolved inorganic P)
ii. Particulate P / bound P (organic and inorganic bound)

The P cycle is based on the equilibrium and interactions of both forms with the lithosphere, the hydrosphere, and the atmosphere.

The pathways of P to open-water ecosystems are manifold. Surface runoff from soils and losses through artificial drainage and internal erosion processes in the soil has been identified as major contributors to P concentrations in rivers and streams (McDowell & Sharpley 2001, Smith et al. 2015). The substantial contribution of sewage treatment works has already been mentioned. Aquaculture is another source of P in rivers and marine ecosystems (Jarvie et al. 2006, Bowes et al. 2009).

In rivers, P is stored in sediments. The retention of lakes and slow-flowing rivers has a remarkable effect on the P concentrations being measured. We can summarize that there is a variety of point and non-point sources contributing to the aquatic environment via different pathways (Figure 1-1). In this thesis, I will focus on the inputs from the agricultural sector (e.g. fertilizer, soil P) as the non-point sources and, in particular, the transport through the soils and the artificial drainage systems.

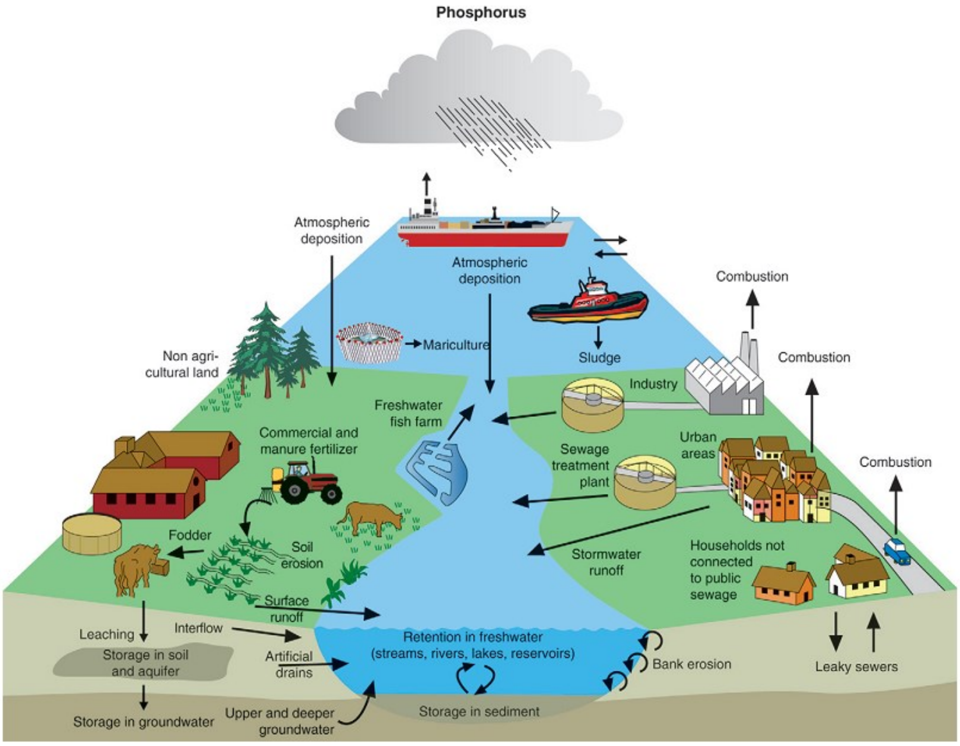

Figure 1-1: *P cycle in agricultural and coastal environments (Kronvang et al. 2009).*

The P cycle was a closed system before industrialization and globalization, and hence, P fertilization from mining sources. However, due to the ongoing use of phosphate reserves for agriculture, larger amounts are leached into surface water bodies and, in consequence, the P cycle is now broken and open (Desmidt et al. 2014).

1.3.3 Plant response to phosphorus fertilization and phosphorus deficit

As stated above, P is an essential macronutrient in plant nutrition (Sharpley et al. 2015), and is one of the 17 critical nutrients required for plant growth (Balemi & Negisho 2012). P fertilizers are widely applied to soils with low P stocks, and the efficiency of these fertilizers is affected by the P immobilization in the soil (Bates & Lynch 2000). However, the total input of P on a societal scale has decreased significantly since lower inputs in the crop production sector were recorded, which is somehow special for Mid- and Eastern European countries (van Dijk et al. 2016).

The supply of P (i.e. plant-available P) is directly linked to the above-soil plant and root-system growths. If P is the limiting nutrient, photosynthesis gets hampered. This leads to reduced leaf area and a prominent dark-green leaf color. The overall plant growth of roots and above-ground plant is significantly inhibited. Thus, the yields from these plants will be minimal even if these develop fully. If the available P stocks are drained, the organic acids in root exudates can mobilize soil-bound P to be transported to the above-ground plant. Root hair growth may be the most immediate morphological response the plants have to changed environmental conditions (e.g. P deficiency, Bates & Lynch 2000). In the presence of iron (Fe) in the soil, this mechanism is hampered, and hence, the root system grows horizontally instead of vertically (Müller et al.

2015). The Fe is transported to the stem cell niche of the plants, and thus, hampers the growth and movement of short roots.

The amount of the available P for plant nutrition is low (approx. 0.1% of soil P Illmer & Schinner 1992)). Phosphate-solubilizing microorganisms (e.g. bacterial and fungal strains) can be an eco-friendly measure to enhance the availability of P and to reduce fertilizer application rates (Illmer & Schinner 1992, Schachtman 1998, Adesemoye et al. 2009, Sharma et al. 2013). However, Freitas et al. (1997) observed a great potential for rhizobacteria to enhance plant growth, but could not give evidence for soil P solubilization.

It is a fine line between optimal P fertilization for maximized crop yield and the minimization of P losses to surface waters through the soil. Balemi & Negisho (2012) approximated that P limits crop yield on 40% of the world's arable land.

If the available P status remains high after fertilization, high levels of P loss can be expected (Juang et al. 2002). However, the P-fixing potential of the soil is highly linked to the sorption of P to the soil, in particular, to Fe and Al oxide surfaces (Vaughan et al. 2007).

1.3.4 Phosphorus scarcity—facing global change

The natural P sources (phosphate rock) are depleting (Desmidt et al. 2014). The annual yield of mined fossil phosphate is around $22 \cdot 10^{12}$ g P. Of all the mined phosphate rock, 95% is used for agricultural applications (Desmidt et al. 2014), whereas 90% is used to produce mineral fertilizer (Cisse & Mrabet 2004). Since fossil phosphate is not an infinite resource, ongoing mining will cause a complete depletion of all P resources. There is ongoing scientific debate when peak P (i.e. the point of the maximum global production rate of P) will be reached. Pessimistic estimates forecast a depletion of P within the next decades whereas more moderate scenarios predict P depletion at the end of the 21st century (van Vuuren et al. 2010). Most recently, it has been realized that in some cases, the phosphate rock reserves might have been overestimated (Edixhoven et al. 2014). Further research is needed to assess the global phosphate rock reserves and deliver better estimates of the depletion scenario.

In contrast to the decreasing trends of agricultural P use in the EU-27 countries (peak stacked inputs of around 8 kg P a^{-1} per capita in 1980 to around 2 kg P a^{-1} per capita in 2010 van Dijk et al. 2016), the global use of P has increased significantly over the last decades to about $175 \cdot 10^{12}$ g phosphate concentrates (van Vuuren et al. 2010)) to achieve or maintain proper agricultural conditions.

In summary, there is a certain trade-off between preventing world hunger and environmental issues regarding the pollution of surface water resources due to the misuse of P in the agricultural sector. Keeping in mind the growing world population and the elevated P concentrations of rivers and marine systems all over the world, one could assume that this trade-off will even increase in future.

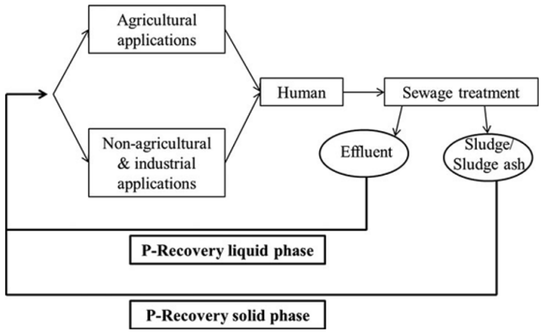

Figure 1-2: *Closed P cycle with a full P recovery from the solid and liquid phase from sewage treatment works (Desmidt et al. 2014).*

P will become scarce and more expensive in the future (Desmidt et al. 2014). Thus, there is an essential need for strategies in P management. On the one hand, we need a better P management in the agricultural sector to prevent and combat eutrophication (Kleinman et al. 2015). On the other hand, techniques are required to recover certain amounts of P from the solid and liquid phases from agriculture and sewage works (Desmidt et al. 2014, see Figure 1-2). There are, up to now, many available techniques—on different scales and of different costs—to decrease P loads in surface waters (Cordell et al. 2011, see chapter 8.5).

1.3.5 The specifics of lowland catchments

According to (Winter 2001), climate, geology, and land-surface form are the main factors that determine the hydrological landscape units. But, the fundamental differentiation is the slope of a catchment area. Hence, the two basic hydrological landscape units are upland and lowland watersheds. If one keeps in mind landscape morphology, there are several differences between upland and lowland watersheds which have been considered in research on hydrological processes (Table 1-1).

A common agricultural practice in lowland watersheds is surface (drainage ditches) and subsurface drainage (tile drainage). Drainage has a significant impact on flow conditions in lowland watersheds (Tiemeyer et al. 2009, Kiesel et al. 2010). The advantages and disadvantages of artificial drainage will be discussed in chapter 1.3.6.

The specifics of lowland catchments play an important role in the adaptation of hydrological models or the assessment of nutrient losses from agricultural catchments. For instance, large amounts of fine sediments are transported into lowland river systems, including the nutrients and contaminants, like heavy metals or organic pollutants (Grabowski & Gurnell 2016).

Table 1-1: *Contrasting juxtaposition of upland and lowland watersheds and their specific morphological, hydrological, and ecological properties. References: Winter (2001), Sophocleous (2002), Schmalz et al. (2008), Schmalz & Fohrer (2009), Lam et al. (2010).*

Property	Lowland watershed	Upland watershed
Soils	Old soils; long periods of pedogenesis; low erosion rates	Young soils; short term pedogenesis; severe soil loss caused by erosion
Watershed shape	Large extent in width and length, large total areas	Smaller extent in width, smaller total areas
Stream velocity	slow	fast
River bed	Fine sediment beds	Bedrock and coarse sediments
Ecology	Fish species with broad temperature tolerance and low oxygen need	Fish species with low temperature tolerances and high oxygen need
Flow pathways	Slow surface runoff; groundwater recharge if soils are permeable; high rates of baseflow	Fast surface runoff; low rates of groundwater recharge; low rates of baseflow, remarkable rates of drainage flow
Groundwater table	High groundwater table	Low groundwater table
Land use	Agriculture (arable farming), grassland, forests	Agriculture (livestock), Forests (below timber line), grassland
Drainage	Drainage (ditches and subsurface) for soil cultivation; river regulation	No drainage practices needed

1.3.6 Artificial drainage of agricultural land

Artificial drainage of soils is a common agricultural practice that significantly reduces the residence time of water in the soil, and improves the aeration and moisture conditions in the soil (Tiemeyer et al. 2006). Additionally, the structural stability of soils with naturally poor drainage conditions will improve (Simard et al. 2000). Artificial drainage can increase crop growth by reducing excess water stress to plants (Blann et al. 2009).

Drainage is common in Europe and North America. In Europe, the portion of drained area exceeds 25%, while only less than 10% of the cultivated area is artificially drained in non-industrial countries (Abbott & Leeds-Harrison February, 1998). In Germany, large proportions of cultivated land are drained for crop production. Therefore, the hydrology of many German streams and rivers is severely influenced by drainage. Kiesel et al. (2010) estimated that 31% of a small north-western German lowland watershed is drained by ditches or subsurface drainage. In agriculturally used catchments, the drained area can exceed the 50% mark in Germany (Gelbrecht et al. 2005). Tetzlaff et al. (2009) estimated that about 56% of the German agricultural land is drained. However, one has to consider that the proportion of the drained area can vary strongly, depending on the soil properties (Hirt et al. 2005). Exemplarily, in the German Mulde watershed, areas with strong waterlogging pseudogleys have a drained area of up to 30% whereas better conducting loess lessivés and glacial sands are only drained up to 16–18% (ibidem).

The drainage distribution in Germany is highly variable. The gradients in drainage density from north to south and west to east are most likely related to the occurrence of near-coastal flat areas and, of course, the interactions of land use, climate, and soil, which are an expression of the demand for drainage (Tetzlaff et al. 2010). As shown in chapter 2.1, a large proportion of the Warnow river basin—which is in focus in this doctoral thesis—is drained by subsurface and surface drainage.

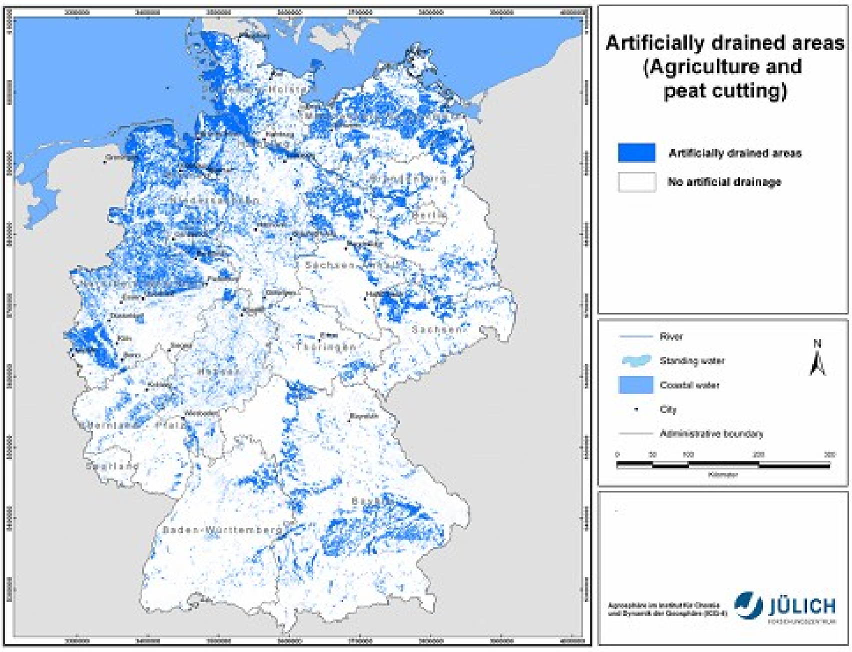

Figure 1-3: *Potentially drained areas in agricultural land and peatlands in Germany (Tetzlaff et al., 2010).*

However, the exact estimation of the drained areas remains challenging. Abbreviated historical documentation and missing digital maps of drainage areas and drainage condition lead to large uncertainties in estimating the drained areas. Different approaches have been tested to estimate the proportion of drained areas. Aerial photographs were used to create a cartographic inventory of artificially drained areas in Germany (Tetzlaff et al. 2010, Figure 1-3). This approach is comprehensively described for the River Ems watershed (Tetzlaff et al. 2009). Another approach has been presented by Mehl et al. (2010). Here, the landscape and soil properties were condensed to deduce the probability of an area being drained.

There are direct and indirect effects of drainage which have to be considered after implementation in agriculture, forestry, and wetland cultivation (Blann et al. 2009).

The primary direct effect is:

i. Habitat loss due to stream channelization and the conversion of wetlands to cropland

Severe effects on the properties of soil can occur when peat lands are drained. Wetlands that are transformed into crop and/or grassland by artificial drainage experience numerous marked impacts on their structure and ecology. The increasing aeration of the peat leads to an immediate increase of peat mineralization. This, together with physical compaction, causes shrinkage of the peat body and a reduction of the height of the wetland (Succow 2001).

Indirect effects include:

i. Water quality impacts

The most severe effects of drainage are, obviously, those influencing flow and (soil) water regime. Although there are several implications for the improvement of soil properties and soil hydrology, there is strong evidence that agricultural drainage and, particularly, tile drainage is accountable for the growing contamination of surface waters with nutrients and contaminants. Subsequent to the reduced waterlogging, there is an increased risk of preferential solute movement and loss through tile drains, as frequently observed (Stamm et al. 1998, Lennartz et al. 1999, Tiemeyer et al. 2009, Ulén et al. 2014). Drainage may, therefore, account for increases in sediment transport and the pollution of surface water bodies (Skaggs et al. 1994).

The current nutrient state of the Baltic Sea directs one's attention to the control of P and N losses from drains to prevent the eutrophication of the receiving waters. Attempts are being made by the European Union to provide a legal framework for all EU member states to achieve "good" water quality (European Water Framework Directive—Directive 2000/60/EC, 7th Environment Action Programme—Decision No 1386/2013/EU).

ii. Hydrological alteration (altered volume and timing of runoff (Blann et al. 2009))

The installation of tile drains and drainage ditches often occur in conjunction with land-use changes (Blann et al. 2009). As stated before, the residence time of water in the soil is shortened by artificial drainage. Hence, usually increased peak runoff rates occur (Skaggs et al. 1994).

1.3.7 Diffuse pollution of surface waters by phosphorus from agriculture

The continuous accumulation of nutrients is called eutrophication. It has been stated that algae bloom production, and hence, eutrophication, is controlled by the availability of nitrogen and P in the waters (Ryther & Dunstan 1971). According to Sharpley et al. (2015), the impairment of surface waters due to P enrichment is still a major environmental concern worldwide.

Trends in many European countries reveal that point sources of pollution—mainly P and ammonium-nitrogen—have been significantly reduced by improved wastewater treatment (Grimvall et al. 2000). Nonetheless, the losses of P to surface waters have remained constant over the last two decades. Hence, the diffuse sources of P attract more attention in environmental science.

The ecological consequences of eutrophication of surface waters are severe. The first and most obvious implication of elevated nutrient concentrations is the dense growth of algal blooms in streams, rivers, and coastal ecosystems. These algal blooms limit light penetration, which hampers the ability of predators to catch prey (Chislock et al. 2013). The depletion of dissolved organic carbon and the rising pH levels can be observed throughout the day, following increased rates of photosynthesis. In the late stages of eutrophication, the algal blooms die and microbial decomposition severely dissipates oxygen in the water. The resulting hypoxic or anoxic zones in rivers and lakes lack sufficient oxygen to support most organisms (Chislock et al. 2013). Another threat is the "harmful algae blooms" (HAB), which are toxic to both plants and animals and make their way up the food chain (Strokal et al. 2014).

Although eutrophication is a natural process—for instance, the eutrophication following the nutrient allocation of drying lakes—it is strongly accelerated by human activities (Ansari & Gill 2014). However, some lakes demonstrate a nutrient reduction with time (Whiteside 1983). Natural eutrophication happens on geological timescales, while anthropogenic eutrophication can occur in months or may take years.

The concentrations of dissolved and particulate P in the surface water depend on catchment and stream bed properties. A study in an English mesoscale catchment shows that sewage work discharge, P, SiO_2, and Al_2O_3 concentrations of bed sediments, and hence, the adsorption to clay minerals based on streambed geology are the most important controlling factors for dissolved P concentrations in the stream water (van der Perk et al. 2006). Additionally, organic carbon content of the sediment bed has a high predictive power for the spatial variation of streambed P concentrations (van der Perk et al. 2007).

Even in catchments where point sources are reduced by wastewater treatment, P concentrations in receiving waters may be high due to diffuse sources from agricultural land (Foy et al. 1995). In Finnish rivers and lakes, decreasing concentrations of chlorophyll and, hence, lower pollution have been observed (Räike et al. 2003). However, they stated that even though point sources of P could be reduced significantly, loads from non-point sources are still threatening the quality of surface waters.

1.3.8 Eutrophication risk of the Baltic Sea

The nutrient status of the Baltic Sea has been of interest to European environmental scientists for a long time. Increased pelagic and benthos primary production following elevated nutrient concentrations (P and nitrogen) has been measured since the 1970s (Bonsdorff et al. 1997).

We clearly perceive the threat of eutrophication to the Baltic Sea, which is promoted by the large area of the Baltic Sea drainage basin, which is around four times larger than the Baltic Sea itself (Stålnacke et al. 2015). Additionally, the retention time of water in the Baltic Sea is large because of the small Kattegat that connects the Baltic and the North seas.

Even though the surface waters of north-eastern Germany contribute to the lowest amount of the overall drainage basin, the area-related export rates of P to the Baltic Sea are remarkable with roughly 600 t a^{-1} (LUNG MV, 2016, personal communication). It has been estimated that about 75% of the total annual P emissions to the Baltic Sea, originating from the Mecklenburg-West Pomeranian watersheds, are from diffuse sources (Behrendt & Bachor 1998). However, it has been observed that P concentrations have increased in north-eastern German rivers in the last decade, contributing to the Baltic Sea. This has been attributed to the increasing number of lairages for animal production, as well as to increased cultivation of energy crops that require elevated P fertilization (LUNG MV, 2016, personal communication).

A strong correlation was found between the concentrations of particulate P and chlorophyll (Stepanauskas et al. 2002). This confirms the idea of the relevance of particulate and sediment-bound P, which will be discussed in the next section.

Efforts have been made in Europe to mitigate Baltic Sea eutrophication. The Helsinki Commission, also known as the Baltic Marine Environment Protection Commission (HELCOM), not only provides monitoring plans, but also releases concrete action plans for decision-makers and governments. Its first successes can be observed now. After a long period of eutrophication in all parts of the Baltic Sea, some parts showed a trend reversal, and an oligotrophication process, in the 2010s, and there were even signs of recovery in the Kattegat (Andersen et al. 2017). However, some parts of the Baltic Sea (Bornholm Basin, Baltic Proper, the Gulf of Riga, and the Gulf of Finland) still show ongoing eutrophication.

Thus, mitigation strategies to face the impairment of surface waters, and, in particular, the Baltic Sea, by non-point sources are essential for sustainable agriculture in future (Jarvie et al. 2013, Kleinman et al. 2015, Sharpley et al. 2015). Possible mitigation strategies have already been implemented by the Federal Ministry of Environment, Environmental Conservation and Geology (Ministerium für Landwirtschaft, Umwelt und Verbraucherschutz Mecklenburg-Vorpommern 2011).

1.3.9 Phosphorus transport through soils and tile drains

Although it has been claimed for long that the primary diffuse P pathway to surface waters from agriculturally used land is surface runoff, there is increasing evidence that marked amounts of P are transported through subsurface drains, either as dissolved or particulate P. The importance of subsurface P pathways was already emphasized by Grant et al. (1996), Sims et al. (1998) and Stamm et al. (1998).

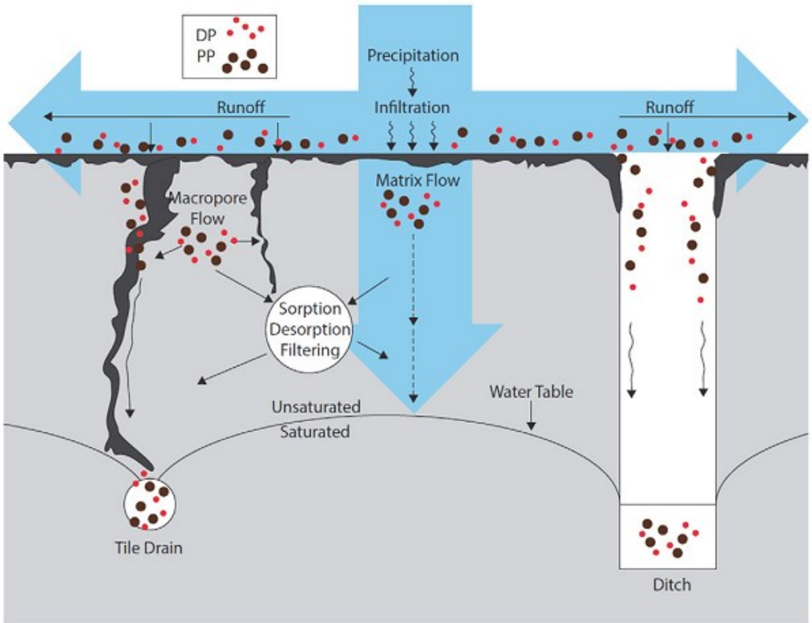

Figure 1-4: *Dissolved P (DP) and particulate P (PP) transport through soils by preferential flow, matrix flow, macro-pore flow, and surface runoff (Kleinman et al. 2015b).*

To reach the tile drains, the particulate P has to bypass the soil matrix, while the dissolved P can also be transported via the matrix flow (Figure 1-4). The transport of both dissolved and particulate P was often attributed to preferential flow pathways in the soil (Gächter et al. 1998, Simard et al. 2000). In a laboratory study, (de Jonge et al. 2004) found that about 75% of the total P was transported by small colloids and nanoparticles (<240nm). The importance of preferential flow and the occurring drainage events has also been emphasized for a region within the study site of this thesis. Up to 68% of the overall losses of DRP and TP can be attributed to event-based flow, which endorses the idea of preferential flow (Tiemeyer et al. 2009).

However, the dissolved P can, besides being transported by preferential flow, also bypass the soil matrix to outreach the drainage pipes. Permanent grasslands might be even more vulnerable to the preferential loss of P due to persistent macro pores that occur after long periods of no-till management (Simard et al. 2000).

The drainage pathway of P into surface waters has been of considerable interest in the literature for a long time. Tetzlaff et al. (2009) conducted model studies and found that 69% of all P inputs to surface waters are discharged through artificial drainage. A similar contribution of 72% of P being transferred through drainage pipes was observed for both dissolved and particulate P under different land uses in Canada (Zhang et al. 2015). Increasing concentrations of dissolved and particulate P with similarly increasing drainage discharge reveal the importance of the drainage pathways for P loads in rivers. These patterns have been frequently observed (Gentry et al. 2007, Tiemeyer et al. 2009).

The key factors affecting P transport through drains include soil characteristics (preferential flow, sorption capacity), drainage design (e.g. tile spacing, tile depth), prevailing conditions, management (e.g. tillage, cropping system, soil-test P level), and the hydrological and climatic variables (e.g. baseflow, eventflow, seasonal differences) (King et al. 2015b).

1.3.10 Hydrological models and their capability for decision-making and management

Properly utilized, hydrological models are vital tools for a better understanding of watershed hydrology. There is a variety of comprehensive and elaborate review articles on eco-hydrological catchment models for different spatial scales (Borah & Bera 2004, Daniel 2011). However, early applications of hydrological models had a greater interest in process research, for instance, the impact of climate change on watershed hydrology (Ficklin et al. 2009). Recently, the focus has shifted to modeling ecosystem services and supporting policy-making (Vigerstol & Aukema 2011, Francesconi et al. 2016), or best management and land-use practices (Xie et al. 2015). The concept of ecosystem services has recently been of tremendous interest in a broad range of sectors, including government, NGOs, and the business community (Vigerstol & Aukema 2011). It was highlighted that the variability in the assessment of hydrological ecosystem services can be explained to a large extent by scoping and the research interest of the studies (Harrison-Atlas et al. 2016). Hence, there is a future need for proper incorporation of ecosystem services to eco-hydrological models to support researchers and decision-makers (Francesconi et al. 2016).

In this thesis, we used the Soil and Water Assessment Tool (SWAT) to understand watershed hydrology and set the fundamental framework for further analysis of DRP and TP data on different spatial scales. A comprehensive review of applications for the SWAT model was presented by Gassman et al. (2007). An introduction into the SWAT model and the used routines in this thesis are given in chapter 2.3 and chapter 3.

1.3.11 The problem of spatial and temporal scales in environmental science

The validation of the process-based assessment of nutrient leaching is not only based on the consideration of different spatial scales, but also the water quality evaluation and courses of decision making. The significance of linking spatial scales and patterns to the development of management strategies and the understanding of ecosystems has often been emphasized (Tiemeyer et al. 2009, Lagzdins et al. 2012, Klaus et al. 2016, Liu et al. 2016).

A recommendation of the concerned spatial scales are (i) the drainage plot scale, (ii) the drainage field scale, (iii) the small agricultural catchment scale, and (iv) the river scale (Lagzdins et al. 2012). Scales i to iii have also been addressed in our study site (Tiemeyer et al. 2009, Bauwe et al. 2015). In the present dissertation, we also addressed scale IV. The consideration of multiple monitoring stations, from the spring to the estuary mouth, to cover the whole watershed area and a variety of spatial scales has been underlined (Minaudo et al. 2015).

The major complexity of assessing different spatial scales is determining the boundary conditions of the considered system. While the constraints are easily perceptible in laboratory studies, the multitude of processes and independent variables become astoundingly high with an increasing spatial scale (Figure 1-5).

However, not considering temporal scales in the same stage might pose a challenge since long-term, intra- and inter-annual variability of P losses might be large, depending on changes in climate, land use, and management. As stated before, P losses from agricultural land may be strongly influenced by rainfall. However, rainfall shows a high inter-annual variability. At our Dummerstorf study site in the Warnow river basin area (see chapter 2.1 and 5), both exceptionally wet years (Tiemeyer et al. 2009) and exceptional dry ones have been recorded (Nausch et al. 2017). Even the short-term variability may have severe influences on the observed processes of P transport. High-frequency measurements play an important role in the understanding of short-term dynamics of P release into surface waters. Bowes et al. (2015) succeeded in assigning P-transport pathways and within-channel mobilization to events in the hydrograph of a British river system.

The aforementioned spatial scales will also get attention in this thesis. However, I used a top-down approach to assess nutrient losses on different spatial and temporal scales, starting at the watershed scale (> 1000 km^2), and moving downwards to the pedon level (<1 m^2). The temporal resolution is addressed less here since the available data for chapter 4 had a low temporal resolution of a bi- or four-weekly sampling. In chapter 5, we employed a sample density of two or more samples a week.

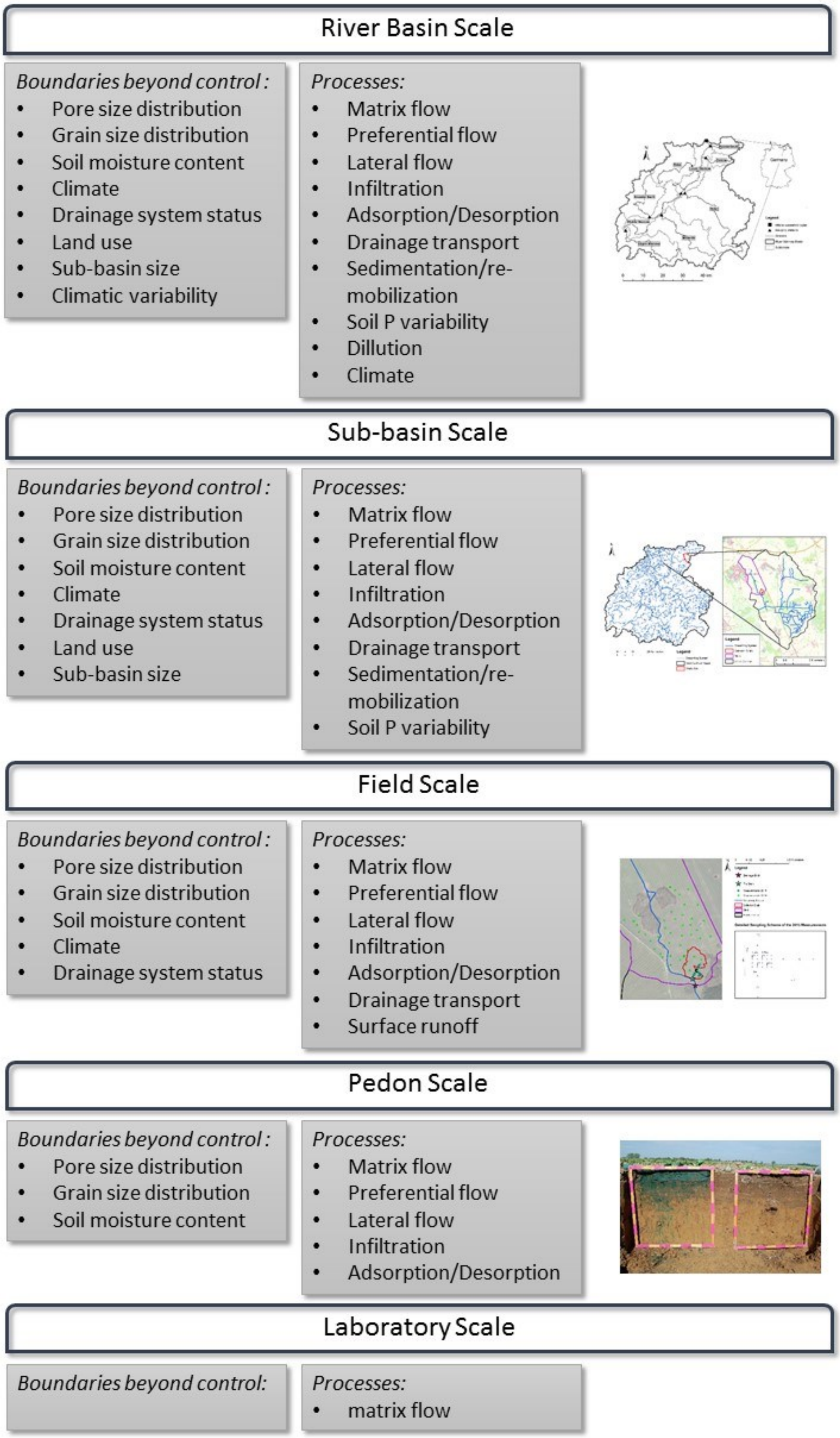

Figure 1-5: *The spatial scales of hydrological process research. Increasing spatial scale is equivalent to a broader range of processes that are involved and more undefined boundary conditions.*

2 Material and methods

2.1 The study sites

The Warnow river basin (Figure 2-1) is a north-eastern German lowland watershed that drains directly into the Baltic Sea. It is located in the federal state of Mecklenburg-West Pomerania, and has a total area of 3038 km^2. The Warnow River is 155 km long from its spring to the estuary mouth. A water-gate and a dam separate the freshwater part of the river system from its brackish stream.

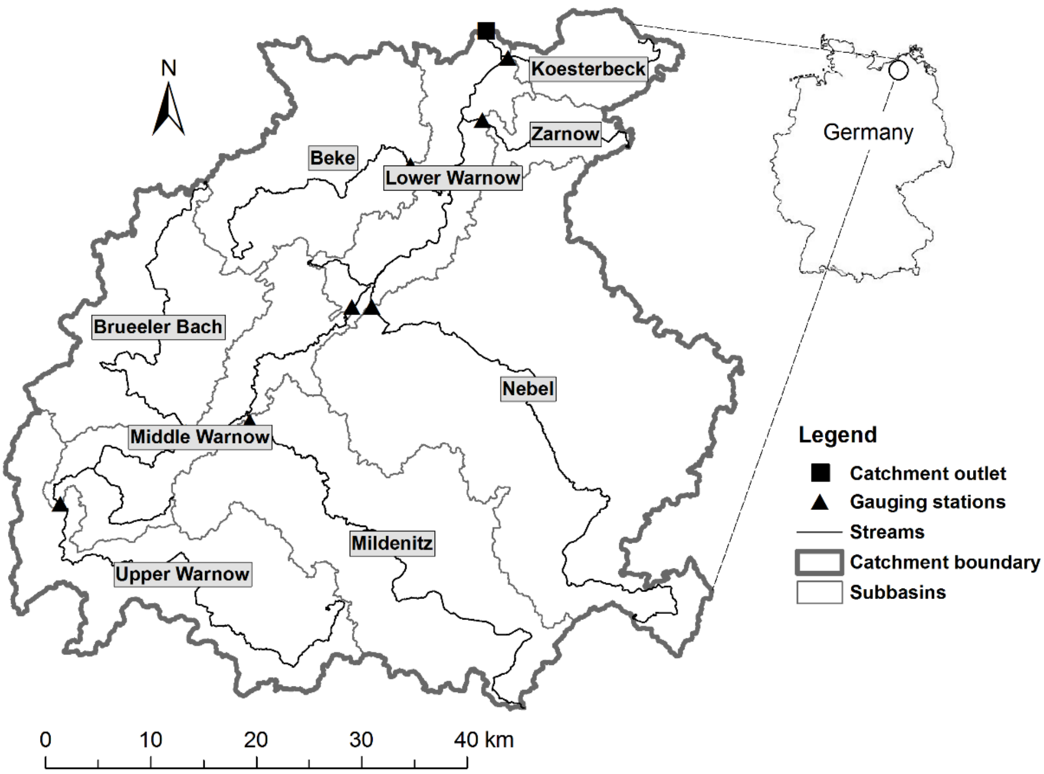

Figure 2-1: *The Warnow river basin (Koch et al. 2013) (Chapter 3).*

We delineated the Warnow river basin using ESRI ArcGIS 10.3 and the Spatial Analyst extension. The basin was sub-divided into sub-basins by using nine gauge stations for stream flow and water quality measurements (NO_3^-, dissolved reactive phosphorus (DRP), and total phosphorus (TP)). From mouth to spring, the sub-basins are: Lower Warnow (whole watershed outlet), Koesterbeck, Zarnow (sub-basin for experiments on the field and plot scale (Chapter 5, 6, 7)), Beke, Middle Warnow (Warnow river stream), Nebel, Mildenitz, Brueler Bach, and Upper Warnow (Warnow river stream). The difference of elevation of the Warnow River from spring to mouth is 68 m.

From the gauge station Bützow (Middle Warnow sub-basin) to the whole watershed outlet, the total difference of elevation is only 0.19 m, with an accordingly low velocity of 0.05 to 0.10 m s^{-1} (Kleeberg & Schlungbaum 1993). The loads of nitrogen and phosphorus, dissolved organic matter, and particulate organic matter are high since the watershed is mainly agriculturally used, and it flows through some eutrophic lakes located upstream (Bahnwart et al. 1999). Hence, the observation and assessment of DP and TP concentrations and loads seem substantial for agricultural management in the watershed.

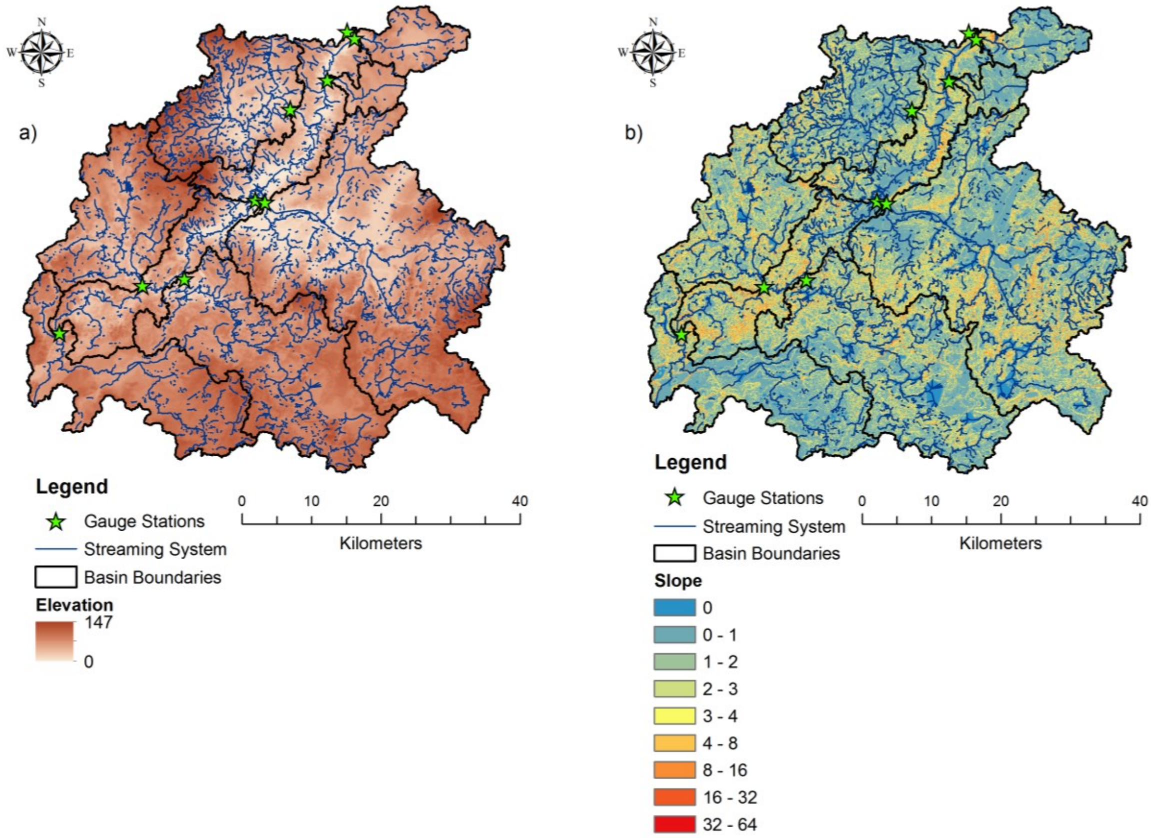

Figure 2-2: *The Warnow river basin: a) Digital elevation model (height given in meter, raster cell size 25 × 25 m) and b) Slope (slope classes given in degrees).*

The Warnow river basin is a typical lowland watershed with a broad spatial extent (Figure 2-1). In contrast, the highland catchments are narrowly shaped. The highest elevation in the Warnow watershed is 146 m (located in the Lower Warnow sub-basin) with a mean elevation of 43 m and a standard deviation of 20 m (Figure 2-2). The highest slopes can be found in the upstream regions and the tributary streams of Brueler Bach and Nebel. In general, the highest slopes are situated near the stream and form the water gaps, which are very attractive to tourists and residents. The morphology of a lowland catchment might be important for the assessment of process-based statistical analysis of stream flow and phosphorus loads, and is discussed in chapter 1.3.5.

The Weichselian ice age has formed the basin and shaped the geology and geomorphology of Mecklenburg-West Pomerania significantly. The major landform in the Warnow river basin is the ground marine landscape with elongated belts of end moraines from the north-west to the south-east of the watershed. Large amounts of peat were formed in the riparian areas of the Warnow River.

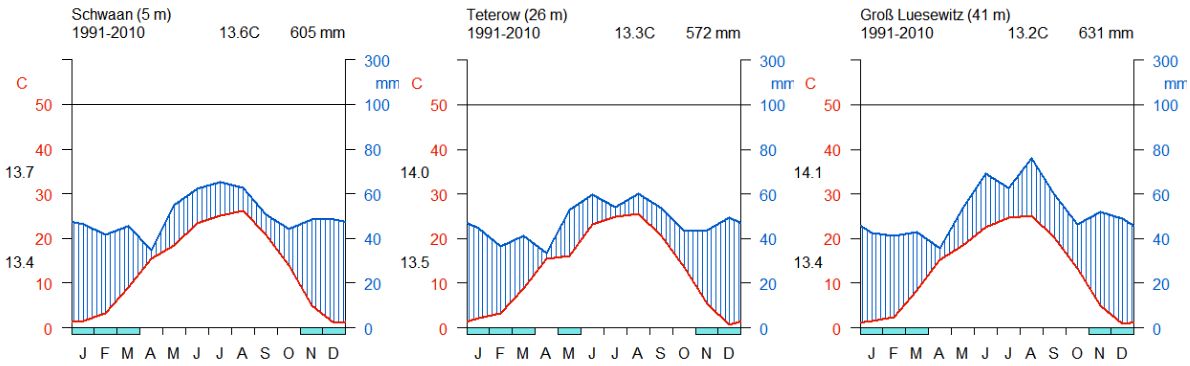

Figure 2-3: *Climate diagrams for three weather stations in the Warnow river basin.*

The climate of the Warnow river basin is shaped by a gradient from Atlantic to continental climate. Warm summers and mild winters are strongly influenced by the slow heating and cooling of the Baltic Sea, which works as a meteorological buffer. The mean temperature in the period from 1991 to 2010 was around 13°C with a mean annual precipitation of around 600 mm and a bimodal distribution of precipitation (Figure 2-3).

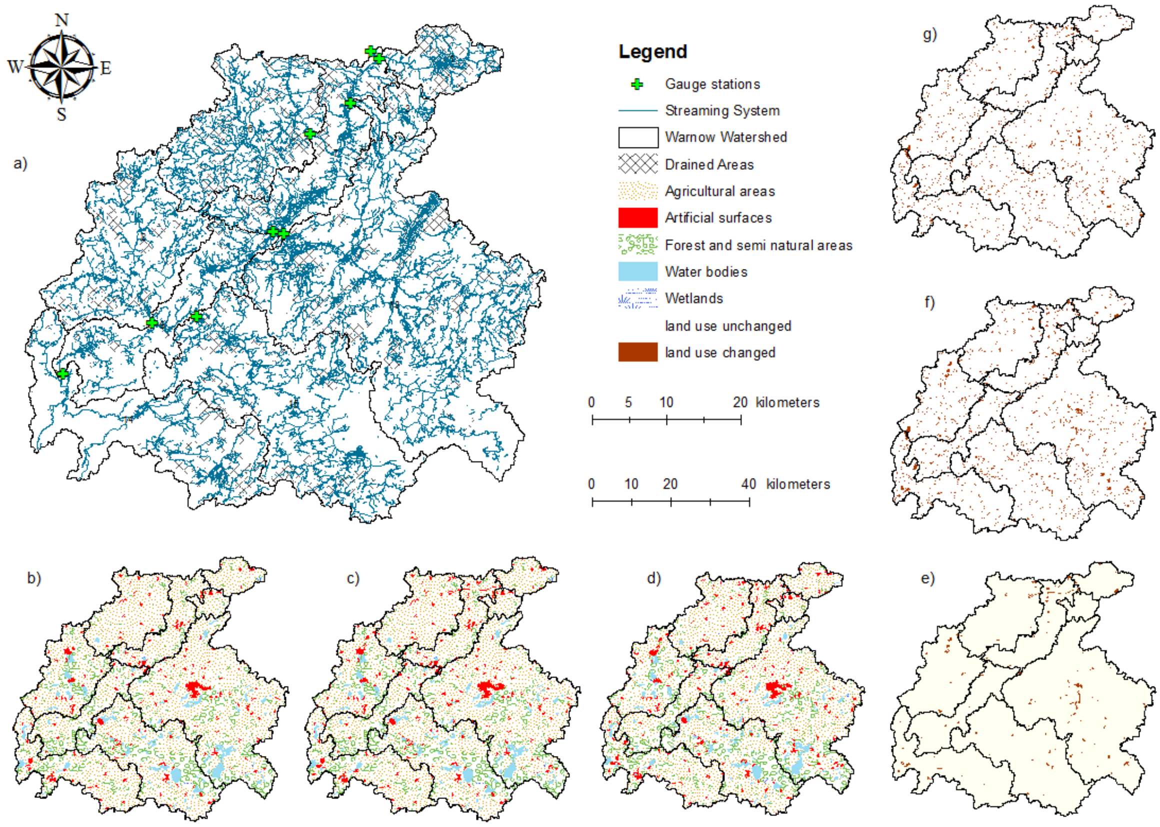

Figure 2-4: *Land use and land use change in the Warnow river basin. Land use data was extracted from CORINE land cover data (1990, 2000, and 2006). a) Warnow river basin with streaming system, gauge stations, and drainage area, b) land use 1990, c) land use 2000, d) land use 2006, e) land use change 1990 to 2000, f) land use change 2000 to 2006, g) land use change 1990 to 2006.*

Land use in the Warnow river basin reflects the general distribution of land use in Northern Germany (Table 2-1). Depending on the considered sub-basin, the major land use is agricultural with a maximum areal portion of roughly 77% in the Beke sub-basin. However, agriculture comprises intensive and extensive crop production, animal farming, and pomiculture. As it is common in rural areas, the proportion of urban areas is small in all sub-basins. Southerly, the total forest area increases with the largest proportion of coniferous forests.

Table 2-1: *Land use distribution in the Warnow river basin and its sub-basins. All values are given in %.*

Land Use	Beke	Brueler Bach	Koester-beck	Lower Warnow	Middle Warnow	Mildenitz	Nebel	Upper Warnow	Zarnow
Urban Areas	2.87	4.50	3.74	5.90	1.98	2.58	3.85	3.59	4.02
Agricutlure	76.88	56.78	66.34	60.65	48.66	49.42	56.74	61.05	65.42
Meadows	11.87	9.06	20.12	20.65	14.99	10.77	12.53	11.13	22.00
Deciduous Forest	4.06	9.87	5.43	5.35	8.92	4.77	7.27	5.43	4.47
Coniferous Forest	1.74	10.40	2.15	5.14	20.84	22.72	12.91	13.08	1.70
Mixed Forest	1.87	4.78	1.30	1.58	3.04	2.39	2.15	2.96	2.39
Wetlands	0.29	0.25	0.65	0.13	0.24	0.84	0.19	0.07	0.00
Open Water	0.41	4.38	0.26	0.60	1.33	6.51	4.35	2.69	0.00

Land use has changed markedly in the Warnow river basin in the last two decades (Figure 2-4). However, these changes are statistically not significant. The most severe changes were recorded for urban areas, with increases up to 62% from 2000 to 2006 in the Koesterbeck sub-basin. The total agricultural area decreased consistently by 2% for all sub-basins. The changes of wetlands and forest areas are below 1% in all the investigated sub-basins.

The soils (data provided by the State Office for Environment, Nature Conservation and Geology of Mecklenburg-West Pomerania, KBK25–Konzeptbodenkarte 1:25,000) in the Warnow river basin were formed on Weichselian glacial till and boulder clay. Hence, the majority of the soils are loamy gleysols, cambisols, and luvisols, with maximum areal proportions of about 19%, 46%, and 58% respectively (Table 2-2). As stated in the introductory chapter, the cultivation of soils with high water capacities requires the installation of subsurface drainage. Less frequent soils are regosols, technosols, anthrosols, and podsols. However, the northern German lowland houses considerable areas of histosols. The total area of peat soils is 367 km^2, equaling a proportion of 12.1%. The deviation of the area of histosols in the KBK25 soil map and the area of peatlands according to the Corine Land Cover map has to be attributed to the fact that many former wetlands have been artificially drained in the past and are now used as green land and pasture.

Another detailed description of the distribution of soils and land use in the Warnow river basin is given in chapter 3.

Table 2-2: *Distribution of soils in the Warnow river basin and its sub-basins. All values are given in %.*

Soil Type	Beke	Brueler Bach	Koester-beck	Lower Warnow	Middle Warnow	Mildenitz	Nebel	Upper Warnow	Zarnow
Anthrosol	0.16	0.00	0.00	0.19	0.00	0.00	0.00	0.00	0.00
Cambisols	13.78	40.77	29.82	20.10	44.23	40.29	31.98	46.22	25.13
Gleysols	19.72	19.63	16.51	13.13	9.60	10.18	18.85	13.40	14.97
Histosols	8.28	10.46	18.98	16.30	15.23	13.57	11.81	12.03	16.77
Luvisols	57.55	23.05	32.96	48.39	28.74	27.61	30.91	24.14	42.96
Open Water	0.51	5.21	0.73	1.11	1.94	7.07	4.82	3.22	0.18
Podsols	0.00	0.00	0.00	0.00	0.00	0.72	0.20	0.00	0.00
Regosols/ Leptosols	0.00	0.00	0.00	0.00	0.00	0.24	0.06	0.00	0.00
Technosols	0.00	0.89	0.99	0.78	0.25	0.33	1.37	0.99	0.00

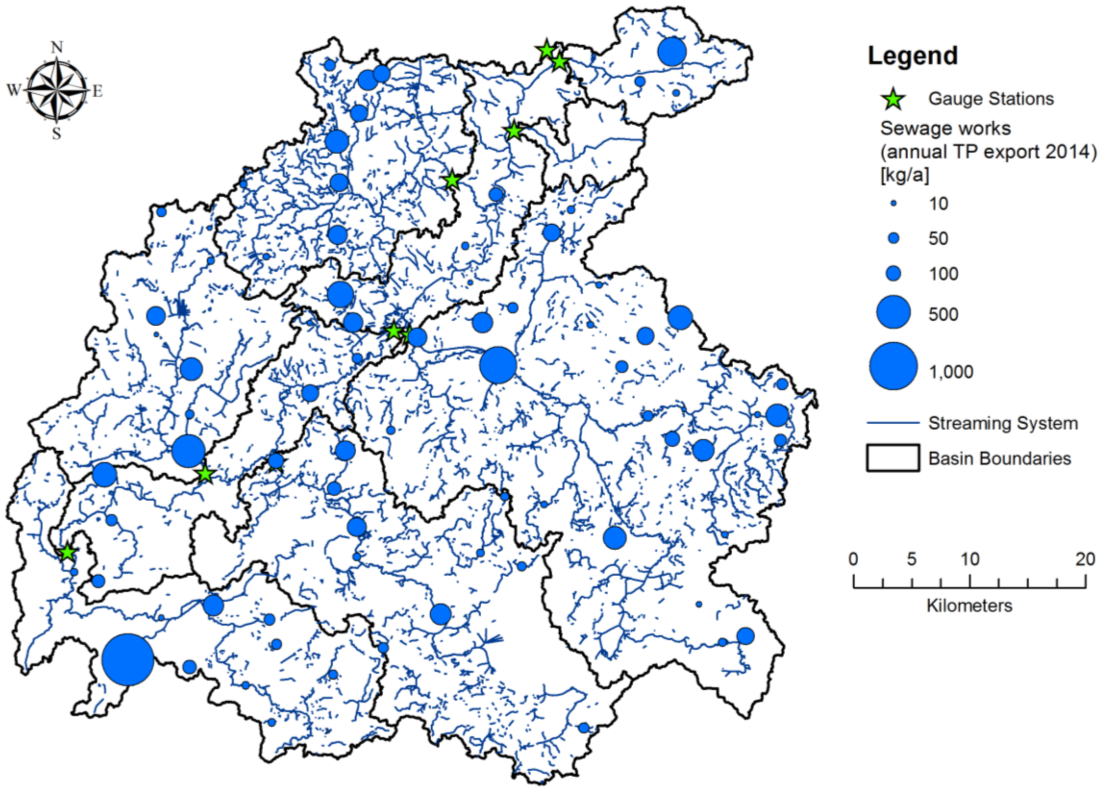

Figure 2-5: *Sewage works and their annual TP export to rivers in the Warnow river basin in 2014.*

The number of sewage works in the Warnow river basin has increased in the last two decades. Around 80 sewage works can be found in the whole watershed (Figure 2-5).

The second study area is a north-eastern sub-basin of the Warnow river basin (Chapter 5, 6, 7). The Zarnow watershed is the smallest sub-basin and about 38 km² large. We subdivided the watershed into three smaller spatial scales with a tile drainage field (4.2 ha), a drainage ditch watershed (179 ha), and a smaller part of the Zarnow watershed of around 1,550 ha (Figure 2-7). The sampling stations at the three spatial units are equipped with automated water samplers and water level loggers (see chapter 5).

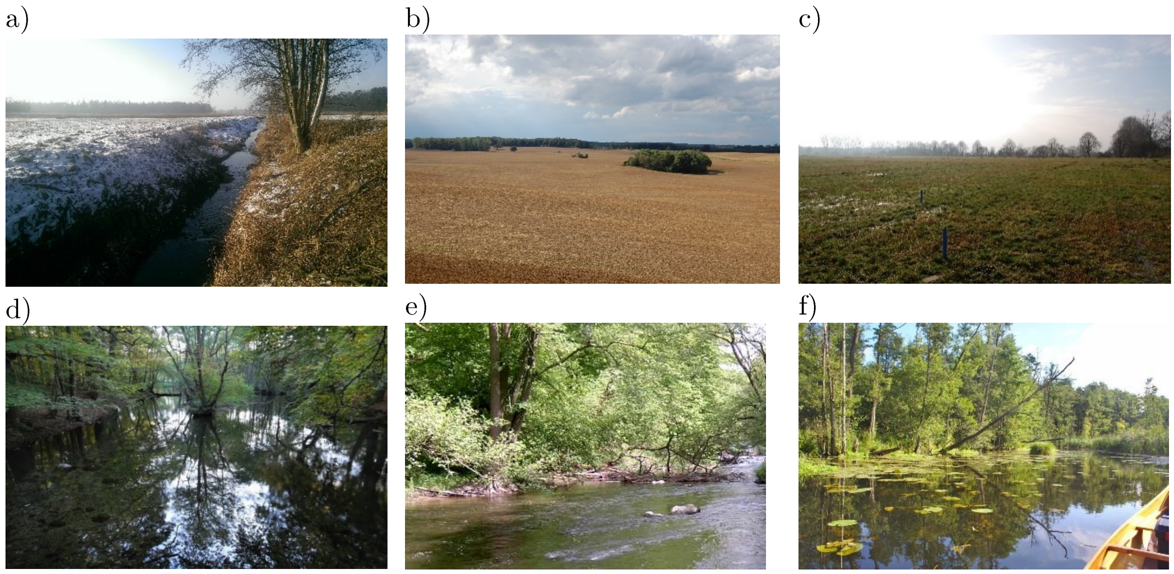

Figure 2-6: *Impressions from the Warnow river basin: Photographs a–c were taken by the author, d is from http://mapio.net/pic/p-42157442/, e was taken by Angelverein Oberwarnow, and f comes from www.flussinfo.net. a) The Zarnow brook near Dummerstorf, b) typical agricultural landscape in the Warnow river basin (near the city of Güstrow), c) an extensively used peatland (grassland) in the Zarnow sub-basin, d) The Nebel river close to Serrahn, e) the Mildenitz, f) The Warnow River ca. 2 km south of the brackiah part of the river.*

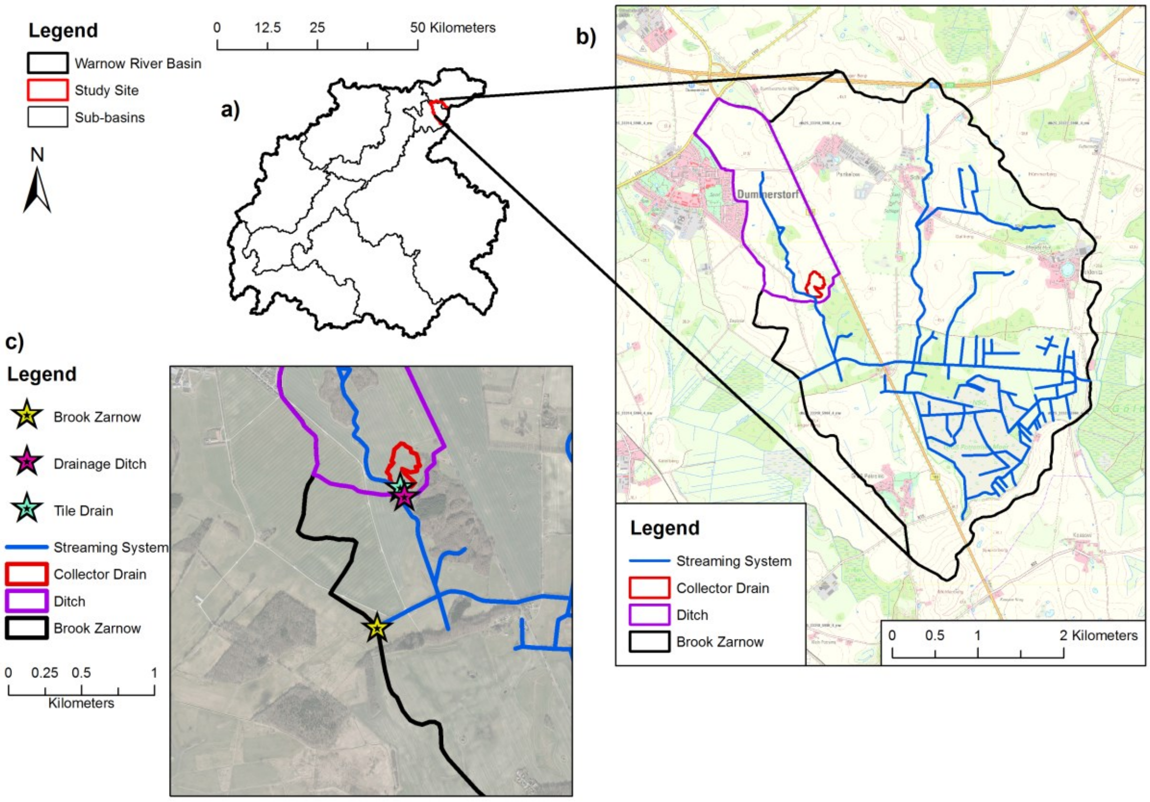

Figure 2-7: *Map of the several investigated scales in this thesis: a) Warnow river basin with Zarnow sub-basin, b) the three sub-scales of tile drain, drainage ditch, and brook, and c) a detailed map of the sampling stations of the three considered scales.*

2.2 Data gathering

Hydrological modeling often requires large amounts of input data to work properly (Table 2-3). Hence, we acquired an extensive set of input data for the SWAT model and the statistical models.

The Corine Land Cover data and the maps of soil and drainage distribution are shown in chapter 3 (Figure 3-3 c and Figure 3-2).

The monitoring network of the State Department of Environment, Nature Conservation, and Geology of Mecklenburg-West Pomerania (LUNG-MV) consists of 372 measurement points. The water quality parameters and discharge are measured every two to four weeks by the employees of the local water and soil organizations of the respective rural districts. Not all measurement stations derive data of all nutrients (phosphate, nitrate, and ammonium), chlorophyll-a, and discharge. Macrobenthos and macrophytes are exclusively measured by private research institutes. However, the nine chosen gauge stations presented in this thesis delivered the data of DRP, TP, and discharge.

Table 2-3: *Input data for statistical modeling of phosphorus concentrations and loads, and modeling using the SWAT model.*

Data	Obtained from	Temporal resolution	Spatial resolution	Data type
Time series of streamflow	LUNG MV	Bi- to four-weekly	Sub-basin	Excel sheet
Time series of DP concentrations	LUNG MV	Bi- to four-weekly	Sub-basin	Excel sheet
Time series of TP concentrations	LUNG MV	Bi- to four-weekly	Sub-basin	Excel sheet
Times series of streamflow 2015/2016 Zarnow sub-basin	Measured by employees of the chair of soil physics and resources conservation at the University of Rostock	Two to four measurements per week	Tile drainage field, drainage ditch and brook	Excel sheet
Times series of DP and TP concentrations 2015/2016 Zarnow sub-basin	Measured by employees of the chair of soil physics and resources conservation at the University of Rostock	Two to four measurements per week	Tile drainage field, drainage ditch and brook	Excel sheet
Land use data	CORINE Land Cover project	Data sets for 1990, 2000 and 2006	1:100,000	Shape file and legend document
Soil data	BÜK200. LUNG MV	Single measurement	1:200,000	Shape file
	Konzeptbodenkarte, KBK25	Single measurement	1:25,000	Shape file
Drainage map	LUNG MV	Single measurement	1:10,000	Shape file
River network map	LUNG MV	Single measurement	1:10,000	Shape file
Digital elevation model (DEM)	LVermA MV	Single measurement	10 × 10 m	Raster file
Numbers and TP export rates of sewage works		Annual (2012/2013)	Sub-basin	XY points file

2.3 The SWAT model

The Soil and Water Asessment Tool (SWAT, Arnold et al. 1998) is a physically based and semi-distributed hydrological model. Its core capabilities are the process-oriented modeling of water and nutrient balances on agriculturally used mesoscale watersheds. Worldwide, it has been applied to a multitude of watersheds on a variety of spatial scales. Small-scale investigations were carried out in the federal state of Schleswig-Holstein in northern Germany (Schmalz et al. 2008, Lam et al. 2010). The calibration of the model has often been in the focus of scientists (Starks & Moriasi 2009, Bacu et al. 2011, Arnold et al. 2012), and so has been the application of special hydrological applications, such as the implementation of landscape depressions (Kiesel et al. 2010), agricultural drainage (Du et al. 2005, Green et al. 2006, Kiesel et al. 2010), and climate change assessment (Ficklin et al. 2009, Awotwi et al. 2015,). Numerous tools and modules have been developed for the SWAT model to increase its performance and scope of work, for instance, SWAT-CUP, a calibration tool developed at the ETH Zürich (Abbaspour et al. 2007, Arnold et al. 2012), an advanced wetland module (Rahman et al. 2016), or a drainage module for dissolved phosphorus transport (Lu et al. 2016).

A detailed description of the approach of sensitivity analysis, calibration, and validation, and the model's application to a tile-drained watershed is given in chapter 3. Although we have not applied the SWAT model for phosphorus modeling so far, we plan a comprehensive P modeling approach for the Warnow river basin.

List of Publications and author contributions

(i) Application of the SWAT Model for a Tile-Drained Lowland Catchment in North-Eastern Germany on Subbasin Scale

Stefan Koch	Study design, data gathering, data analysis, writing, editing
Andreas Bauwe	Study design, data gathering, editing
Bernd Lennartz	Study design, editing

Koch, Stefan; Bauwe, A; Lennartz, B (2013): Application of the SWAT Model for a Tile-Drained Lowland Catchment in North-Eastern Germany on Subbasin Scale. In: *Water Resources Management* 27(3), 791–805.

(ii) Long-term phosphorus dynamics in a North-Eastern German lowland river basin

Stefan Koch	Study design, data gathering, data analysis, writing, editing
Petra Kahle	Study design, data gathering, editing
Bernd Lennartz	Study design, editing

Koch, Stefan; Bauwe, A; Lennartz, B: Long-term phosphorus dynamics in a North-Eastern German lowland river basin. *Ambio.* Submitted in 2016. Revision submitted in 2017.

(iii) Visualization of colloid transport pathways using Titanium(IV) oxide as a tracer

Stefan Koch	Study design, data gathering, data analysis, writing, editing
Petra Kahle	Study design, data gathering, editing
Bernd Lennartz	Study design, editing

Koch, Stefan; Kahle, P; Lennartz, B (2013): Visualization of colloid transport pathways using Titanium(IV) oxide as a tracer. In: *Journal of Environmental Quality* 45(6), 2053-2059

3 Application of the SWAT model for a tile-drained lowland catchment in north-eastern Germany on sub-basin scale

Abstract

Tile drainage is a widespread practice in agriculturally dominated lowlands with naturally high groundwater tables. A realistic estimation of the stream flow composition including tile drainage is an essential precondition for identifying major flow sources of nutrients. In this study, the Soil Water Assessment Tool (SWAT) was applied to the partially tile-drained Warnow catchment in North-Eastern Germany to evaluate the effect of tile drainage systems on stream flow composition on a sub-basin scale. In addition, model performance was tested after excluding tile drainages from the calibrated model setup. A sensitivity analysis revealed the highest sensitivities for parameters concerning evapotranspiration, soil characteristics, and groundwater flow, with a large variability in sensitivity ranks among the sub-basins. Nash-Suttcliffe-Efficiencies (NSE) varied strongly among the sub-basins for the tile-drained model setup ranging from 0.22 to 0.81 for the calibration and from -0.81 to 0.66 for the validation period. The percentage of tile flow varied between 0.3 and 31.9%, and reflected statistically significantly ($p<0.05$) the spatial extent of tile-drained areas within the sub-basins. Excluding tile drainages from the model setup led to a strong decrease in model quality and to a changed stream flow constitution dominated by groundwater. The results of our study indicate that the SWAT model realistically represented the actual fractions of tile flow on discharge on the sub-basin scale within the Warnow catchment. Therefore, we conclude that the incorporation of tile drainage systems is essential to calculate flow components accurately.

Keywords: *hydrological modeling, artificial drainage, stream flow constitution, subcatchment*

3.1 Introduction

Artificial drainage, either as subsurface tile drainage or as surface ditch systems, is a common practice to improve moisture and aeration conditions of the soil in agriculturally dominated lowlands with naturally high groundwater tables. According to Werner et al. (1991), 16% of the agricultural land in Germany is tile-drained with substantial consequences for catchment hydrology and solute leaching. Tile drainage systems lead to a shortened retention time for soil water and can therefore be important pathways for mobile nutrients, in particular nitrate (Kladivko et al. 1999, Tomer et al. 2003). It is estimated that 47% of the total nitrate load in Mecklenburg-West Pomerania, North-Eastern Germany, originates from tile drainage (Behrendt & Bachor 1998, Tiemeyer et al. 2008). Water from tile drainage systems contributes to discharge as a fast subsurface flow component (Northcott et al. 2002, Zajíček 2011), while groundwater is the major source of the slow baseflow component. Surface runoff plays only a minor role in the stream flow composition of lowland catchments (Gonzales et al. 2009). Therefore, a realistic estimation of the contribution of the different flow components, including tile drainage, is an essential precondition for identifying major sources of nutrient loads in lowland catchments.

Eco-hydrological catchment models are suitable tools to partition the discharge into individual flow components. Daniel et al. (2011) give an excellent overview of watershed models and their applications. Several models such as DRAINMOD (Skaggs 1978), MIKE SHE (Refsgaard & Storm 1995), or the Soil Water Assessment Tool (SWAT) (Arnold et al. 1998) have implemented algorithms to describe the hydrological processes in tile-drained catchments. The SWAT model is a popular eco-hydrological watershed model to predict river discharge, sediment, and chemical yields (Neitsch et al. 2005), and has been successfully applied in many studies around the globe (Gassman et al. 2007). However, most investigations to predict discharge only consider the catchment outlet. Santhi et al. (2008) emphasize the need for a spatially distributed approach to capture the spatial variations in hydrological parameters within the sub-basins. Du et al. (2005) validated the drainage module of SWAT and stated a solid functionality for discharge modeling in tile-drained watersheds. Studies applying the SWAT model to lowland catchments with flat topography in combination with a considerable amount of tile drainages, are rare. Kiesel et al. (2010) performed a tile drainage case study for a lowland catchment in northern Germany that showed a significantly improved model performance after the incorporation of tile drainage into the SWAT model setup. The high impact of the inclusion of tile drainages on stream flow constitution and water balance has been described by Green et al. (2006).

In the present study, the SWAT model was applied to the Warnow catchment, a tile-drained, agriculturally dominated, mesoscale lowland watershed in north-eastern Germany. The objectives were to estimate the proportions of tile flow on total stream flow on a sub-basin scale, to analyze the effect of the inclusion of tile drainage both on the model performance and on stream flow constitution, and to identify the parameters controlling the runoff processes.

3.3 Materials and methods

3.3.1 Study area

The 3,038 km² Warnow catchment is located in north-eastern Germany in the federal state of Mecklenburg-West Pomerania (Figure 3-1). The river Warnow drains into the Baltic Sea with an elevation difference of 68 m from the spring to the mouth, and a total length of 155 km. The highest elevation of the catchment is 146 m a.s.l., while the mean elevation is 42 m a.s.l. (Figure 3-3 a). The discharge gauge at the catchment's outlet is situated to the south of the city of Rostock near the northern boundary of the total catchment.

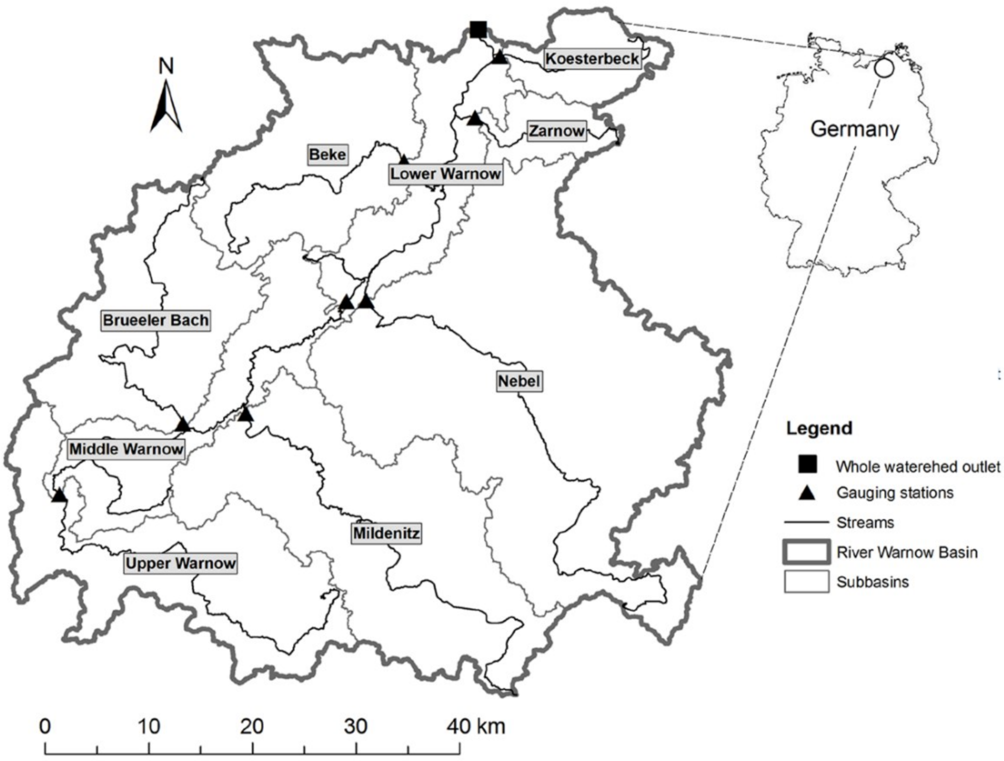

Figure 3-1: *The Warnow catchment including sub-basins.*

The climate is mainly Atlantic influenced with a mean annual precipitation sum of 647 mm and a mean annual temperature of 9.1 °C. Land use is dominated by arable land (58%), forests (21%), and grassland (13%) Figure 3-3 c). Less prominent are wetlands (4%), urban structures (3%), and open water areas (<1%) (DLR 2000). According to the current digital drainage map, provided by the State Office of Environment, Nature Conservation, and Geology of Mecklenburg-West Pomerania (LUNG-MV), 11% of the catchment is estimated to be artificially drained by tile drainage systems (Figure 3-2). Subsurface drainage was mainly installed under arable land with a naturally high groundwater table. The drainage systems are usually several decades old, whereby the exact location and the spatial extent have not always been known. The main soil types are Cambisols (30%), Lessivés (27%), Stagnosolos (17%), and Gleysols (6%) (Figure 3-3b). Histosols account for 10%, and the percentage of Regosols is negligible (LUNG 2010). The geomorphology was formed by the glacial movement of the

European continental ice sheet during the last ice age. As a consequence, the area is dotted with landscape elements typical for glacial ground and end moraines, such as kettle holes.

3.3.2 SWAT model and modeling approach

The Soil Water Assessment Tool is a physically based, semi-distributed and process-oriented eco-hydrological model to predict discharge, sediment yield, and nutrient and pesticide loads under different land use or climate change scenarios (Neitsch et al. 2005). For this study, we used the SWAT2005 version (Arnold et al. 1998) with the GIS interface ArcSWAT (Olivera et al. 2006). The hydrological cycle simulated in SWAT includes precipitation (comprising snowfall), evapotranspiration, discharge, and groundwater recharge. The maximum temporal resolution is one day. The water balance in SWAT is based on a simple water balance equation (Neitsch et al. 2005):

$$SW_t = SW_0 + \sum_{i=1}^{t} \left(P_{day} - Q_{surf} - ET_a - w_{seep} - Q_{gw}\right)$$

where SW_t is the final soil water content (mm), SW_0 is the initial soil water content on day I (mm), t is the time (days), P_{day} is the amount of precipitation on day I (mm), Q_{surf} is the amount of surface runoff on day I (mm), ET_a is the amount of evapotranspiration on day I (mm), w_{seep} is the amount of water entering the vadose zone from the soil profile on day I (mm), and Q_{gw} is the amount of return flow on day I (mm).

Discharge is calculated as the sum of all flow components according to the following equation:

$$WYLD = GWQ + LATQ + TILEQ + SURQ$$

where *WYLD* is discharge, *GWQ* is groundwater flow, *LATQ* is lateral flow, *TILEQ* is tile flow, and *SURQ* is surface runoff. The units are mm.

In SWAT, tile drainage flow occurs when the groundwater table exceeds the depth of the tile drains. Tile flow is calculated as follows:

$$tile_{wtr} = \frac{h_{wtbl} - h_{drain}}{h_{wtbl}} \cdot (SW\text{-}FC) \cdot \left(1\text{-}\exp\left[\frac{-24}{t_{drain}}\right]\right) \text{if } h_{wtbl} > h_{drain}$$

where $tile_{wtr}$ is the amount of water removed from the soil layer by tile drainage (mm), h_{wtbl} is the water table height above the impermeable layer (mm), h_{drain} is the tile drain height above the impermeable layer (mm), SW is the water content of the profile on a given day (mm), FC is the field capacity water content of the profile (mm), and t_{drain} is the time required to drain the soil to field capacity (hrs). A detailed description of the tile drainage algorithm can be found in Du et al. (2005). To simulate tile flow, it is necessary to specify the depth from the soil surface to the drains (DDRAIN), the amount of time required to drain the soil to field capacity (TDRAIN), the time lag between the water entry to the tile and to the main channel (GDRAIN), and the depth from the soil surface to the impervious layer (DEP_IMP). In this study, we defined the drainage parameters DDRAIN with 800 mm, TDRAIN with 23 hrs, and GDRAIN with 23 hrs. DEP_IMP was set to 2.000 mm.

The minimal spatial object in SWAT is the hydrologic response unit (HRU), which is defined as a unique intersection of soil type, land use type, and slope class for each sub-basin, resulting in identical hydrologic properties. Tile drainage was introduced as a fourth component in order to distinguish drained and non-drained HRUs. To this end, the tile drainage map was intersected with the soil map. Soils influenced by tile drainage were subsequently marked in the SWAT-implemented soil database. A similar approach has been described by Kiesel et al. (2010).

3.3.3 Input data

Weather data from four climate and seven precipitation stations across the Warnow catchment—obtained from the German Weather Service—served as meteorological input variables. The data included daily values of precipitation, minimum and maximum air temperature, solar radiation (calculated from sunshine duration), wind speed, and relative humidity. Depending on the season and the position of the rain gauges, precipitation measurement errors vary from 10 to 25% in north-eastern Germany. The measured precipitation was thus corrected by applying corresponding correction factors (Richter 1995). CORINE land cover data (DLR 2000) with a scale of 1:100,000 formed the basis of land use classification. Land use from the CORINE land cover data was assigned to the corresponding SWAT plant and land cover codes. The soil map is twofold with regard to its spatial accuracy. A map with a spatial resolution of 1:200,000 (LUNG 2010) was available for the northern and the central part of the catchment. The associated database contained detailed information about physical soil properties for different soil horizons. A soil map with a resolution of 1:500,000 (LUNG 1995) was used for the very southern part of the catchment, since the more precise map was still being processed. The statewide map of tile drainage systems was analyzed for plausibility and eventually integrated into the SWAT model as described in the previous section. The proportion of tile-drained areas (Figure 3-2) varied strongly among the sub-basins and ranged from 1.3% (Mildenitz) to 49.0% (Koesterbeck). The spatial extent of these areas is a source of uncertainty and should be considered a rough estimation.

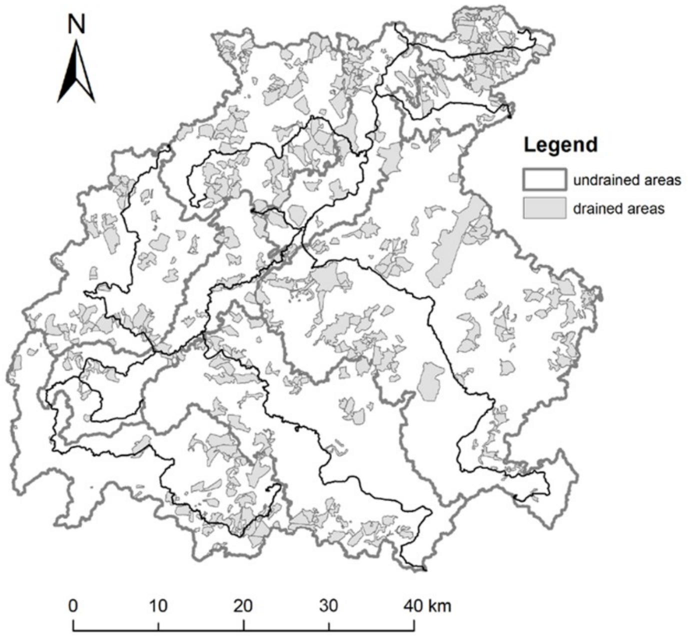

Figure 3-2: *Distribution of tile-drained and non-tile-drained areas within the Warnow river basin.*

A digital elevation model with a 25 × 25 m grid cell resolution (LVA M-V 2000) formed the basis for delineating the catchment, the sub-basins, and the river network. Nine discharge gauges, run by the State Office of Agriculture and Environment of Mecklenburg-West Pomerania, are located within the catchment (Figure 3-1). Based on these gauges, the entire watershed was divided into nine sub-basins covering areas from 68 km² (Zarnow) to 939 km² (Nebel). Associated stream flow data from 2002 to 2008 were used to calibrate and validate the model.

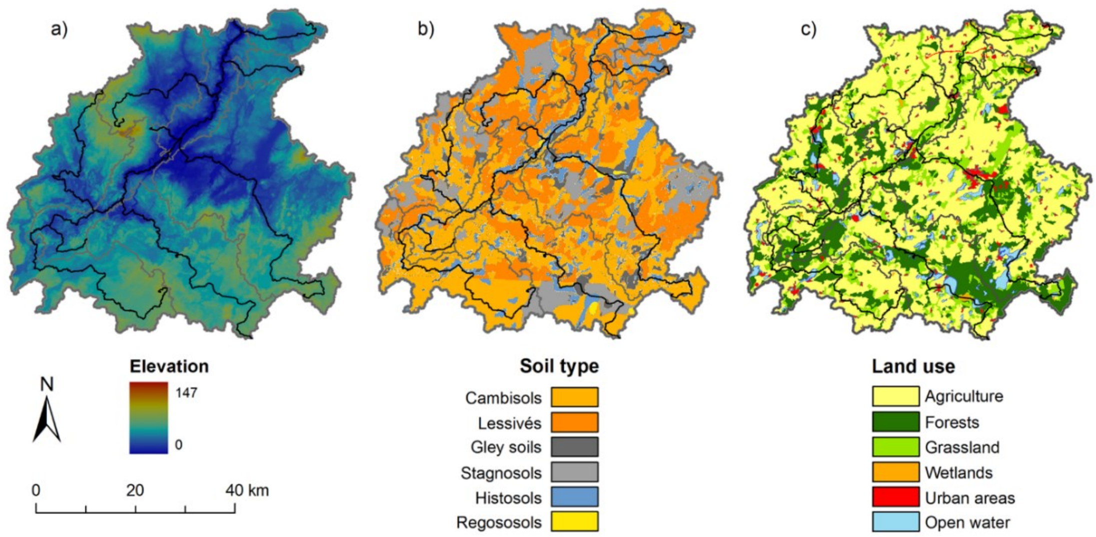

Figure 3-3: *The Warnow river basin with (a) DEM, (b) soil types, and (c) land uses.*

3.3.4 Sensitivity analysis and calibration

Automatic sensitivity analysis was performed for 26 hydrologic related model parameters for each sub-basin by using the “Latin Hypercube – One-factor-At-a-Time” algorithm implemented in SWAT. With this method, one parameter is changed within allowable boundaries, while all other parameters remain invariant. The parameters were ranked by the level of their effect on the model output for each sub-basin, and the median rank was determined. The most sensitive parameters were then chosen for further calibration.

The calibration period was defined as the three hydrological years from November 2002 to October 2005, while the validation period was set to the three subsequent hydrological years from November 2005 to October 2008. The discharge was calibrated on a daily basis separately for each sub-basin, beginning upstream. The parameterization was executed manually in the first step and afterwards automatically by applying the parameter solutions (PARASOL) approach according to van Griensven et al. (2001). We used the Nash-Suttcliffe-Efficiency (NSE, Nash and Suttcliffe 1970) and the coefficient of determination (R^2) to evaluate the goodness-of-fit for the calibration and the validation period.

Two model runs were performed to test the impact of the inclusion of tile drainages on the model performance and the flow components. First, the model was calibrated by including tile drainage. Afterwards, a simulation run was carried out without tile drainage by using the calibrated parameterization of the tile-drained model setup.

In order to enable a comparison between modeled and observed values at the catchment outlet, a seven-day running mean of the daily discharge was calculated to minimize the watergate- and tailback-affected variability in the hydrograph (Figure 3-4).

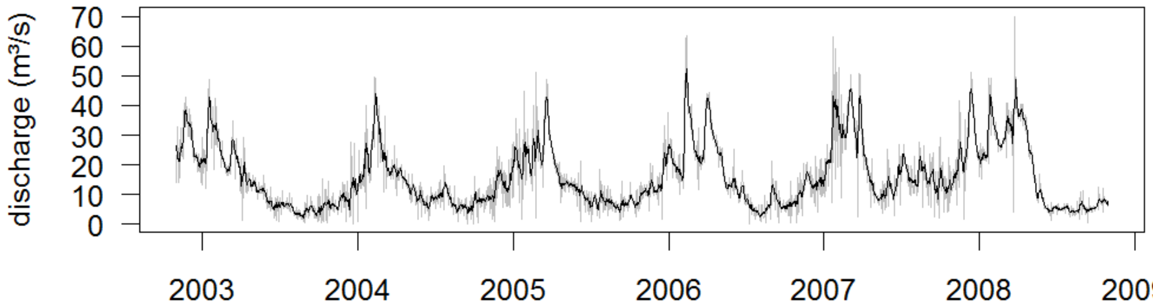

Figure 3-4: *Daily discharge (gray line) and seven-day running mean discharge (black line) at the catchment outlet.*

3.4 Results and discussion

3.4.1 Sensitivity analysis

An overview of the results of the sensitivity analysis is given in Figure 3-5 and Table 3-1. The evaporation parameter ESCO was the most sensitive parameter for five out of nine sub-basins. This is in accordance with Schmalz and Fohrer (2009), who found in a comparative study that the parameter ESCO is very sensitive in both lowland and mountainous catchments. The sensitive baseflow recession coefficient ALPHA_BF had the highest variability among the sub-basins, which could be attributed to differences in relief energy among the sub-basins. In addition, the soil physical properties available water capacity (SOL_AWC) and saturated hydraulic conductivity (SOL_K) were identified to be very sensitive, which indicates that these parameters influence the vertical flow of water through the unsaturated zone to a large degree. The choice of an appropriate soil parameter SOL_Z also affected the quality of the model substantially. The SCS curve number CN2 was found to be very sensitive, as it determines to a large extent the proportion of surface to subsurface flow. The sensitivity rank for CN2 varied between two and eight among the sub-basins, whereby it was most sensitive in the hilly Beke sub-basin (Table 3-1). Vegetation parameters such as initial leaf area index (BLAI) or maximum canopy storage (CANMX) were also among the ten most sensitive parameters (6 and 9).

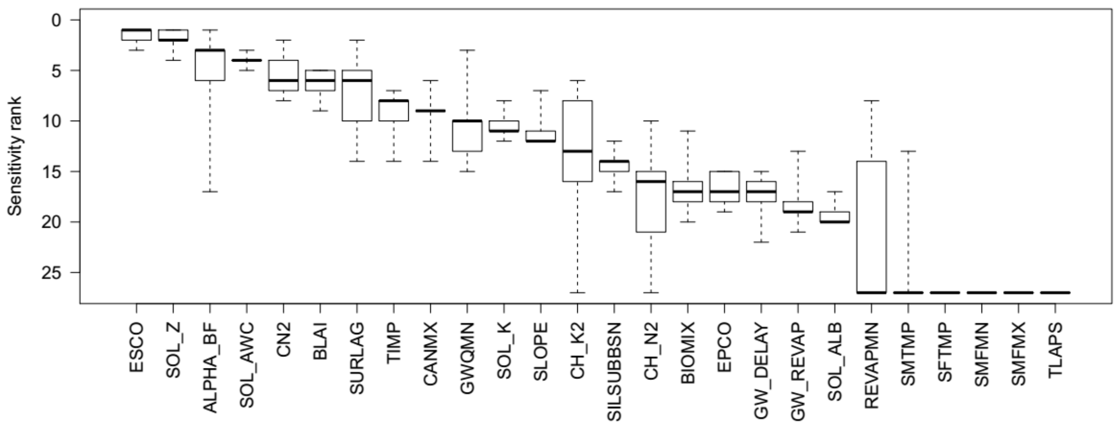

Figure 3-5: *Box-whisker-plots of the sensitivity analysis for all nine sub-basins. Model parameters are shown on the x-axis with decreasing sensitivity.*

The spatial variability of the parameters' sensitivity within the Warnow catchment (Table 3-1) underlined the heterogeneity of the catchment and the need for a spatially distributed calibration. For example, while the parameter ALPHA_BF was most sensitive in the Upper Warnow sub-basin, this parameter had the sensitivity rank of 17 in the Beke sub-basin. These differences can be explained by the differences in the topography within the Warnow catchment, in particular with varying slopes. Despite this variability, sensitivity analysis showed, in general, that parameters for baseflow and surface runoff as well as parameters affecting percolation and evapotranspiration played the most important roles in the catchment. In contrast to similar catchments in northern Germany (Schmalz and Fohrer 2009), the hydrology of north-eastern German lowlands seems to be more affected by a slightly higher relief energy, which has been expressed by the high sensitivities of the surface runoff parameters CN2 and SURLAG. These parameters become crucial when modeling mountainous watersheds (e.g. Thampi et al. 2010; Xu et al. 2009; Hörmann et al. 2009).

Table 3-1: *Sensitivity ranks of the parameters used for calibration in each sub-basin.*

Parameter	Lower Warnow	Koesterbeck	Zarnow	Beke	Nebel	Middle Warnow	Brueeler Bach	Mildenitz	Upper Warnow
BLAI	7	9	5	6	5	5	9	5	7
CANMX	9	14	9	7	9	9	13	6	9
CN2	6	5	4	2	7	7	6	3	8
ESCO	2	2	1	1	1	1	2	1	3
GWQMN	10	13	7	3	10	10	15	12	15
SOL_K	12	11	11	9	11	11	11	8	10
SOL_Z	1	1	2	4	2	2	1	2	4
SURLAG	5	7	14	11	6	6	5	10	2

As a result of the sensitivity analysis, excluding the snow pack temperature lag factor TIMP, the most sensitive parameters ESCO, SOL_Z, ALPHA_BF, CN2, BLAI, SURLAG, CANMX, GWQMN, and SOL_K (Table 3-2) were calibrated. RCHRG_DP was included as an additional parameter. According to Schmalz et al. (2008), this parameter is profoundly sensitive for lowland catchments. No calibration was carried out for the available water capacity (SOL_AWC), since data from the soil map could be used.

Table 3-2: *Parameters used for calibration.*

Parameter	Description	Allowable Range	Unit	Calibration Range
ALPHA_BF	Baseflow recession coefficient	0–1	1	0–1
BLAI	Initial leaf area index	0–8	1	0–4
CANMX	Maximum canopy storage	0–100	mm	0–15
CN2	SCS curve number for moisture condition II	35–98	1	± 15%
ESCO	Soil evaporation compensation factor	0–1	1	0–1
GWQMN	threshold water level in shallow aquifer for baseflow	0–5000	mm	0–1000
RCHRG_DP	Deep aquifer percolation coefficient	0–1	1	0–0.5
SOL_K	saturated hydraulic conductivity	0–2000	Mm h^{-1}	± 15%
SOL_Z	Depth from soil surface to bottom of layer	0–2000	mm	± 15%
SURLAG	Surface runoff lag time	0–24	d	0–12

3.4.2 Model performance

NSE-values for the calibration (0.86) and the validation period (0.66) of the catchment outlet indicated a good model fit to the observed values (Figure 3-6). During the calibration period, baseflow was slightly underestimated and peak flows were non-uniformly under- and overestimated. During the validation period, both baseflow and peak flows were constantly overestimated by the model. This led to a less satisfactory NSE-value for the validation period compared to the calibration period.

The model fit differed considerably among the sub-basins. The NSE-values for the single sub-basins ranged from 0.22 to 0.86 for the calibration and from -0.82 to 0.77 for the validation period (Table 3-3), whereby negative NSE-values occurred in the sub-basins Nebel, Upper Warnow, and Middle Warnow.

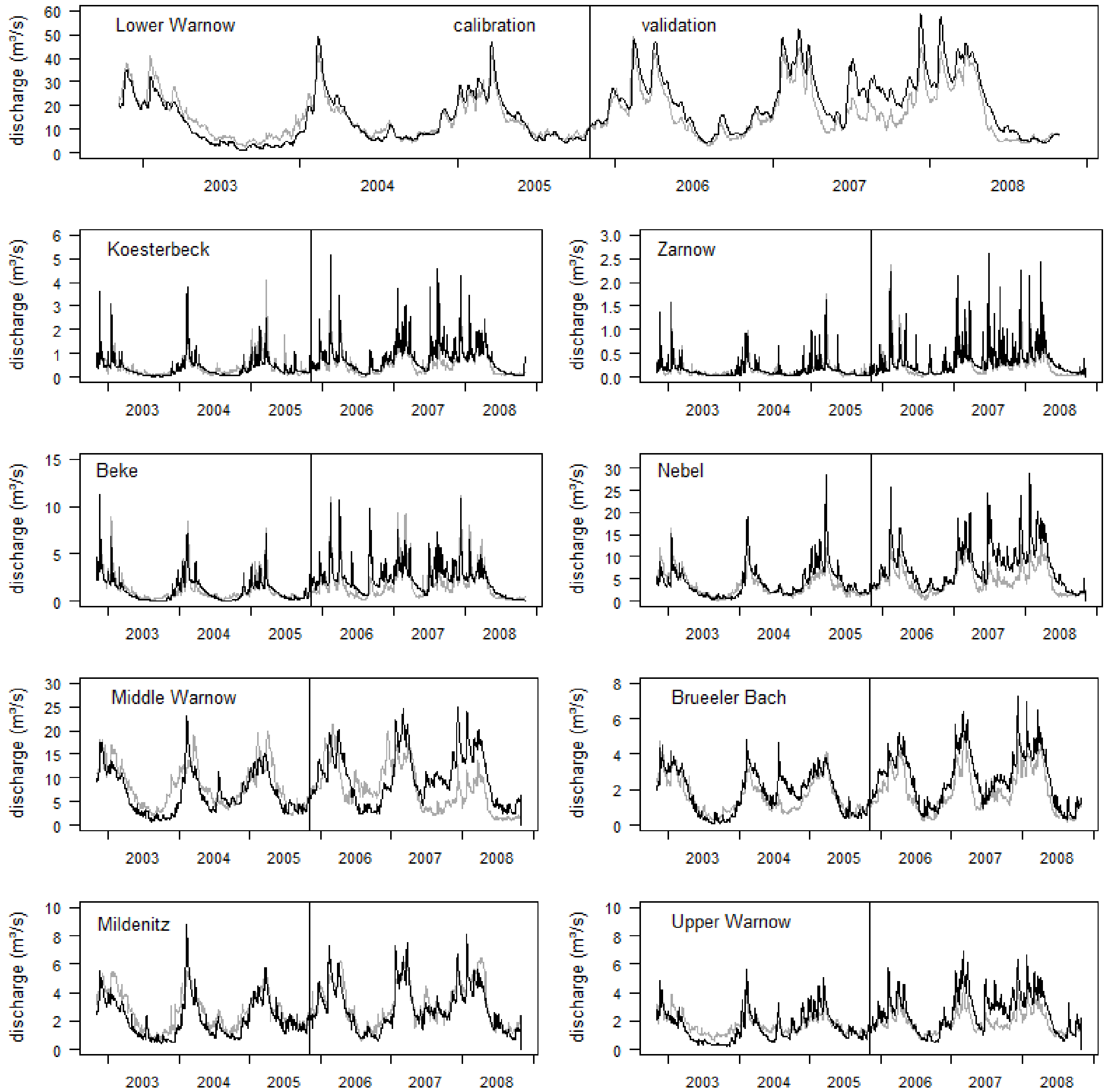

Figure 3-6: *Observed (gray lines) and predicted (black lines) hydrographs of the simulation period for each sub-basin. The catchment outlet is presented by the Lower Warnow sub-basin. Note the varying y-axis scaling.*

Table 3-3: *Model fits (NSE and R^2) for the calibration period, validation period, and whole simulation period for all sub-basins with incorporated tile drains. NSE-quality according to Xu et al. (2009), modified: *** very good, ** good, * satisfactory, + poor, ‘ very poor*

	calibration period		validation period		whole simulation period	
Sub-basin	NSE	R^2	NSE	R^2	NSE	R^2
Lower Warnow	0.86***	0.90	0.66**	0.87	0.74**	0.87
Koesterbeck	0.48*	0.53	0.45*	0.65	0.48*	0.65
Zarnow	0.34*	0.47	0.02^{+}	0.46	0.15^{+}	0.46
Beke	0.71**	0.73	0.49*	0.64	0.59**	0.64
Nebel	0.26*	0.64	-0.82‘	0.70	-0.32‘	0.70
Middle Warnow	0.50**	0.65	-0.31‘	0.35	0.06^{+}	0.35
Brueeler Bach	0.55**	0.74	0.43*	0.80	0.49*	0.80
Mildenitz	0.59**	0.79	0.77***	0.80	0.71**	0.80
Upper Warnow	0.22^{+}	0.72	-0.43‘	0.77	-0.15‘	0.77

According to Holvoet et al. (2005), model results can be profoundly influenced by the degree of detail of the maps used. For example, Romanowicz et al. (2005) emphasized the high impact of the soil map on the model predictions for an agricultural watershed in Belgium. Especially the less detailed soil map used in the southern part of the catchment was a source of uncertainty in our study. Nevertheless, other studies reported that the impact of the spatial aggregation of the soil map is limited, compared to land use and DEM data (Di Luzio et al. 2005). Backwater effects within a catchment can be a fundamental problem in hydrologic modeling. At different points inside the Warnow catchment, dams and weirs were constructed to regulate discharge. The eco-hydrological SWAT model is not designed to model these hydrodynamic conditions, which may have caused dissatisfactory model results for some sub-basins. Zhang et al. (2008) reported that the model prediction can significantly decrease when applying the same parameterization for each sub-basin in multi-gauged catchments. Following this finding and taking into account the heterogeneity of the Warnow catchment in terms of soil, land use, slope, and tile drainage, we calibrated each sub-basin separately. Kumar and Merwade (2009) showed, despite this approach, that model results can differ markedly among the sub-basins. The slightly inferior validation results compared with the validation results in our study could be attributed to the wetter weather conditions during the validation period, with an average annual precipitation sum of 735.4 mm compared to 623.3 mm for the calibration period (see also Shrestha et al. 2010).

3.3.3 Impact of tile drainage on the model performance

The effect of incorporating tile drainage into the SWAT model was tested by excluding the tile drainages from the calibrated model setup (Figure 3-7). Eliminating the tile drainages led to reduced and constantly underestimated discharge rates in almost all sub-basins.

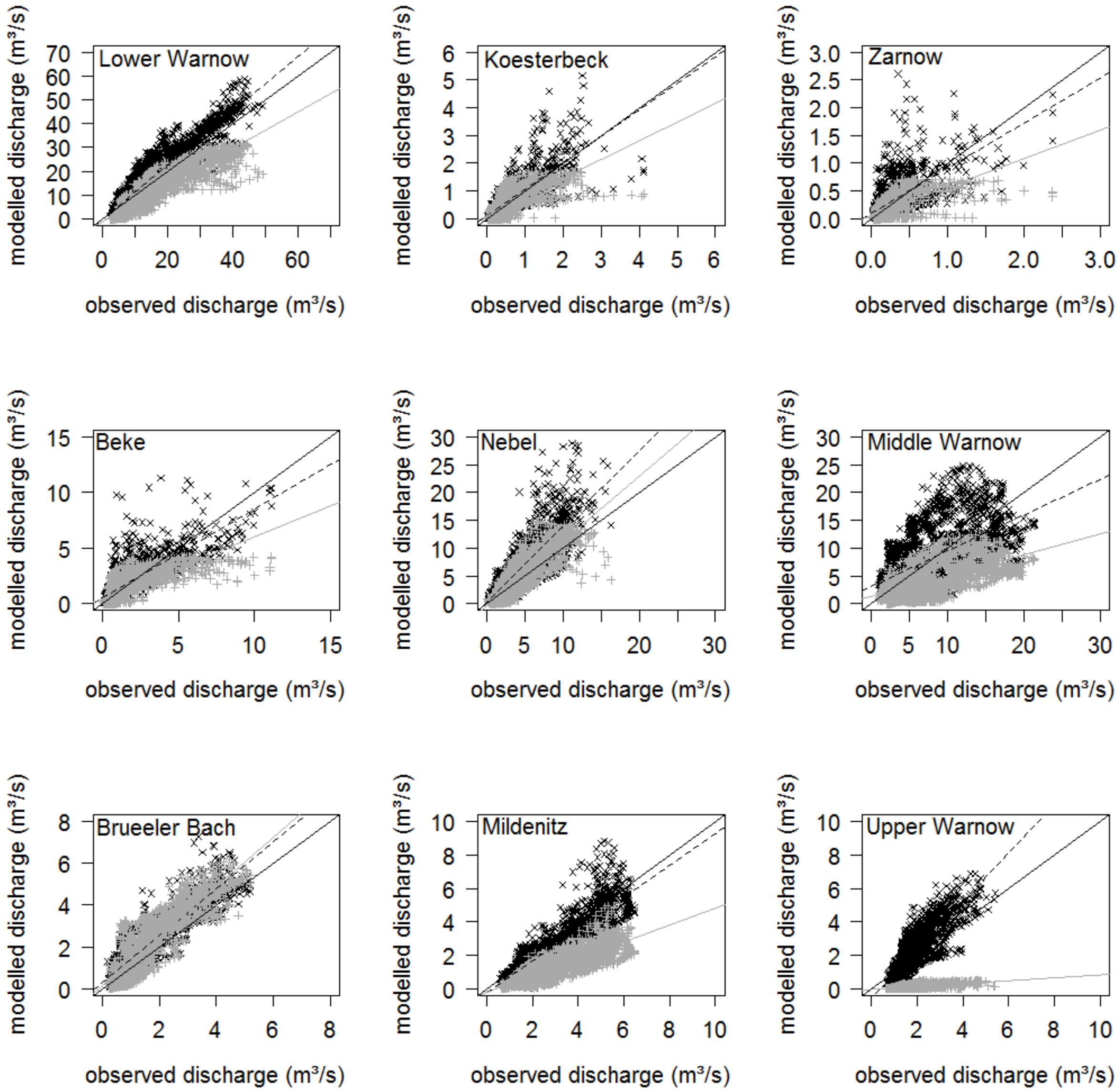

Figure 3-7: *Daily modeled vs. observed discharge, and model fits for the tile-drained (black crosses, black dashed line) and non-tile-drained (gray crosses, gray solid line) model runs covering the complete simulation period. The black solid line shows the best potential model fit (R^2 = 1).*

Tile drainages act as a fast interflow component and shorten the retention time of soil water with increased flow rates when the groundwater table exceeds the depth of the drainage pipes. Increased discharge rates due to the consideration of tile drainage systems were also simulated by Green et al. (2006), who emphasized the importance of including tile flow in water yield calculations for tile-drained affected catchments. Regression lines in Figure 3-7 indicate that the inclusion of tile drainages substantially enhanced the model performance. This is in accordance with Kiesel et al. (2010), who reported a strongly improved model performance after including tile drainages into a calibrated model setup. A closer inspection of our data revealed that the impact of tile drainages on the model quality was variable among the sub-basins. For example, while the model quality increased dramatically through the incorporation of tile drainages in the Upper Warnow sub-basin, almost no alteration was observed in the Brueeler Bach sub-basin.

The percentage of tile flow varied between 0.3% and 31.9% and mirrored the spatial extent of tile-drained areas within the sub-basins (Figure 3-8). Sub-basins with a high proportion of tile-drained areas had, in general, higher tile flow rates than sub-basins with lower proportions of tile-drained areas. This relationship was statistically significant both for the calibration ($p<0.05$) and the validation period ($p<0.01$).

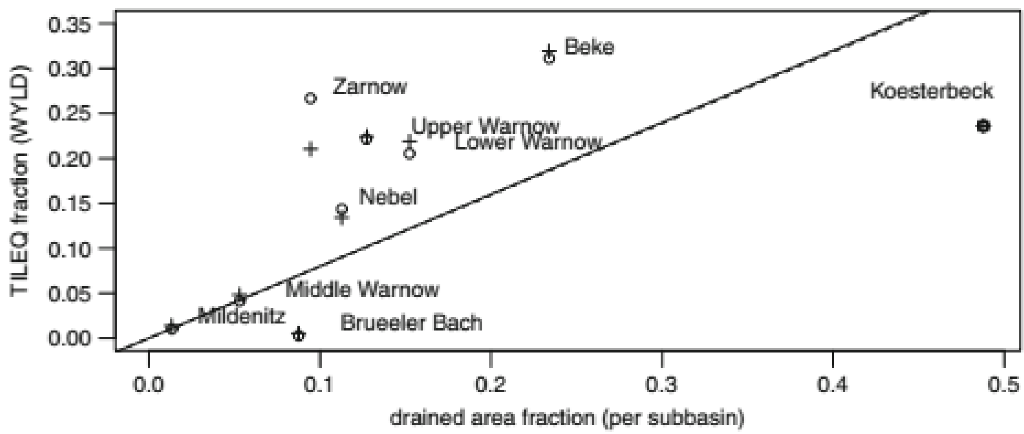

Figure 3-8: *Tile flow (TILEQ) as a function of the tile-drained area per sub-basin covering the calibration (△, solid line shows linear trend, r^2 = 0.65) and the validation period (+, dashed line shows linear trend, r^2 = 0.76). The Koesterbeck sub-basin as an outlier was not taken into account for the regression model.*

For the tile-drained model run, the fraction of surface runoff contributing to stream flow ranged from 1.5% to 24.4%, whereby higher fractions were calculated in the validation period. This could be attributed to higher amounts of precipitation during this time span. For the non-tile-drained model run, surface runoff was negligibly small in all sub-basins (<0.35%), and thus distinctly lower than in the model run with tile drainage, which is in contrast to Green et al. (2006), who calculated higher surface runoff fractions without the incorporation of tile drainage systems.

Results indicate that the presence of tile drains increased the model quality dramatically. The tile flow fraction was strongly dependent on the input data concerning the tile-drained areas (Figure 3-8). Adequate drainage maps are, therefore, essential to cover tile flow realistically. Current investigations with GIS-based probability approaches (Mehl et al. 2010) may lead to more exact drainage maps and, consequently, to improved model results in the near future.

3.4 Conclusions

In this study, we used the SWAT model to analyze the effect of tile drainages on stream flow constitution and on the model performance on a subcatchment scale for a partially tile-drained lowland catchment in north-eastern Germany. Sensitivity analysis showed that the hydrological processes in the Warnow catchment are controlled by parameters affecting baseflow, percolation, and evapotranspiration. Because of the partially hilly landscape structure, parameters that control surface runoff also played an important role. The results of our study indicate that the SWAT model was capable of representing the actual fractions of tile flow on discharge more or less accurately in the Warnow catchment. Differences on the sub-basin scale were visible, and the performance of the model was variable among the sub-basins. The proportion of tile flow on total stream flow was strongly dependent on the extent of tile-drained areas within the sub-basins. The exclusion of tile drainages from the model setup led to a completely changed stream flow constitution. Therefore, the conclusion can be drawn that incorporating tile drainage systems into the model setup is essential to calculate flow components realistically in the relevant catchments. The quality of the SWAT model was substantially lower when eliminating the tile drains from the calibrated model setup. This result underlines the enormous influence that the inclusion of tile drainages may have on modeling results.

A significant step forward in modeling the hydrology of tile-drained catchments would be the generation of more accurate maps to identify tile-drained areas as exactly as possible. Future research will focus on the identification of the most important flow paths for solutes, in particular nitrate, in tile-drained catchments, to derive appropriate management strategies with the aim of reducing the risk of eutrophication of surface water bodies.

Acknowledgements

We greatly acknowledge the State Office for Environment, Nature Conservation and Geology of Mecklenburg-West Pomerania, especially Alexander Bachor, Frank Idler, and Stefan Klitzsch, for providing soil and discharge data.

4 Long-term phosphorus dynamics in an agricultural watershed in North-Eastern Germany

Abstract

We analyzed a 21-year data set (1990-2010) of dissolved reactive (DRP) and total phosphorus (TP) concentrations in surface waters of an agricultural used watershed (> 3,000 km^2) in North-Eastern Germany aiming at identifying dominant P-pathways in artificially drained lowland landscapes.

Phosphorus concentrations were only moderate spatially variable. Mean annual DRP and TP loads ranged from 0.04±0.01 to 0.15±0.05 and 0.12±0.05 to 0.27±0.06 kg ha^{-1} a^{-1} respectively. We detected significant negative temporal trends in the first investigated decade, which are most likely related to installed sewage plants. DRP concentrations decreased with increasing discharge whereas TP concentrations tend to increase at higher discharge rates. We assume that the soluble P fraction in surface waters is diluted by less P-laden groundwater, whereas TP dynamics reflect artificial drainage and internal erosion effects. Future work should concentrate on high P export rates during storm events and the role of artificial drainage systems in particulate P-transport.

Keywords: *catchment hydrology; dissolved and particulate phosphorus, eutrophication; monitoring; sub-basin scale*

4.1 Introduction

Eutrophication of surface waters was and still is a major environmental concern and agriculture is often the dominant diffuse source of phosphorus (P) (Sharpley et al. 2013). A successful cultivation of crops as well as the preservation of soil fertility is, however, bound to a sustainable nutrient management, including the use of mineral and organic fertilizers (Cordell et al. 2009). Although the application of mineral P fertilizer can be realized with satisfying precision, the application of manure remains challenging regarding application rates and application technique (Nkebiwe et al. 2016). In this context, the risk of high P mobilization rates for manure-amended soils needs special attention (Dodd & Sharpley 2015)

The enrichment of P in surface waters following leaching from arable soils generally leads to an increased growth rate of algae and inferential consumption of oxygen (Carpenter 2005). The reduction of point and non-point sources of P is therefore a priority for future land use (Daniel et al. 1998).

The European Water Framework Directive (Directive 2000/60/EC) commits European Union member states to achieve a good qualitative status of all surface water bodies. Although, eutrophication is a general concern in Europe, the Baltic Sea is, in particular, threatened by eutrophication through its geographical situation. The total area of the Baltic Sea drainage basin is about 1,745,000 km^2, which is approximately four times larger than the Baltic Sea itself (Stålnacke et al. 2015)

Long-term observations of the concentrations of P and other nutrients (e.g. nitrogen) and contaminants (e.g. heavy metals) in the surface water bodies are a valuable source for the evaluation of the development of riverine ecology and water quality. Data from land use and fertilizer management, from soils (soil types and tillage) and drainage systems should be recorded to evaluate the development of water quality over time and to improve the understanding of interactions between agriculture and other human activities on water quality on basin and sub-basin scale.

Kronvang et al. (2007) analyzed multiple European rivers different in catchment scale (from $<$30 km^2 to $>$50,000 km^2) and highlighted the relevance of diffuse sources for the pollution of rivers. However, we noticed a substantial under-representation of lowland watersheds.

Under the different pathways of P transport from agricultural fields to rivers and streams, the relevance of erosion and the surface runoff of dissolved and particulate P transport have been widely documented (Sharpley et al. 1994; Carpenter 2005). There is also increasing evidence that particle facilitated P transport through the soil profile and the subsequent release to surface water bodies by tile drainage systems may be important (Outram et al. 2014; Zimmer et al. 2016).

A differentiation between transport mechanisms and pathways of dissolved reactive phosphorus (DRP) and total phosphorus (TP) seems indicated. Bowes et al. (2005) as well as Zimmer et al. (2016) highlighted the importance of storm events for the release of TP in lowland catchments and through subsurface drainage. In this context, Grant et al. (1996) emphasized the importance of a high frequency sampling strategy during storm events for a realistic estimation of annual P loads via tile drainage.

The aim of this study was to evaluate the temporal trends of the P concentrations and the P loads exported to surface water bodies in an agricultural lowland watershed with considerable extent of artificial drainage in North-Eastern Germany (1990–2010) and to detect the regional drivers and pathways of P losses using multiple linear regression and non-linear regression models.

4.2 Material and methods

4.4.1 Study site

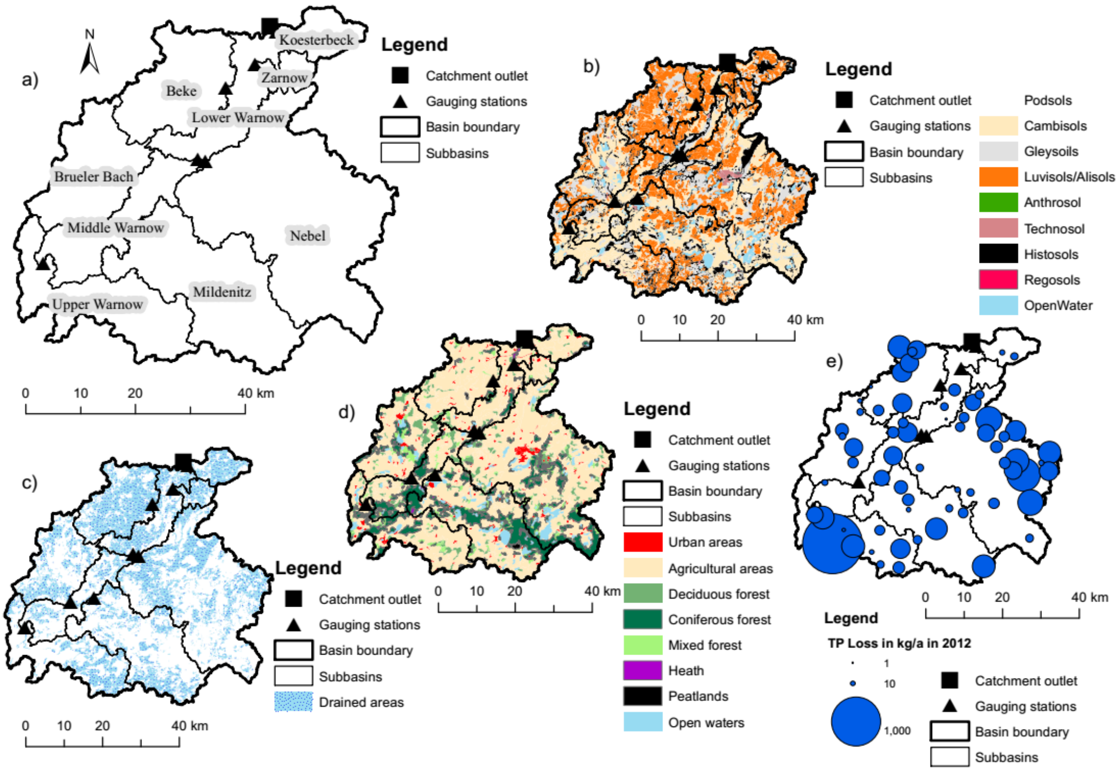

Figure 4-1: *The Warnow river basin and its sub-basins (a) and maps with b) soil types (data provided by LUNG MV), c) estimated areas of artificial drainage (data provided by LUNG MV), d) land use based on Corine Land Cover 2006 data (CLC 2006), and e) sewage works and their annual loss of TP in the year 2012 (data provided by LUNG MV, no other data available).*

The Warnow river basin (3,028 km²) is located in the federal state of Mecklenburg-West Pomerania in North-Eastern Germany (Figure 4-1) and consists of nine sub-basins (Table 4-1). The climate is atlantic influenced with a mean annual precipitation of 636 mm and a mean annual temperature of 10.4°C (1990–2010). The basin is characterized by gentle slopes with a maximum elevation of 146 m. The land use of the Warnow river basin is dominated by agriculture (71% of the total area). Further uses are forests, wetlands, open water areas, and artificial surfaces (e.g. settlements and impervious layers, Table 4-1). The land use distribution changed within the last 20 years by a reduction of arable land and an increase of the portion of sealed surfaces. About 42% of the watershed area is artificially drained by subsurface drainage systems or drainage ditches. Approximately 100 sewage works of varying sizes are located in the watershed (Figure 4-1e).

Soil types are dominated by cambisols, lessivés, gley soils and stagnosols. A comprehensive characterization of land use and soil composition of the Warnow river basin is given by Koch et al. (2013) (see chapter 3).

The Warnow River (143 km length) discharges into the Baltic Sea. The mean discharge was 16.73 $m^3 s^{-1}$ in the period from 1990 to 2010. The elevation difference from spring to the mouth is 68 m. A watergate and a dam at the Warnow River gauge station “Rostock” strongly influence the discharge measurements at this point (sub-basin Upper Warnow).

4.4.2 Data collection

The study is based on a set of daily stream flow and biweekly phosphorus concentration data of dissolved (DRP) and total phosphorus (TP) of the Warnow river basin (Mecklenburg-West Pomerania), provided by the State Office of Environment, Nature Conservation, and Geology of Mecklenburg-West Pomerania (LUNG-MV). The data set originates from 141 gauge stations within the Warnow river basin with nine sub-basins (Figure 4-1) for the period from 1990 to 2010. The onset and the temporal resolution of the concentration measurements varied depending on the gauging station and the tributary river system. The total number of samples for the study period was 3,674 and 2,948 for DRP and TP, respectively, over the entire study period.

Water levels were recorded on a daily basis by using pressure sensors. Discharge was measured by ultrasonic flow measurement devices once a month to generate daily stream flow data based on seasonal rating curves. Water sampling was performed manually once a month or biweekly by employees of the LUNG-MV. All water samples were analyzed for DRP and TP without freezing immediately after sample collection. Dissolved reactive phosphorus was determined of the filtered samples (<0.45 µm) colorimetrically with a flow injection analyzer according to DIN EN ISO (2005). Total phosphorus (TP) was determined using unfiltered samples after alkaline digestion colorimetrically (Ganimede-P-Analysator) according to DIN EN ISO (2004).

Meteorological data were provided by the German Weather Service (DWD) with daily resolution of precipitation and air temperature for seven stations within the Warnow river basin. Land use data were obtained from the Corine land cover (CLR 2006) with a resolution of 1:100,000 and grouped land use classes of agricultural areas (arable land and grassland), artificial areas (urban and sealed areas), forests (including heathland), wetlands and open water (i. e. lakes). Additional data include the number and the coordinates of sewage works (Online server, Government of Mecklenburg-West Pomerania) and the tile-drainage maps (LUNG MV, 2010).

The delineation of the watershed was achieved using the Spatial analyst extension for ESRI ArcGIS 10.3. Additional input data comprised the streaming network and a digital elevation model with a resolution of 5 × 5 m (LVermA MV, 2008). The sub-basins were delineated by the position of the measurement stations for stream flow and P concentrations.

4.4.3 Statistical analyses

As presented by Baker et al. (2004) and used for phosphorus modeling by Ulén et al. (2016), we calculated the Richard-Baker-Flashiness Index (R-B flashiness index) for each year (1990–2010) by using the following equation:

$$\text{R-B Index}=\frac{\sum_{i=1}^{n}(q_i-q_{i-1})}{\sum_{i=1}^{n} q_i} \qquad (1)$$

, where q is the discharge at a given time step. According to Baker et al. (2004) the flashiness index reflects frequency and rapidity of short term changes in stream flow in a defined period of time.

We used a simple baseflow segmentation to subdivide stream flow data into a fast and slow component presuming that the fast stream flow signal is generated by tile-drainage discharge. The baseflow component of the stream flow data was calculated according to Nathan and McMahon (1990):

$$q_{d(i)}=\alpha q_{d(i-1)}+\beta(1+\alpha)(q_{r(i)}\text{-}q) \quad (2)$$

, where q_d is the quickflow part of the stream flow which is subject to $q_d \geq 0$ for the time I in days, q_r is the total flow (baseflow + quickflow) and α and β are flow coefficients.

We used Mann-Kendall seasonal trend tests (Hirsch et al. 1982) as insensitive to the existence of seasonality with monthly medians of P concentrations. Mann-Kendall trend tests were used to test the annual P loads for temporal trends and were performed for the overall dataset.

Non-linear models were used for the characterization of relationships between stream flow and concentrations of DRP and TP. We used long-term weekly means of discharge and corresponding long-term means of DRP and TP concentrations for the study period 1990–2010. Models of the form $y = a + b / x^2$ for DRP concentrations and models of the form $y = 1 / a + bx + cx^2$ and $y = a + bx$ (simple linear model) for TP concentrations were chosen.

Annual loads of DRP and TP were calculated by a bootstrapping approach. We calculated the integral for the P concentration curves for each year. This estimation was repeated 100 times by randomly leaving two measurements out. The mean of the individual estimations per year was taken as the annual P load. We fitted simple polynomial models of the form $y = ax^2 + bx + c$ to the P-discharge-relationships. A stepwise multiple linear regression approach was employed to model annual DRP and TP loads. Parameters used for the regression analysis were annual precipitation, annual discharge, annual baseflow, annual peak flow and annual R-B flashiness index, and the number of days on which precipitation exceeded 0, 10, 15 and 20 mm, respectively.

The non-linear models of P concentrations and the linear regression models of P loads were evaluated by the coefficient of determination of measured and predicted values of P concentrations and annual P loads, respectively.

Prior linear and non-linear modeling we smoothed the hydrograph at the watershed outlet with a 10-day moving average to minimize the effects of the dam and watergate. All statistical analyses were conducted employing the statistical software package R (R Core Team 2015).

4.5 Results

4.5.1 Dynamics and trends of discharge, phosphorus concentrations and phosphorus loads

The mean stream flow of the investigated tributaries varied strongly from 0.2 $m^3 s^{-1}$ to 16.7 $m^3 s^{-1}$ depending significantly on the sub-basin area ($R^2 = 0.99$, $p<0.001$, linear regression; Table 4-1). The concentrations of DRP and TP were in the same order of magnitude across all sub-basins with a mean concentration of 70 µg l^{-1} DRP and 132 µg l^{-1} TP over the study period, respectively. Solely the Zarnow sub-basin showed articulately higher mean concentrations of DRP and TP of 132 µg l^{-1} and 184 µg l^{-1}, respectively. The concentrations of DRP and TP range between 3 and 1,458 µg l^{-1} and 13 and 2,040 µg l^{-1}, respectively

The Richards-Baker flashiness index of stream flow varied strongly across all investigated sub-basins. However, with the exception for the watershed outlet ($R^2 = 0.24$, $p<0.05$, linear regression model) we found no significant relationships between annual Richards-Baker flashiness index and the annual runoff in mm for all sub-basins.

Significant negative temporal trends for DRP were observed in seven sub-basins according to a Mann-Kendall seasonal trend test. The trend for the Beke sub-basin had a level of significance of $p<0.1$ whilst the sub-basins Nebel, Mildenitz, Brueler Bach, Upper Warnow, Middle Warnow and Lower Warnow showed trends with levels of significances of $p<0.05$. In six sub-basins (Nebel, Mildenitz, Brueler Bach, Upper Warnow, Middle Warnow and Lower Warnow) we found significant temporal trends for the entire data set (1990–2010) with levels of significances of at least $p<0.05$ for both TP and DRP.

DRP concentrations exhibited a strong seasonal pattern over the entire study period (Figure 4-2), independent from the year and the sub-basin. The highest concentrations of DRP were recorded in the summer and autumn months (weeks 25–45), whereas the concentrations in winter and spring were the lowest (weeks 46–24). The patterns of TP were ambiguous and less distinct compared to DRP with discontinuous regional peaks over time. With the exception of two sub-basins (Zarnow, Mildenitz), the differences of seasonal minima and maxima were lower for TP than for DRP.

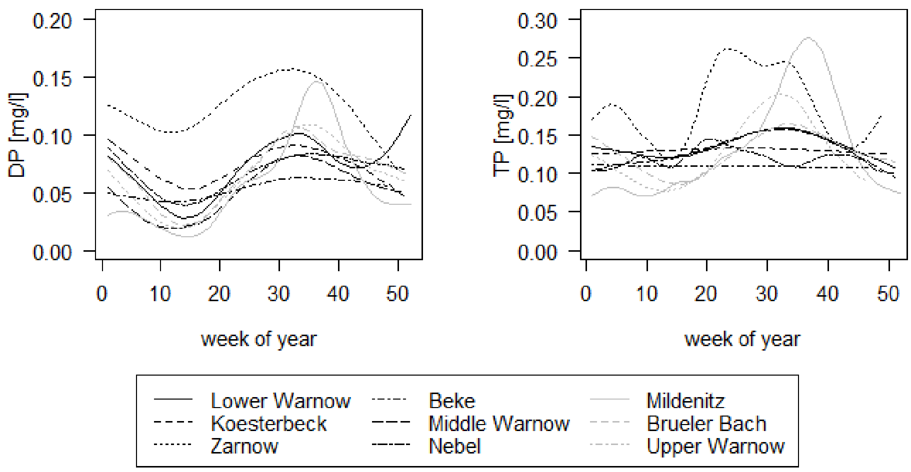

Figure 4-2: *Seasonal patterns of weekly means of P concentrations for the entire study period*

Table 4-1: *Watershed characterization including size of sub-basins, land use (agricultural and forest area fractions based on Corine Land Cover 2006 data), artificially drainage area, Mean annual discharge (Q mean), concentrations of dissolve phosphorus (DRP) and total phosphorus (TP) (mean, min, max) and mean annual discharge of the tributaries of the Warnow river system over the study period 1990–2010 (data provided by the State Office of Environment, Nature Conservation, and Geology of Mecklenburg-West Pomerania) and precipitation (data provided by German Weather Service).*

Sub-basin	Area	Agricultural Area	Forest Area	Drainage Area	Preci-pitation	Streamflow ($m^3 s^{-1}$)			DRP concentrations (µg l^{-1})			TP concentrations (µg l^{-1})			Q mean
						mean	min	max	mean	min	max	mean	min	max	
Lower Warnow	216	0.8	0.13	0.68	656	16.7	2	73.5	60	3	1,054	136	13	790	175
Koesterbeck	97	0.86	0.1	0.78	702	0.5	0	4.1	64	3	475	126	30	590	174
Zarnow	52	0.87	0.09	0.88	665	0.2	0	2	132	21	1,458	184	50	520	95
Beke	305	0.89	0.08	0.73	637	1.7	0.1	13.6	62	7	730	114	40	610	178
Middle Warnow	223	0.63	0.33	0.28	638	8.4	1.6	35	57	3	290	128	30	1,640	92
Nebel	944	0.69	0.23	0.36	628	4.6	0.2	24	64	5	570	119	20	550	65
Mildenitz	536	0.59	0.31	0.32	626	3	0.5	8.6	54	3	420	132	20	2,040	175
Brueler	308	0.66	0.25	0.34	620	1.8	0.2	7.3	69	4	409	124	20	570	187
Upper Warnow	349	0.72	0.22	0.35	619	1.7	0.4	6.8	71	2	650	126	30	0.39	158
Warnow river basin	**3,028**	**0.71**	**0.22**	**0.42**	**643**	**16.7**	**2**	**73.5**	**60**	**3**	**1,054**	**136**	**13**	**790**	**175**

We fitted a non-linear model in the form of $y = a + b / x^2$ to long term weekly means of stream flow and DRP concentrations. Although the quality of the model fits varied strongly among the nine sub-basins, the patterns were similar for all monitoring stations (Figure 4-3) with a marked decrease of DRP concentrations with increasing discharge.

The non-linear model was also taken for the TP concentration-discharge relationships. The model optimization revealed a satisfactory strength of the relationships; only for the Koesterbeck, the Zarnow and the Beke sub-basins a reciprocal quadratic ($y = 1 / a + bx + cx^2$, Koesterbeck and Zarnow) and a linear model ($y = a + bx$, Beke) gave better optimization results. These three sub-basins were those with the highest portion of artificial drainage (Table 4-1). However, we clearly saw the tendency of TP to increase at high discharge events.

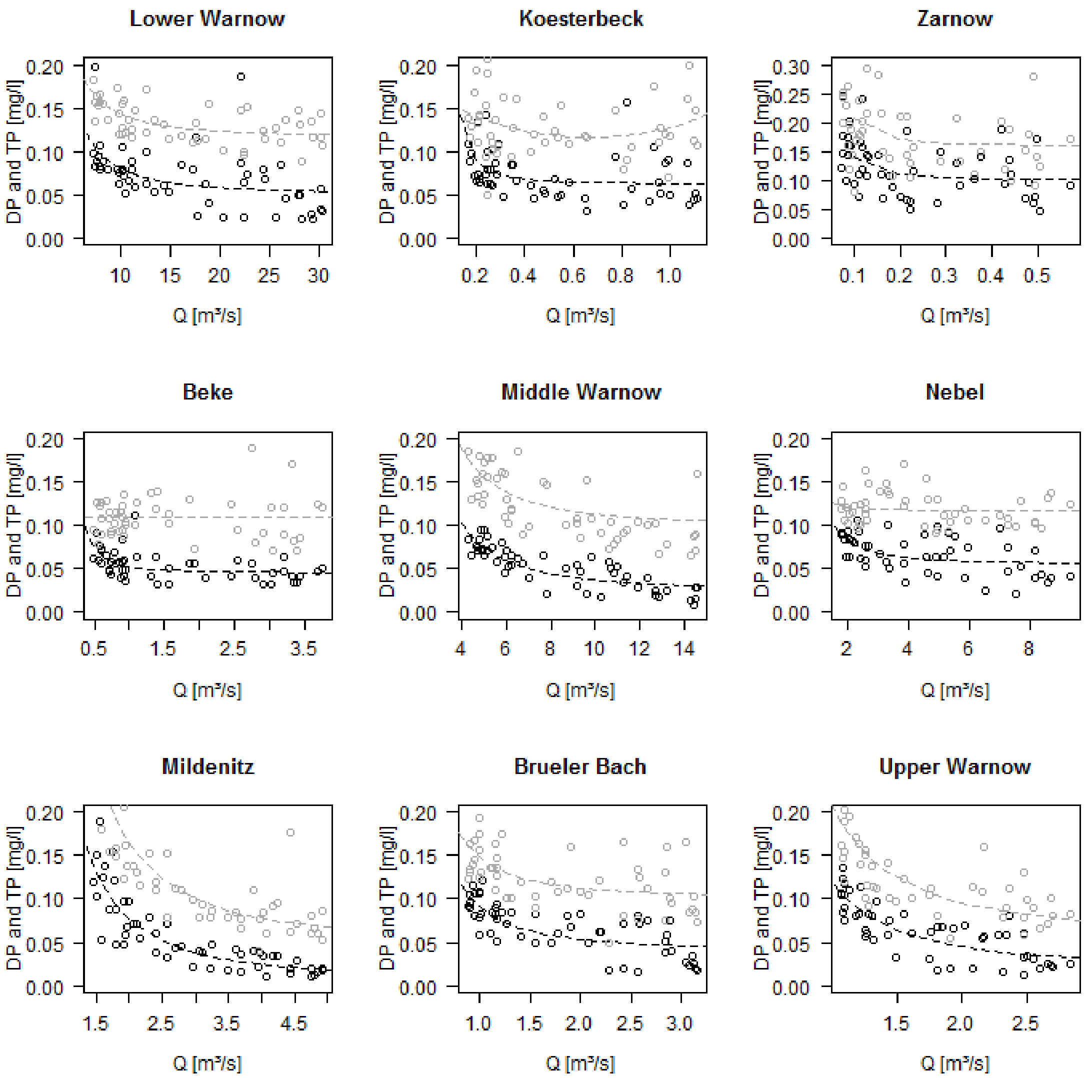

Figure 4-3: *Mean concentrations of dissolved (DRP) and total phosphorus (TP) in all sub-basins of the Warnow river basin. The dashed line displays the non-linear models of the form $y = a + b / x^2$ with the exception of the Koesterbeck (grey dashed line: $y = 1 / a + bx + cx^2$) and the Beke sub-basin (grey dashed line: $y = a + bx$). Black points and black dashed line represent dissolved P concentrations. Grey points and dashed line represent total P concentrations. Notice the differing y-axis.*

The loads of DRP and TP varied strongly across all sub-basins and resulted in mean annual loads of 30,380 kg DRP and 82,026 kg TP at the Warnow river basin outlet equaling 0.10 and 0.27 kg ha^{-1} a^{-1} DRP and TP, respectively, for the period from 1990 to 1999 (Table 4-2). The loads for the period 2000 to 2010 were 21,266 kg DRP and 51,646 kg TP corresponding to 0.07 and 0.17 kg ha^{-1} a^{-1} DRP and TP, respectively.

Table 4-2: *Mean annual loads and standard deviation (SD) in kg ha^{-1} a^{-1} of DRP and TP for the periods 1990–1999 and 2000–2010 (missing values are caused by missing discharge measurements in the Middle Warnow and Nebel sub-basins).*

Sub-basin	1990–1999 period				2000–2010 period			
	DRP	SD	TP	SD	DRP	SD	TP	SD
Lower Warnow	0.10	0.02	0.27	0.06	0.07	0.02	0.17	0.05
Koesterbeck	0.15	0.06	0.22	0.07	0.08	0.03	0.19	0.08
Zarnow	0.14	0.06	0.27	0.11	0.06	0.03	0.14	0.07
Beke	0.07	0.01	0.20	0.07	0.07	0.01	0.19	0.08
Middle Warnow	no data	no data	no data	no data	0.07	0.02	0.15	0.05
Nebel	no data	no data	no data	no data	0.04	0.01	0.12	0.05
Mildenitz	0.10	0.02	0.25	0.03	0.05	0.01	0.14	0.03
Brueler Bach	0.11	0.03	0.22	0.08	0.09	0.03	0.23	0.07
Upper Warnow	0.09	0.01	0.15	0.05	0.09	0.01	0.18	0.03

4.5.2 Modeling annual phosphorus loads

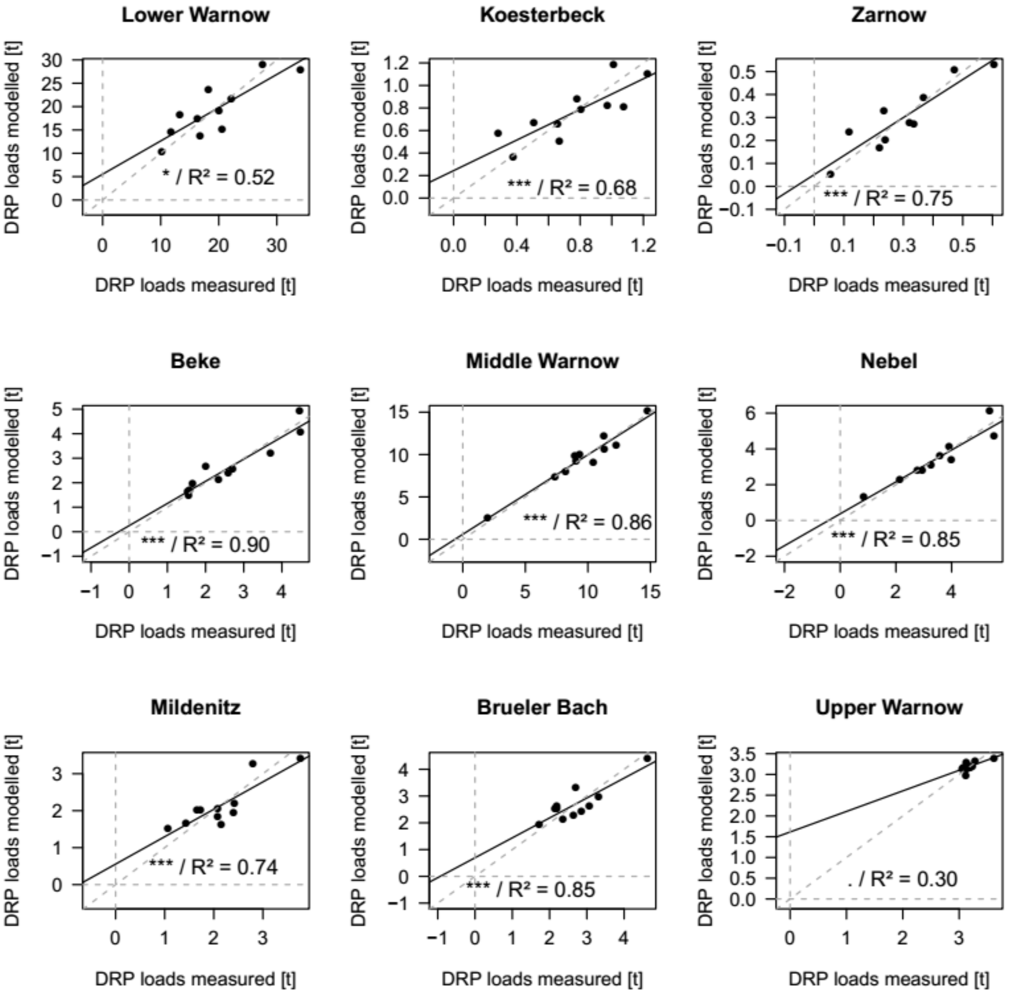

Figure 4-4: *Modelled vs. measured annual phosphorus DRP loads in all sub-basins of the Warnow River watershed. The dashed grey line shows a perfect model fit of r^2=1. Values left of the perfect model fit overestimate, while those on the right underestimate the real (measured) situation. The figure shows modeling results for the 2000-2010 data set. Notice the differing y-axis.*

The stepwise multiple linear regression of DRP (Figure 4-4) and TP (Figure 4-5) loads produced simple linear models with shifting parameters for each sub-basin (Table 4-3). Regression analysis was conducted with the overall data set from 1990 to 2010 (data not shown) and additionally with a truncated data set from 2000 to 2010.

The model quality varied clearly across sub-basins for the data set 1990-2010 for DRP. We could not find any independent driver of P loads at the river basin outlet (Lower Warnow) and the Beke sub-basin yielding statistically significant relationships between measured and modelled values (Table 4-3). Baseflow was a significant predictor in five sub-basins. However, there was at least one sub-basin (Nebel) with Richards-Baker flashiness index, Number of rainfall days in a given year as significant variables. Quickflow was the significant driving force for P export in two sub-basins (Zarnow, Nebel).

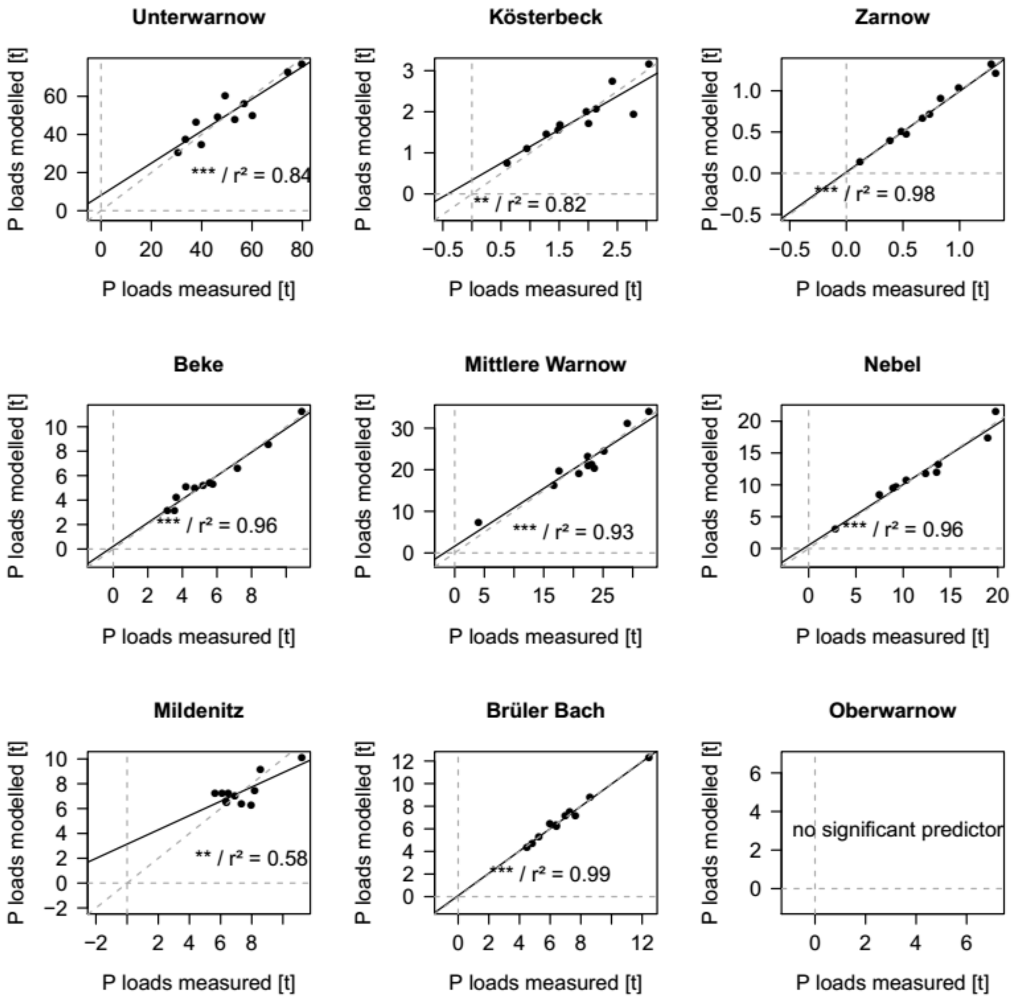

Figure 4-5: *Modelled vs. predicted annual phosphorus TP loads in all sub-basins of the Warnow river basin. The dashed grey line show a perfect model fit of r^2=1. Values left of the perfect fit model are overestimated while those on the right are underestimated. The figure shows the modeling results for the 2000-2010 data. Notice the differing y-axis.*

The linear models for the period 2000–2010 showed a distinct increase of predictive power. All sub-basins achieved a satisfactory model quality with coefficients of determination higher than 0.5 (Table 4-1). For three sub-basins (Middle Warnow, Brueler Bach, Upper Warnow) the model parameters did not change for the shortened data set. Baseflow was the single predictive variable for five sub-basins considering the truncated data-set (2000–2010). Richards-Baker flashiness index had a high predictive power for the Beke and the Mildenitz sub-basins. Quickflow and the Number of days exceeding a precipitation of 15 mm showed predictive power for at least one sub-basin (Mildenitz).

Table 4-3: *Results of the stepwise multiple linear regression models of DRP and TP loads showing sub-basins, the parameters used for the regression model and their respective level of significance for the reduced data set (2000-2010). Levels of significance are *** 0.001, ** 0.01, * 0.05, . 0.1*

sub-basin	Parameters used for multiple regression of DRP (2000-2010)	R^2	Parameters used for multiple regression of TP (2000-2010)	R^2
Lower Warnow	Baseflow (***)	0.69	Quickflow (**), RB-Index	0.84
Koesterbeck	Baseflow	0.77	Quickflow (***), RB-Index (**)	0.82
Zarnow	Quickflow (**)	0.88	Quickflow (**)	0.98
Beke	RB-Index (***)	0.81	Quickflow (***), No of days with P > 15mm (***)	0.96
Middle Warnow	Baseflow (**)	0.94	Quickflow (***), RB-Index (***)	0.93
Nebel	No significant parameters found	-	Baseflow (***)	0.96
Mildenitz	RB-Index (**), No of days with P > 15mm (.)	0.70	RB-Index (*), No of days with P > 15mm (.)	0.58
Brueler Bach	Baseflow (***)	0.76	Baseflow (***), RB-Index (.)	0.99
Upper Warnow	Baseflow (***)	0.93	No significant parameters	-

The linear models for the data set 1990–2010 tended to underestimate the annual P loads (graphs not shown). Annual P loads could be much better described if applying a multiple linear regression model to the data set 2000–2010.

The models derived for TP indicated a higher impact of the fast flow components of stream flow (Table 4-1). Quickflow was a significant predictor for four sub-basins. Likewise, Richards-Baker-flashines-index, precipitation and the Number of days with precipitation exceeding 20 mm were significant predictors in the linear models. However, baseflow was a valid predictor for four sub-basins.

The quality of the TP models increased significantly if the data set 2000–2010 was considered. The fast flow component was an important driver for five sub-basins, the baseflow, in opposite, was a significant predictor in only two sub-basins.

4.6 Discussion

4.6.1 Dynamics of discharge, phosphorus concentrations and phosphorus loads

The mean DRP and TP concentrations ranged from 60 to 132 and 114 to 184 µg l^{-1} respectively. The German Länderarbeitsgemeinschaft Wasser (1998) demand concentrations for DRP and TP of lower than 150 µg l^{-1} and 100 µg l^{-1} respectively. In total, 796 and 791 measurements of DRP and TP respectively, are higher than these target values. However, with consideration of the observed downward trends in DRP and TP concentrations, the recent concentrations of DRP and TP fulfill the requirements of a “good” quality status below the afore mentioned target values.

The observed low DRP and TP concentrations presented here are in accordance with findings from other agricultural watersheds in Europe. Kronvang et al. (2007) analyzed a large data set from European catchments and found DRP concentrations ranging from 10 µg l^{-1} to 140 µg l^{-1}. Long term observations of phosphorus concentrations in the agricultural Loire River watershed in France show slightly higher concentrations for DRP of around 150 µg l^{-1} in the 2000’s (Minaudo et al. 2015). Mellander et al. (2015) measured a mean DRP concentration of 25 µg l^{-1} in surface water from arable land in Ireland. In a Polish river, used as a source for drinking water, mean DRP concentrations of 144 µg l^{-1} were found (Dabrowska et al. 2016). The one-year mean from high-frequency measurements in an English river basin showed DRP concentrations of 178 µg l^{-1} (Bowes et al. 2015). Another study by Bowes et al. (2009) reports DRP concentrations of 140 µg l^{-1} from the 1970’s to 2000 and 88 µg l^{-1} from 2002 to 2005.

TP concentrations of numerous European catchments representing a variety of spatial scales ranged from 30 µg l^{-1} to 680 µg l^{-1} (Kronvang et al. 2007). The TP concentrations shown by Mellander et al. (2015) were on average 61 µg l^{-1} in surface water bodies of an arable watershed. Elevated TP concentrations of 206 µg l^{-1} were presented by Bowes et al. (2015) for an English watershed. Mean TP concentrations of 36 µg l^{-1} to 200 µg l^{-1} for well drained arable catchments in Ireland were measured by Jordan et al. (2012). Although there is some serious spatial variation in the DRP and TP concentrations across European rivers, the concentrations are in the same order of magnitude and reflect the effort to reduce P leaching from agricultural land and waste water alike.

Although the DRP and TP concentrations in the Warnow river basin seem to be generally low, the total loads draining into the Baltic Sea are still considerable with roughly 30,000 and 70,000 kg DRP and TP annually (0.09 and 0.22 and kg ha a^{-1}) respectively. In accordance to our results, annual loads of 0.08 to 0.23 kg ha^{-1} a^{-1} (DRP) and 0.13 to 0.62 kg ha^{-1} a^{-1} (TP) coming from an arable catchment were found in an Irish watershed (Mellander et al. 2015). Another study from Ireland estimated a range from 0.18 to 0.79 kg ha^{-1} a^{-1} of TP loads in arable watersheds (Jordan et al. 2012). The TP loads determined in Finnish catchments were twice as high and varied between 0.28 and 0.34 kg ha^{-1} a^{-1} (Ekholm et al. 2015). Data from the United States and Europe showed TP loads for arable land in a remarkable range from 0.06 to 2.90 kg ha^{-1} a^{-1} (Johnes et al. 1996). Although the comparison of P losses from different watersheds is challenging because of differences in land use, soil pedogenesis, climate and other variables, it allows an insight in the variability of P losses to surface waters in general. The investigation of different surface waters shows that the annual P loads might be substantial even with low mean riverine concentrations and may pose a threat to the receiving seas. It has to be taken into account that uncertainty remains in the estimation of annual P loads, because of the often low temporal resolution of concentration measurements and a possible under-representation of hot moments of P export.

In the Warnow river basin we found significant decreasing temporal trends for DRP and TP, although these trends become blurred with the beginning of the 21st century. In the Darß-Zingst-Bodden-Chain, a brackish bay of the Baltic Sea situated approximately 30 to 70 km east of the Warnow river basin, the loads of tributary streams decreased markedly in the 1990’s whereas until the 1980’s the inputs of anthropogenic P increased constantly (Selig et al. 2006).

Decreasing trends in TP were likewise reported from 20 Finnish watersheds and attributed to the decrease in grassland area (Ekholm et al. 2015). Downward trends of DRP concentrations were also found in the French Loire watershed and were assigned to improved P control in sewage treatment works (Minaudo et al. 2015). Long-term data from various catchments draining into the Baltic Sea showed that even with severe changes in land use, atmospheric deposition and waste water treatment, the loads of phosphorus remained almost constant from the 1980's to the mid 1990's (Stålnacke et al. 1998). Hence, the reasons for upward or downward temporal trends strongly depend on catchment properties and anthropogenic activities.

The reasons for the widely observed negative temporal trends of DRP and TP loadings are various. The P-inputs per capita in the crop production sector constantly decreased since 1980 in the EU-27 countries which might be explanatory for decreasing TP and DRP trends in agricultural watersheds in Europe in general (van Dijk et al. 2016).

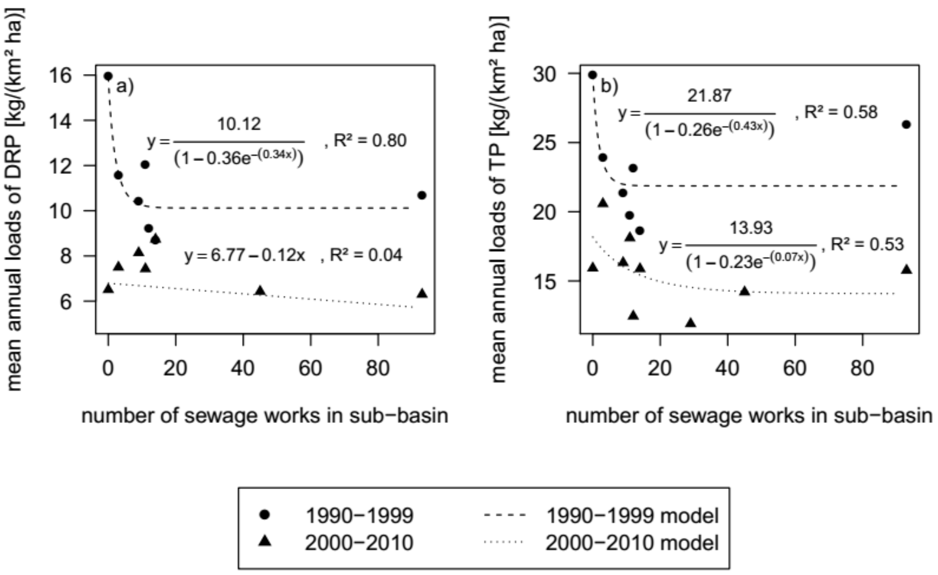

Figure 4-6: *Relationship of mean annual loads of a) DRP and b) TP to the total number of sewage works in the according sub-basins.*

Our data reveal that the number and quality of sewage plants may be the reason for reduced stream flow DRP and TP concentrations which is confirmed by the literature (Bowes et al. 2009). In Germany, roughly 95% of all inhabitants are connected to a state-of-the-art waste water treatment (Ott and Rechberger 2012). This, in particular, explains the downward trend in P concentrations of receiving waters. We found a marked relationship between DRP (1990–1999) as well as DRP and TP (2000–2010) and the number of sewage works (Figure 4-6). In the years 2012 and 2013 the portion of TP originating from sewage works was 26% and 18%, respectively, which equals a TP load of approximately 9,000 kg a^{-1}. Thus, 74% and 82% of the TP load that were released to the Baltic Sea originated from diffuse sources.

Phosphorus in stream flow may originate from: (1) Bank erosion and suspended sediment. The net P input from bank erosion equaled 17% to 29% in a Danish watershed (Kronvang et al. 2015). This observation fits quite well to our unexplained diffuse source P; we assume that TP leaching from surface runoff and overland flow is negligible in lowland watersheds. (2) Leaching of P-laden sediment originating from internal soil erosion through tile drains. Losses of TP through tile lines have been studied earlier and can predominantly be attributed to preferential flow processes (Outram et al. 2014).

Low concentrations of TP can also be attributed to lakes which may operate as sedimentation traps (Arnheimer & Liden 2000). In the Warnow river basin, only the Nebel River traverses a lake (Lake Krakow) and has slightly lower TP concentrations compared to other sub-basins which might support the hypothesis. Missing information on in- and outflow P concentrations for Lake Krakow hinders a more in-depth analysis.

The relationship of discharge to DRP and TP concentrations—with high concentrations of DRP and TP at low discharge and low DRP and TP concentrations at high discharge, with TP tending to increase at peak discharge in some sub-basins—confirms earlier findings. A relationship between DRP and river discharge was found from high resolution measurements in Britain with maximum of not flow-related DRP release in summer months and clearly flow-related DRP export in winter and spring (Bowes et al. 2015). An analogical relationship was also found for a French catchment (Thomas et al. 2016). Discharge-phosphorus relationships may show a variety of functions in different catchments and different landscapes settings (Kronvang et al. 2007). DRP concentrations are seemingly diluted at high rates of discharge. Increasing TP concentrations at high flow rates in the Thames watershed in Great Britain were presented by Bowes et al. (2014). The authors attribute their findings to a rainfall related source of phosphorus and to a remobilization of within-channel P. We assume that high concentrations of TP at low flow rates are related to sewage treatment works, whereas high TP concentrations at discharge events may be connected to bank erosion. However, the event based DRP and TP losses could not be analyzed in more detail in this study because of the coarse, bi- or even four-weekly sampling schemes.

4.6.2 Modeling annual stream flow phosphorus loads

Modeling of P losses into rivers requires detailed knowledge of watershed characteristics and underlying processes. The multitude of biogeochemical processes regarding P loss often impedes precise and satisfactory modeling (Collick et al. 2015). However, simple statistical models may reveal insight to major transport pathways on the basin scale.

The model result for the outlet of the entire basin, might be impaired by effects as caused by a dam and a watergate that segregates the freshwater section of the Warnow river from its brackish course (inflow from the Baltic Sea). The derived P models are probably affected although the hydrograph was smoothened by a 10-day moving average. The employed statistical models for the depiction of annual DRP and TP loads reflect the characteristics of the investigated sub-basins with satisfactory accuracy (Table 4-3). After a comprehensive analysis of morphology, land use, fraction of artificially drained areas, a direct linkage of the processes as identified through the statistical models to watershed properties could not be established (Table 4-4). In sub-basins with a large fraction of artificial drainage, baseflow was identified as the main driver of DRP. Solute dilution occurs at high flow rates. For the Nebel sub-basin where the baseflow was found a predictive variable also for TP, we assume that the retention potential of Lake Krakow has smoothened peak flow TP concentrations.

The flashiness is strongly correlated with increasing frequency and magnitude of storm events (Baker et al. 2004). On a smaller spatial scale (<1 km^2), the RB flashiness index was used to predict P leaching from different fields of former swine farms in Sweden (Ulén et al. 2016). We assume that the flashiness is primarily an expression for increased runoff from tile drains and soil surface following rainfall events. Thus, hillslopes and artificially drained areas near the watershed outlet may stimulate this relationship, if the P retention potential of the river is low. However, there might be additional processes that play an important role in P leaching independent from morphological or land use aspects. An important process in loamy and clay soils is preferential flow and internal erosion through the soil profile to tile drains as observed previously; its contribution to losses of TP might be substantial (Makris et al. 2006; Williams et al. 2016).

Table 4-4: *Significant predictors for DRP loads and corresponding watershed characteristics for the 2000-2010 data set for all sub-basins.*

Sub-basin	Predictor variable DRP	Predictor variable TP	Watershed characteristics
Lower Warnow	Baseflow (***)	Quickflow (**), RB-Index	sum of all sub-basins
Koesterbeck	Baseflow	Quickflow (***), RB-Index (**)	large portion of drained areas stream near hillslopes near outlet
Zarnow	Quickflow (**)	Quickflow (**)	flat and homogenous morphology baseflow exceeds quickflow
Beke	RB-Index (***)	Quickflow (***), No of days with P > 15mm (***)	flat and homogenous morphology large proportion of drained areas
Middle Warnow	Baseflow (**)	Quickflow (***), RB-Index (***)	sum of sub-basins Brueler Bach, Mildenitz and Upper Warnow most tumular morphology across all sub-basins
Nebel	No significant parameters found	Baseflow (***)	large portion of drained areas tumular morphology
Mildenitz	RB-Index (**), No of days with P > 15mm (.)	RB-Index (*), No of days with P > 15mm (.)	stream near hillslopes large portion of drained areas near stream outlet
Brueler Bach	Baseflow (***)	Baseflow (***), RB-Index (.)	stream near hillslopes large portion of drained areas near stream outlet
Upper Warnow	Baseflow (***)	No significant parameters	stream near hillslopes near outlet large portion of drained areas near spring

However, the statistical regression models showed that DRP concentration follow a baseflow component in almost all sub-basins of the Warnow river basin whereas TP concentration are strongly impaired by an event-based quickflow component.

4.7 Conclusion

The analysis of a 21-year dataset of phosphorus concentrations and discharge from a mid-size river basin including its sub-basins revealed that the surface water quality has in general improved over the last decades, which can most likely be attributed to newly installed sewage plants. The annual phosphorus loads of around 30 tons per year at the watershed outlet put the ecological services of the receiving Baltic Sea, however, still at risk and a phosphorus pathway related management is suggested.

Simple linear regression analyses revealed with an amazing consistency that the groundwater contribution to stream flow highly impacts the dissolved phosphorus fraction in brooks and rivers. The concentration of total phosphorus, which includes the particulate fraction, strongly depends on the fast flow component although differences between sub-basins exist. In lowland catchments with reduced surface runoff, quickflow originates basically from the widespread artificial drainage systems. It is concluded that mobile soil particles that are transported by preferential flow to the tile-drainage system may play a major role in the overall phosphorus loading of surface water bodies. Additionally, within drainage pipes and channel mobilization of sediment is a substantial diffuse source of P. Further studies should investigate the role of internal and bank erosion processes and their relation to rainfall/runoff intensity. Sampling strategies with a high temporal resolution (hourly or even at the minute) are required to fully unveil the flow rate dependent relation between dissolved and particulate phosphorus.

Acknowledgements

We kindly acknowledge the work of the State Office of Environment, Nature Conservation, and Geology Mecklenburg-West Pomerania, in particular Dr. Alexander Bachor for the considerable amount of data that was committed. The authors gratefully acknowledge the German Federal Ministry of Education and Research (BMBF) for funding both the BonaRes project InnoSoilPhos (No. 031A558) and the ReWaM project PhosWaM (No. 033W042B).

5 Spatio-temporal variability of phosphorus (losses) in a small agricultural watershed on three different Scales

Abstract

We analyzed a one-year data set of concentrations of dissolved reactive phosphorus (DRP) and total phosphorus (TP) for spatial and temporal patterns on three spatial scales: a tile drainage field (4.2 ha), a drainage ditch (drainage area 179 ha), and a brook (drainage area 1,550 ha).

The mean DRP concentrations were 0.017, 0.019, and 0.015 mg l^{-1} for the tile-drain, the drainage ditch, and the brook respectively. The mean TP concentrations were 0.045, 0.056, and 0.057 mg l^{-1} in the corresponding spatial scales. The increase in TP concentration with increasing drainage area suggests the constant inflow of sediment-rich drainage water.

The contribution of the loads of DRP and TP to the tile drain, the drainage ditch, and the brook was 48%, 77%, and 15%, and 50%, 68%, and 49% respectively. The loads of TP per hectare decreased with increasing drainage area (98.88, 79.81, and 24.39 g for tile drain, drainage ditch, and the brook respectively). This supports the idea of rapid sedimentation even during runoff events due to the low hydraulic energy in the drainage ditch and the brook.

The double lactate-extractable soil P content in the topsoil and subsoil showed similar spatial patterns with a theoretical range of 220 m and 150 m. We could not address the origin of the observed spatial patterns but literature indicates a strong relationship with the content of iron and aluminum hydroxides in the soil.

Our study indicates that more research is needed to understand the interaction of P pools in the landscape, and the adsorption-desorption behavior of streambank sediments in response to hydraulic events.

Keywords: *spatial scale, dissolved reactive phosphorus, total phosphorus, variogram, patterns*

5.1 Introduction

Phosphorus (P) is an essential nutrient for crop production. Nonetheless, the runoff of P to rivers and streams, and the potential of eutrophication of surface waters also give rise to environmental concerns. The mitigation of surface water pollution is, therefore, one of most challenging issues in future agricultural P management (Kleinman et al. 2015).

A reduction of point source inputs to surface waters is quantifiable in recent years (Gelbrecht et al. 2005). However, diffuse sources of P are still threatening surface waters (Gelbrecht et al. 2005, Heathwaite et al. 2005).

A common agricultural practice in Germany is artificial drainage. The drainage of loamy soils—with a high water-holding capacity—reduces the residence time of water in the soil. Furthermore, it improves aeration conditions and promotes agricultural production (Skaggs et al. 1999, Tiemeyer et al. 2010). However, it has been frequently reported that its contribution to surface water pollution may be severe (Gentry et al. 2007, King et al. 2015a, Christianson et al. 2016). Although it has been thought for a long time that surface runoff might be one of the major pathways of P release into rivers, recent studies reveal a significant contribution of tile drains to riverine P loads (Tiemeyer et al. 2009, Nash et al. 2015, Bhadha et al. 2016). Even more, a single storm can severely release preferentially transported particulate P from tile drainage (King et al. 2015b, Zimmer et al. 2016, Williams et al. 2016). Particularly, following manure and fertilizer application, these outputs can be fatal (Geohring et al. 2001).

P management is not only crucial for the mitigation of eutrophication but also for productivity and agricultural yield (Balemi & Negisho 2012). The question arises as to how P is distributed in agricultural landscapes and the landscapes shaped by human activities. The spatial variability of the soil P content may be large and has been subject to several studies (Corazza et al. 2003, Page et al. 2005, Roger et al. 2014). A better understanding in soil P distribution may help in the development of the best management practices for future agriculture (Roger et al. 2014). Studies on the relevance of colloid-bound P (Makris et al. 2006, Gottselig et al. 2014) reveal the idea of the soil P spatial variability being associated to the distribution of fine soil material (Wang et al. 2009). The variability of soil P may be large and dependent on the addressed spatial scale. Grunwald et al. (2006) and Leopold et al. (2006) found changes in variability over several kilometers whereas smaller ranges of spatial variability of several meters have been observed too (Heilmann et al. 2005, Vaughan et al. 2007). These observed differences in spatial patterns can be attributed to differences in other soil chemical properties, different land uses and, of course, different experimental approaches.

This problem of soil P and spatial variability explain the problem of different spatial scales in environmental sciences. The role of scale-dependent processes has been illustrated for agricultural ecosystems (Sharpley et al. 2002).

We measured discharge and concentrations of dissolved reactive P (DRP) and total P (TP) on three spatial scales: a tile drainage field (4.2 ha), a drainage ditch (179 ha), and a brook (1,550 ha). We assessed the spatial variability of double lactate-extractable (DL-extractable) P content on the drainage ditch scale. The aim was to determine temporal (event-based) and spatial patterns of P losses to surface waters from an agricultural watershed in north-eastern Germany.

5.2 Material and methods

5.2.1 Study site

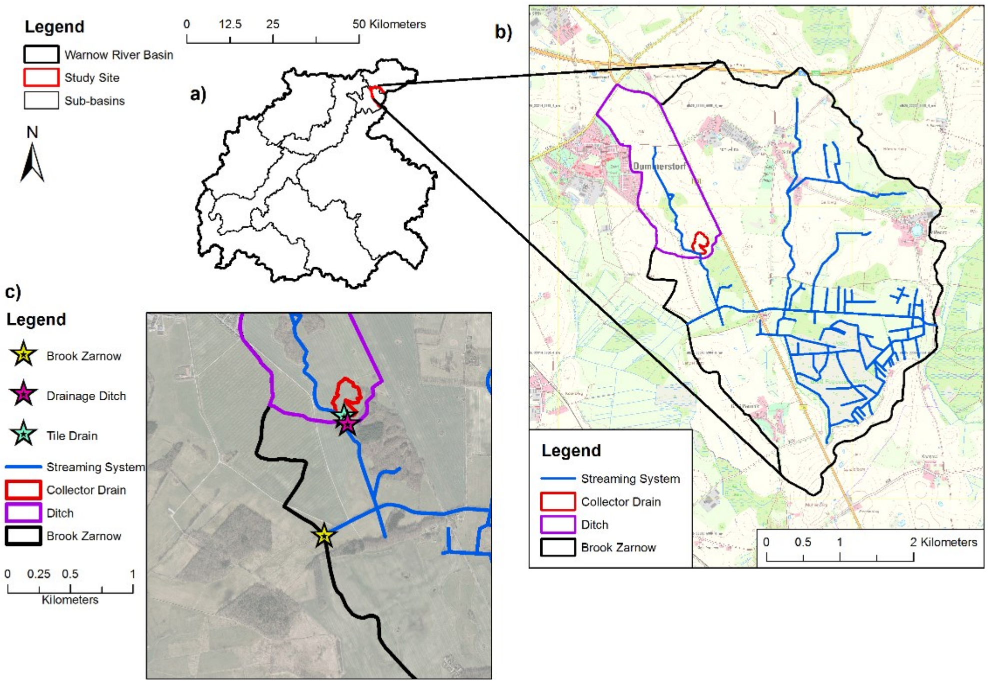

Figure 5-1: *Study Site of the Zarnow brook (b and c) within the boundaries of the Warnow river basin (a).*

The study site is an agriculturally used lowland catchment in north-eastern Germany in the federal state of Mecklenburg-West Pomerania, situated about 15 km southeast of the city of Rostock at the Dummerstorf monitoring site of the Chair of Soil Physics of the University of Rostock.

The investigated watershed is part of the Zarnow sub-basin of the Warnow river basin (Figure 5-1, compare Figure 3-1, chapter 5). In 2003, a monitoring program was introduced to observe long-term developments of discharge, and nitrate, chloride, and sulfate losses along with several cations. In the past, attempts have been made to extend the monitoring system, and implement measurements of P losses from arable land. P concentrations at all considered spatial scales were ended after the runoff season 2005/2006. The monitoring of DRP and TP was re-established in the runoff season 2015/2016.

The major soil types in the study watershed are loamy cambisols, gleysols, and drained peatlands. The climate is characterized by warm summers and mild winters. The mean annual precipitation is 636 mm and the mean average temperature is 10.4°C (reference period 1990–2010). The major land use is agriculture. The forms of agriculture are extensive arable farming and grassland on drained peatland.

We conducted all the measurements on three spatial scales: a tile drain (4.2 ha drainage area), a drainage ditch (179 ha drainage area), and the brook Zarnow (1,550 ha). In all, 19 collector drains are emptied into the ditch. Tile drains are about 1.1-m deep, and the distance between individual drainage pipes varies between 8 and 22 meters. A detailed description of the three sites is given by Bauwe et al. (2015). The crop rotation and fertilization rates are presented in Table 5-1. The P application rates reflect a conservation fertilization.

Table 5-1: *Crop rotation and N and P fertilization rates for the study period and the contributing acres.*

Acre #	area (ha)	crop 2015	Previous crop	N fertilization (kg/ha)	P-fertilization (kg/ha)
5.1	55	Winter oilseed rape	Winter barley	26 (2015) 185 (2016)	13 (2015) 13 (2016)
5.2	26	Winter oilseed rape	Winter barley	26 (2015) 185 (2016)	13 (2015) 13 (2016)
6.1	55	Winter wheat	Winter oilseed rape	156 (2015) 223 (2016)	13 (2015) 13 (2016)
7.1	12	Alfalfa	Winter wheat	211 (2015) 33 (2016)	35 (2016)
7.2	22	Alfalfa	Winter wheat	211 (2015) 30 (2016)	35 (2016)
7.3	13	Alfalfa	Winter wheat	211 (2015) 31 (2016)	35 (2016)
8.2	39	Winter wheat	Maize	130 (2015) 223 (2016)	13 (2016)
8.3	8	Maize	Winter wheat	144 (2015)	26 (2015)
8.4	55	Winter wheat	Winter oilseed rape	156 (2015) 210 (2016)	13 (2016)

5.2.2 Data collection

The discharge and concentrations of DRP and TP were measured on the three considered spatial scales. Samples were taken during the runoff period of the hydrological year 2015/2016 from November 2015 to April 2016.

Water samples at all the scales were taken automatically (Teledyne Isco, Inc., Lincoln, NE) every six hours and mixed to a daily sample. Two to four samples per week were then randomly chosen to be analyzed in the lab every Thursday. The DRP samples were filtered with pre-combusted (6h, 450°C) 0.7 µm membrane-filter and stored in the fridge at -25°C, together with the non-filtered samples of TP until further processing. The samples were colorimetrically analyzed with a photometer (Specord40, Analytic Jena). The DRP and TP samples were dyed using ammonium heptamolybdate. Prior-dyeing TP samples were decomposed by microwave exposure.

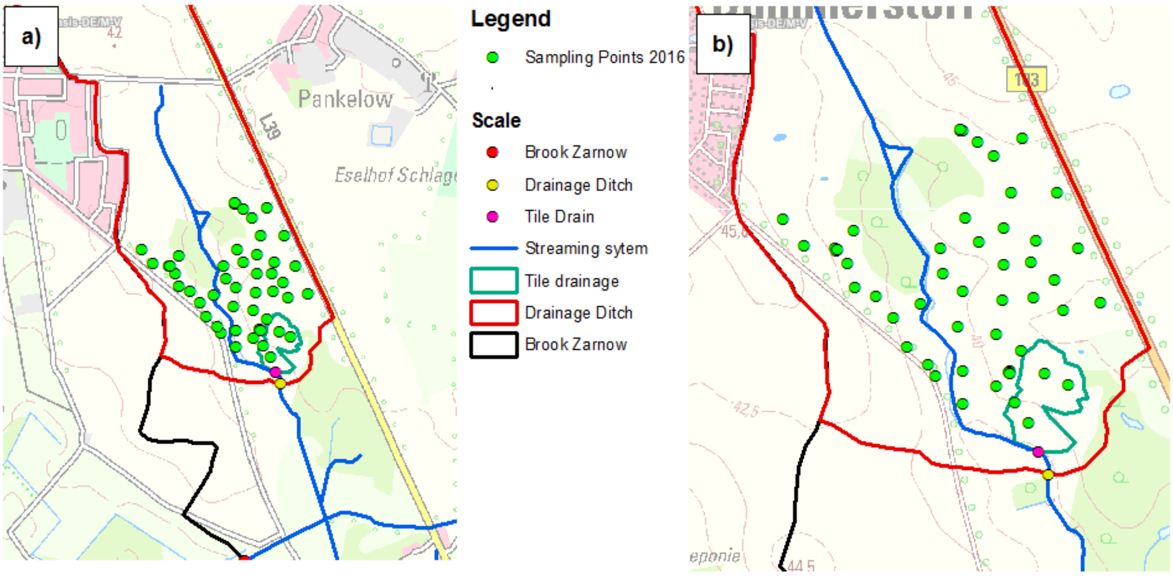

Figure 5-2: *Sampling points for the measurements of DL-extractable soil P content.*

Precipitation was recorded directly at the field site (Seba Hydrometrie GmbH, Kaufbeuren, Germany). The discharge of the tile drain was measured with a Venturi-Flume (Eijkelkamp Agrisearch Equipment, Giesbeek, Netherlands). The drainage ditch measurement station is equipped with an ultrasonic water-level measurement device (Teledyne ISCO, Inc., Lincoln, NE). Discharge was measured using an inductive flowmeter (Flo-MateTM, Marsh-McBirney, Inc. Frederick, MD) to set-up the rating curves for the ditch and brook stations. A detailed description of the measurement techniques and the equipment of the sampling stations have been given by (Bauwe et al. 2015).

Furthermore, we collected soil samples from a random grid (Figure 5-2), and plant-available P was determined by DL extraction (Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten e.V. 1991) from mixed samples in November 2016. At each of the 50 sampling points (Figure 5-2), three core samples were taken in 0–30-cm and 30–60-cm depths and mashed into one sample.

5.2.3 Statistical analyses

We analyzed the hydrograph of the three spatial scales—the tile drain, drainage ditch, and the brook—and located four remarkable peak flow events. Furthermore, we added the initial flow event to the list of events we analyzed. Although the overall runoff in the initial flow event was low, we expected a remarkable release of TP through this first event. The events were determined manually by selecting four peaks from the hydrograph. The beginning and the end of the events were defined as changes in the direction of the slope of the hydrograph.

Non-linear and linear models were used to test for relationships of DRP and TP to discharge.

The P loads were estimated using discharge-concentration relationships for both the events and the whole runoff period. The runoff period was subdivided into two periods (November–February, and March–April). These models were used to calculate daily loads of DRP and TP. The seasonal and event-based total loads were calculated as the sum of the daily loads.

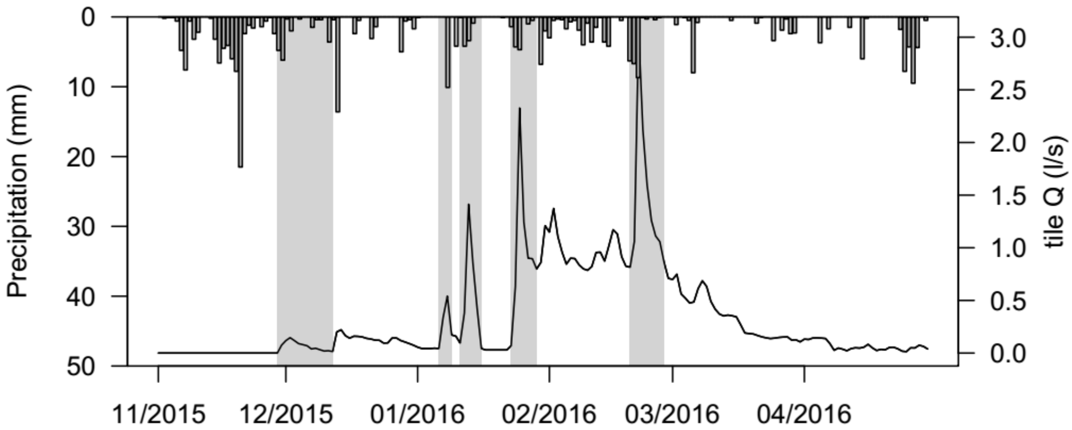

Figure 5-3: *Hydrograph of the 2015/2016 runoff season and the five analyzed events and daily precipitation for the tile drainage field.*

Certainly, the consideration of only one runoff period does not guarantee representative results, in particular, in watersheds with a marked variability in annual precipitation. However, since the measurements of P have just started at the Dummerstorf field site, the results may gain a first insight into the temporal variability of P losses from agricultural land in lowland catchments and to the effects of different spatial scales.

The spatial variability of DL-extractable soil P content was assessed using geo-statistical methods. Empirical semi-variograms were calculated based on the soil P content from DL extraction. The equations used for the empirical semi-variograms and the theoretical (spherical) semi-variogram models can be reconstructed from chapter 6.

5.3 Results

5.3.1 General results and temporal patterns of phosphorus concentrations

Table 5-2: *Mean, minimum, and maximum concentrations of DRP and TP, and mean, minimum, and maximum discharge at all three spatial scales.*

Scale	DRP (mg l^{-1})			TP (mg l^{-1})			Q (l s^{-1})		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Tile Drain	0.017	0.005	0.145	0.045	0.010	0.307	0.339	0.000	3.070
Drainage Ditch	0.019	0.000	0.176	0.056	0.021	0.297	9.987	0.240	22.63
Brook Zarnow	0.015	0.003	0.113	0.057	0.004	0.272	43.18	3.3	297.3

The mean DRP concentrations were 0.017, 0.019, and 0.15 mg l^{-1} for the three spatial scales of tile drain, drainage ditch, and the brook respectively (Table 5-2). The minimum and maximum concentrations can likewise be extracted from the table. The coefficients of variation for DRP, TP, and discharge for the three spatial scales of tile drain, drainage ditch, and the brook were 1.25, 1.16, and 1.41, 1.49, 0.88, and 2.32, and 1.05, 0.69, and 0.88 respectively.

The overall population of the DRP concentrations at the three spatial scales did not differ significantly from each other according to a Mann-Whitney-U-Test ($p>0.1$). Otherwise, the TP concentrations of the drainage ditch and the brook differed significantly ($p<0.1$), and so was the case for the tile drain and the brook ($p<0.001$), and the drainage ditch and the tile drain ($p<0.05$). The TP concentrations were consistently significantly higher than the DRP concentrations ($p<0.001$). Although the mean concentrations of TP increased with increasing spatial scale, the highest maximum TP concentration was recorded in the fourth event in the tile drain.

It can be seen from the hydrographs (Figure 5-4) that the concentrations of DRP and TP followed peak flow events, which means that the P concentrations were most likely low during low discharge and higher at higher discharge. Furthermore, it can be extracted from the hydrographs that the drainage ditch and the brook started carrying water earlier compared to the tile drain, which started delivering discharge to the drainage ditch with the beginning of the first considered event.

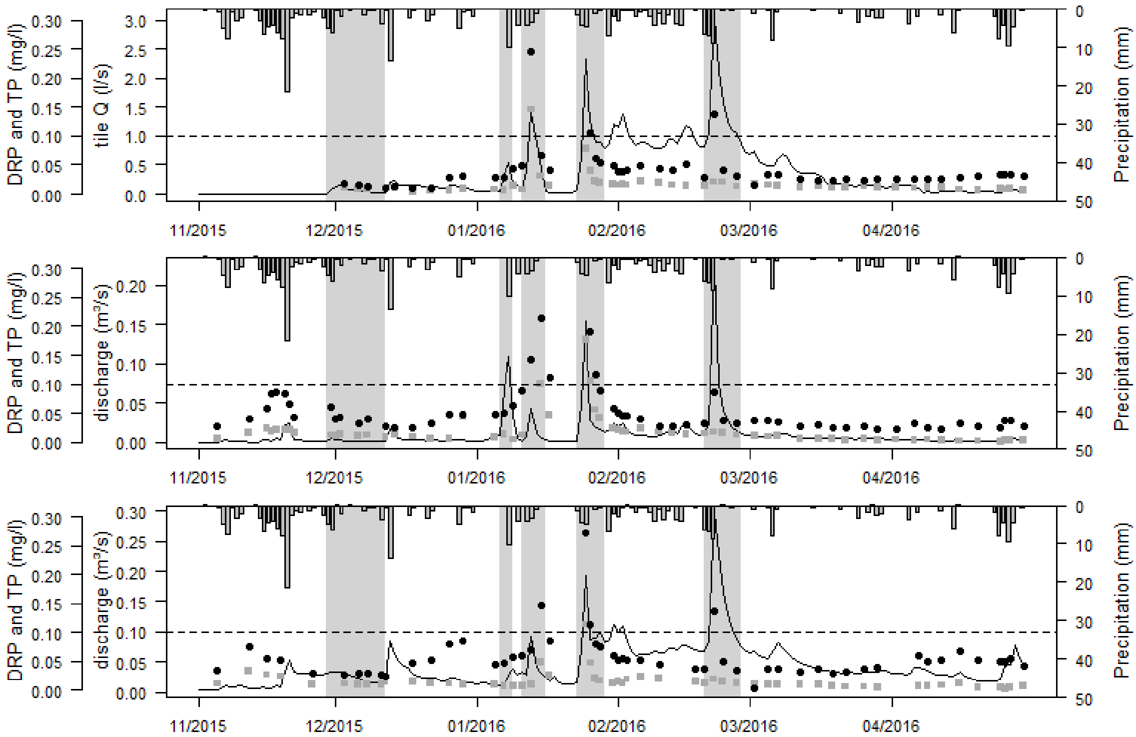

Figure 5-4: *Hydrographs of all spatial scales and DRP and TP concentrations, and the five considered events. Black dots: TP concentrations; grey dots: DRP concentrations. Upper row: tile drain; middle row: drainage ditch; lower row: Brook Zarnow. The dashed line represents the intended target value according to the LAWA (Länderarbeitsgemeinschaft Wasser 1998)*

The DRP and TP concentrations as a non-linear function of discharge showed marked increases of DRP and TP concentrations with increasing runoff (Figure 5-5). The model fits, in terms of the coefficient of determination, were slightly better for the TP concentrations than for the DRP concentrations ($R^2 = 0.22$, 0.17, and 0.17 for DRP at drain, ditch, and brook respectively, and 0.22, 0.51, and 0.34 for TP at drain, ditch, and brook respectively). The highest concentrations of DRP and TP were measured in January and February. Although the runoff was highest in the February event, the concentrations of DRP and TP were lower than in the two earlier events.

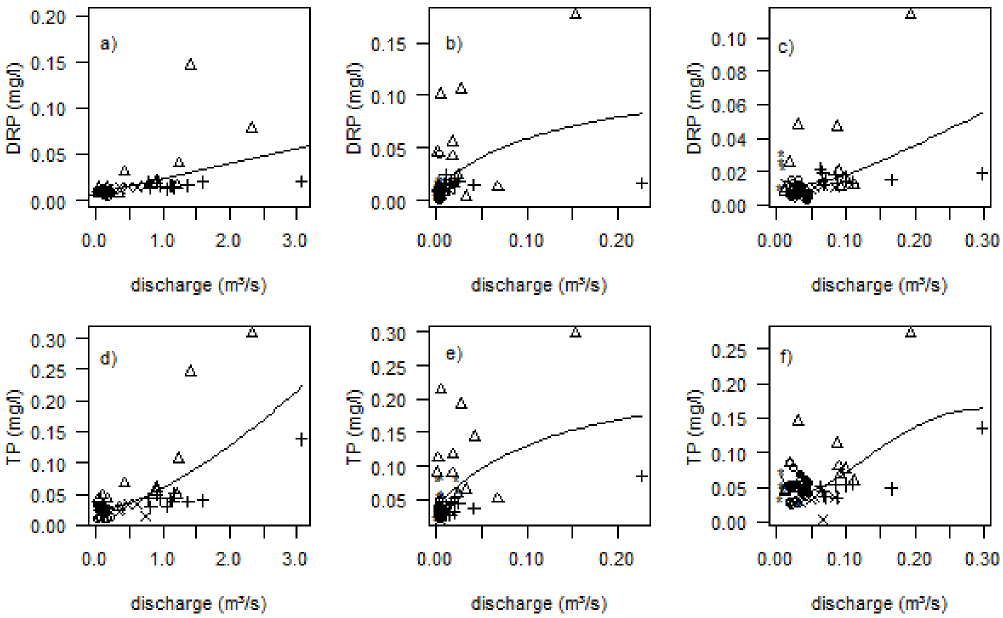

Figure 5-5: *The variety of non-linear models of discharge and P concentrations. a), b), and c) show DRP concentrations for drain, ditch, and brook respectively; d), e), and f) show TP concentrations for drain, ditch, and brook respectively. * – November, ○ – December, Δ – January, + – February, ×– March*

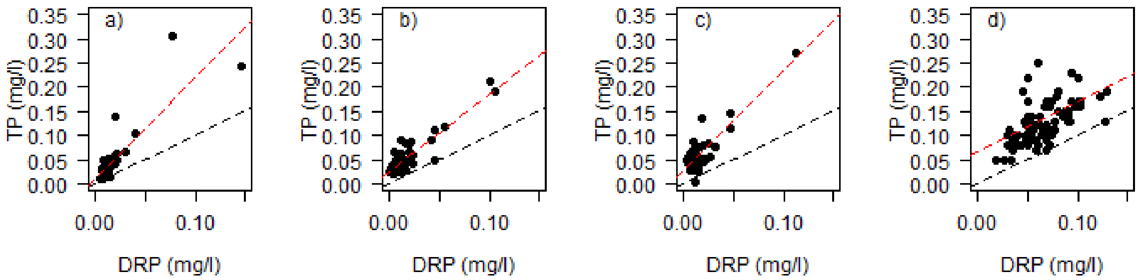

Figure 5-6: *Relationships of DRP and TP in a) tile drain, b) drainage ditch, c) brook, and d) the whole Zarnow River sub-basin. The black dashed line represents the perfect model fit. The red dashed line represents the particular linear models of DRP and TP.*

Moving up the spatial scales from the tile drain to the drainage ditch to the brook to the whole sub-basin of the Warnow river basin, we observed a downward shift of the ratios of TP and DRP. The slope of the linear model of TP in relationship to the DRP decreased from the tile drain to the drainage ditch, and then increased again to the Brook Zarnow. This result is substantiated by the relationship of TP and DRP loads during the considered discharge events. The ratios of mean TP to mean DRP are 3.04, 2.34, and 3.49 for tile drainage, drainage ditch, and the Brook Zarnow respectively.

The estimation of the DRP and TP loads for all five considered events showed a large contribution of these to the overall DRP and TP loads for the whole runoff season (Table 5-3). During the five events, 25% of the season's precipitation was recorded. The contribution of the loads of DRP and TP to the smaller spatial scale of the tile drain and drainage ditch was 48% and 50%, and 77% and 68% respectively. At the Brook Zarnow, the overall contribution of the events to the total loads of DRP and TP decreased to 15% and 49% respectively. Interestingly, the loads per hectare decreased with increasing spatial scale.

Table 5-3: *Precipitation, DRP loads and TP loads of all investigated events and their contribution to the whole season outputs.*

		Tile Drain		Drainage Ditch		Brook Zarnow	
Event	PCP (mm)	DRP Load (g)	TP Load (g)	DRP Load (g)	TP Load (g)	DRP Load (g)	TP Load (g)
1	19.82	0.83	1.22	28.66	103.58	449.77	1463.22
2	10.08	0.39	3.30	260.54	888.09	84.61	426.71
3	8.64	22.47	41.42	48.11	723.93	253.12	873.65
4	12.05	24.96	86.98	3213.64	5621.43	2796.22	7604.86
5	22.74	19.36	74.35	601.24	2402.28	1662.94	7982.52
all events	73.33	68.00	207.28	4152.19	9739.30	5246.67	18350.96
whole season	289.71	140.76	415.29	5387.87	14286.27	35347.68	37819.86
all events (g ha^{-1})		16.19	49.35	23.19	54.41	3.38	11.83
whole season (g ha^{-1})		33.51	98.88	30.10	79.81	22.80	24.39
proportion	0.25	0.48	0.50	0.77	0.68	0.15	0.49

The loads of TP at the tile drainage and the drainage ditch scale were almost three times higher than the DRP loads in the according scales. At the brook scale, the loads of DRP and TP do not differ markedly. The highest loads of DRP and TP have been estimated for the fourth event for all spatial scales, and the lowest loads were recorded for the first initial and second events.

5.3.2 Spatial Variability of double lactate-extractable soil phosphorus and organic matter content

The mean (± standard deviation), maximum and minimum organic matter contents of the topsoil were 1.41%, 2.37%, and 0.92% respectively. The DL-extractable soil P differs significantly between the topsoil and the subsoil (Mann-Whitney-U-Test, $p<0.001$, $n=50$). The mean (± standard deviation), maximum, and minimum DL-extractable P contents of the topsoil were 8.76(±5.09), 32.70, and 4.70 mg P/100 g soil respectively. The corresponding DL-extractable P contents for the subsoil were 6.42(±3.28), 20.70, and 2.7 mg P/100 g soil respectively. The highest DL-extractable P contents of the topsoil and the subsoil were measured south-east of the drainage ditch (see Figure 5-2).

In all, 35 samples are within the boundaries of class C according to the VD-LUFA classification system (Kerschberger et al. 1997). These P-content classes represent the status of fertilizer requirements of the soil (Table 5-4). Class C represents the target value. Thus, classes A and B imply a fertilizer demand and classes D and E express a surplus of soil P. Eleven and four samples are within the boundaries of VD-LUFA classes D and E respectively.

The DL-extractable P content is directly and significantly correlated to that from the subsoil ($R^2 = 0.63$, $p<0.001$, linear model). The DL-extractable P content of the topsoil is likewise significantly correlated to the organic matter content of the topsoil, though this correlation is slightly weaker ($R^2 = 0.22$, $p<0.001$, linear model).

Table 5-4: *Plant available P content classes according to the VD-LUFA (Kerschberger et al. 1997).*

P content class	Double lactate extractable P (mg/100mg soil)	Number of samples in this boundaries
A	≤ 2.0	0
B	2.1 – 4.4	0
C	4.5 – 9.0	35
D	9.1 – 15.0	11
E	≥ 15.1	4

The spatial analysis of the DL-extractable soil P revealed a high spatial variability on the small spatial scale (maximum distance about 800 meters).

The theoretical semi-variogram model showed a zero-nugget DL-extractable P for topsoil and subsoil, and likewise for the soil organic matter (Figure 5-7). The asymptotic range for DL-extractable P content in the topsoil and subsoil, and organic matter content in the topsoil were 220, 150, and 255 m, respectively. The respective sills were 22.3, 8.8, and 0.1. The models were calculated for the omni-directional semi-variogram cloud. However, there were no changes in the spatial patterns for directional semi-variograms.

Although the theoretical semi-variogram models revealed a sill for DL-extractable soil P content in the topsoil, subsoil, and organic matter content, the variance tended to decrease at greater distances. It appeared as the variance increased again at the maximum distance we recorded.

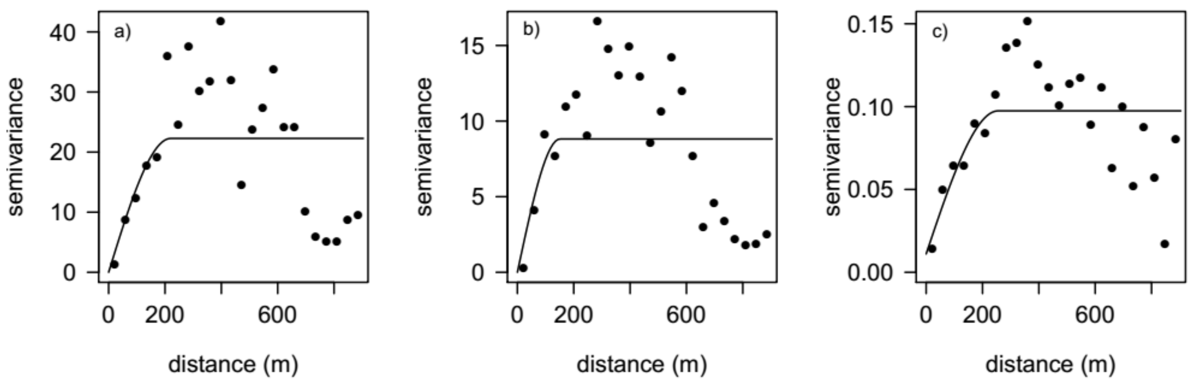

Figure 5-7: *Omni-directional empirical semi-variograms (black dots) and theoretical semi-variogram spherical models (solid line) for DL-extractable P content of a) topsoil, and b) subsoil for the whole data set; c) shows the empirical variogram cloud and the theoretical variogram model for soil organic matter in the topsoil.*

5.4 Discussion

The concentrations of DRP and TP presented here are in conjunction to those presented in the literature. Nonetheless, a larger intra-annual variation was shown at the same study site

10 years ago (Tiemeyer et al. 2009). The water quality varies on the three spatial scales. The 90th percentile of DRP at the drainage ditch was lower than 0.6 mg l^{-1} whereas the 90th percentiles of the tile drain and the brook were lower than 0.4 mg l^{-1}. This is equivalent to water quality class I-II, and II, which are classified as 'slightly polluted' and 'moderately polluted' respectively (Länderarbeitsgemeinschaft Wasser 1998). High concentrations of P in English watersheds are often contributed to point sources like sewage works (Jarvie et al. 2006, Bowes et al. 2008, Bowes et al. 2015). In a French watershed, the increased water quality is attributed to improved quality of sewage works. One has to be aware that the quality of P removal from wastewater varies strongly and so does water quality along rivers (Minaudo et al. 2015).

The satisfactory water quality discovered in the study period 2015/2016 reflects the low inputs of P (see Table 5-2) on the agricultural land at our study site and confirms the negative P budget observed 10 years ago (Tiemeyer et al. 2009). However, no point sources are located in the small 15.5 km^2 watershed.

The increase of DRP from the tile-drain scale to the ditch scale may be attributed to the inflow of P-laden groundwater. Measurements by the Leibnitz Institute of Baltic Sea Research confirm the idea of high concentrations of DRP in the groundwater at our monitoring site (personal communication, data not published yet). There is no further increase of DRP concentrations from the ditch to the brook scale, which indicates a dilution of the DRP concentration. Hence, we have to conclude that groundwater P concentrations have a high spatial variability. We assume that the increase of the TP concentrations with increasing spatial scale is related to the mobilization of P-enriched bed sediments in the drainage ditch and the brook. This idea is supported by the discharge-TP relationships (Figure 5-5). The idea of bank erosion as a main source of diffuse TP in surface waters was also portrayed in the literature (Kronvang et al. 2012, Lu et al. 2015). We assume that the low concentration of TP at low discharge is caused by the lack of point sources in this catchment. High concentrations of TP related to sewage effluents at low discharge have been observed earlier (Bowes et al. 2015).

A variety of discharge-P relationships has been found in the past. In chapter 4, we found a decreasing relationship of DRP and TP, and increasing discharge using long-term weekly means of P concentrations. However, in some Warnow River sub-basins, we detected that TP concentrations tended to increase at high rates of runoff. In conjunction to the variety of discharge-P relationships presented in the literature, there is even a large intra- and inter-annual variety. According to the findings of this study, increasing DRP concentrations with increasing discharge were found in a Polish river, which was attributed to rainfall (Dąbrowska et al. 2016). In contrast, decreasing DRP concentrations with increasing discharge was found frequently in a large number of European watersheds (Thomas et al. 2016). The TP concentrations in a river in England were strongly correlated to rainfall events with high rates of surface runoff, and within-river remobilization of P (Bowes et al. 2015). However, a high number of data points revealed a dilution curve of P and discharge, which was related to constant point source inputs (e.g. sewage works). A weak relationship, but with a significant decrease in TP concentrations, was found in a meta-study for the eastern American states (Christianson et al. 2016). Both increasing DRP and TP concentrations with increasing discharge, as presented here, was likewise confirmed for a watershed in south-western Sweden (Djodjic et al. 2000). However, we have to highlight that the relationships of DRP and TP are strongly colored by specific watershed properties, land use, and climate. In our study region, we assume that high rates of bank erosion and remobilization of sediment with high DRP and TP concentrations at all three spatial scales occur at high-discharge events related to rainfall. Even in the tile drainage system, sediment may be deposited at the baseflow and released during an event-related flow. Additionally, we have to emphasize that the measurement scheme and intervals might strongly influence the observed patterns of DRP and TP in relation to discharge. A higher temporal resolution will reveal a deeper insight into the processes related to event-related runoff in drains and rivers.

Event-based discharge can release high total loads of DRP and TP. At the same study site, 53%, 60%, and 56% of the TP losses from tile drain, drainage ditch, and brook were related to the fast flow component 10 years ago (Tiemeyer et al. 2009). A study from an English watershed estimated 68% of the P load in a river coming from event-related diffuse sources (Bowes, 2014). In a south-eastern US agricultural area, a single storm event exported up to 61% of the total annual P load (Bhadha et al. 2016). In our study, at least 50% of the overall seasonal P load was exported during the five investigated events with the highest proportion observed in the drainage ditch. We assume that especially in the drainage ditch, the event-based re-suspension of bed sediment is the key pathway of TP. However, at greater spatial scales, the dilution effect of less P-laden groundwater to the brook may decrease the effect of bank erosion. Although the concentration of TP increased from scale to scale, the loads per hectare decreased from the tile drainage to the brook scale. While the TP loads were three times higher than the DRP loads at the tile drainage and drainage ditch scales, the differences in the loads of DRP and TP were not marked at the brook scale. We assume that rainfall has a big influence on internal soil erosion of particles to tile drains and the re-mobilization of bed sediments in the drainage ditch, which is vulnerable to hydraulic pressure caused by high discharge (e.g. following recurring dredging). At the brook scale, the plants and the structure of the stream can buffer the re-mobilization of sediment. However, the low amount of DRP at the Brook scale may be a consequence of the sorption of soluble P fractions into sediment particles.

These findings can also be revealed by the relationship of DRP and TP. The slope of the linear model between TP and DRP, which is larger than the slope of the ideal 1:1 model of DRP and TP (Figure 5-6), likewise indicates a higher contribution of TP at high discharge events. The highest slope at the tile drainage scale may highlight the marked contribution of the particulate P at the peakflow in drainage pipes caused by internal erosion and the preferential transport of colloid-bound P.

The spatial variability of soil P has often been addressed in the literature. However, the outcomes show some noticeable discordance. It is known that the spatial variability of soil P may be large but little is known about actual drivers of P variability. The comparison of different studies is challenging since the extraction methods vary markedly. However, relative P contents are more important for the assessment of spatial variability than absolute values are.

It has also been reported that no significant change could be observed in the variance over distance (Kozar et al. 2002). The reported ranges of spatial autocorrelation vary strongly. At a Taiwanese study site, a range of spatial autocorrelation of about 1500 m was observed. Contrastingly, low ranges of spatial autocorrelation were reported for different land use types in the US. The observed ranges varied between 7m and 60m in an organic field, and between 47m and 78m in a conventional field (Cambardella & Karlen 1999). The difference in the spatial range of spatial autocorrelation was confirmed in a Chinese study, in which the ranges of the theoretical variograms varied strongly in relation to land use (Wang et al. 2009), as well as in Switzerland (Roger et al. 2014). These findings approved that a general evaluation of the spatial variability of soil P is challenging. A study in Maryland, USA, suggested that the spatial autocorrelation is strongly related to soil Al and soil Fe contents (Vaughan et al. 2007). The spatial patterns strongly depend on land use, soil properties, soil organic matter content, Ph, Fe, and Al content) and topography. However even chemical properties of the soil may strongly influence the spatial distribution of the soil P (Vaughan et al. 2007). Since we did not measure the Fe and the Al contents of the soil, we cannot clearly address the origin of the spatial patterns of DL-extractable soil P. Nonetheless, we could demonstrate that the general patterns of DL-extractable soil P content are similar for the topsoil and the subsoil. Even the spatial patterns for soil organic matter in the topsoil showed similarities to those from DL-extractable soil P content.

The distribution of soil P in the subsoil has not been of considerable interest compared to the topsoil. However, it was found that the soil P content in the subsoil is significantly lower than that in the topsoil (Page et al. 2005). This is confirmed by our findings in chapter 7.

5.5 Conclusion

We analyzed a data set of discharge, DRP, and TP concentrations and DL-extractable soil P from a one-year runoff period in an agriculturally used watershed in north-eastern Germany.

Our results indicate that the considered spatial and temporal scale can essentially influence the detected processes of P leaching from agricultural fields to the receiving surface waters. Furthermore, we could show that bank erosion may be an important source of TP loads in rivers and streams, and their contributing drainage ditches and tile drainages. The transport of particle-bound P through internal erosion and its release through tile drains is a significant contributor to diffuse P pollution of surface waters in agricultural lowland watersheds.

We assume that a reliable assessment of P losses from agricultural land can only be achieved considering high-frequency measurements of DRP and TP concentrations on different spatial scales, as well as event-based sampling of bed sediments.

Taking our findings into account, future studies should, besides concentrating on small-scale process research, also try to find practical solutions for the mitigation of elevated P losses from agricultural watersheds to the receiving waters. Likewise, more research is needed on the adsorption potential of bed sediments and techniques to mitigate streambank erosion during runoff events.

6 Visualization of colloid transport pathways using Titanium(IV) oxide as a tracer

Abstract

In soils, colloidal transport has been identified as the most important pathway for strong adsorbing, environmental contaminants like pesticides, heavy metals and phosphorus. We conducted a comparative dye tracer experiment using a Brilliant Blue (BB) solution and a Titanium(IV) oxide (TiO_2) colloid suspension (average particle size = 0.3 µm) aiming at visualizing and quantifying colloid pathways in soils.

Both dye tracers showed comparable general flow patterns with preferred transport over the deepest part of the soil profile independent of clay content. However, the stained area was generally smaller for TiO_2 than for BB by a factor of ten and there was no TiO_2 to be found at all in the low clay content soil. The travel distance was almost identical for the solution and the suspension (0.7 m) giving evidence that environmentally critical compounds bound to micro-particles may be vertically transported over longer distances in soils even within single rainfall events. The spatial variability of the dye patterns was large on a small scale with a range of 0.35 m for TiO_2 in the horizontal plane, which was taken as a general proof for a pronounced preferential transport situation.

The study indicates that TiO_2 is transported exclusively through singular macropores of biogenetic nature while BB passes also through the soil matrix of coarse bedded soils, the secondary pore system or inter-aggregate pore space. The results emphasize the general suitability of TiO_2 for the visualization of colloid transport pathways in soils opening up new research opportunities for contaminant transport in soils.

Keywords: *TiO_2, BB, particle-facilitated transport, macropore flow, preferential transport*

6.1 Introduction

It has been an unanimous doctrine in soil science for a long time that strong adsorbing compounds such as phosphate are transported via erosion bound to soil particles (Sharpley and Syers 1979, Daniel et al. 1994, Sharpley et al. 1994). Recently, there occurred increasing evidence that colloids are also transported vertically through the soil. The particle-facilitated transport has been identified as important pathway for leaching of contaminants like pesticides, heavy metals and phosphorous (Jacobsen et al. 1997, de Jonge et al. 2004, Makris et al. 2006). Jiang et al. (2015) investigated the phosphorous contents of soil aggregate-sized fractions from <0.45 µm to >20 µm and found a significant increase of the overall phosphorous content with decreasing aggregate-sized fractions. Heathwaite et al. (2005) stated that total and reactive phosphorus is favorably transported in fractions of 2 µm or smaller than 0.001 µm. The authors highlighted the potential of P colloids to be leached out through subsurface drainage by rainfall events.

McGechan and Lewis (2002) reviewed a multitude of research papers and sum up that macropore and preferential flow are the main processes of colloid and particle transport. Although particle transport in soils has often been studied, it is not known as to what extent colloidal transport patterns compare to the travel pathways of dissolved substances. No attempt has been made to visualize the migration of colloids in soils and therewith to obtain further insight into potential contaminant transport.

The application of dye tracers in infiltration experiments aiming at the visualization of transport processes in soils is well established in soil science. Since decades, dye tracers are used to identify flow pathways in different soils and land use types (Stamm et al. 1998, Janssen & Lennartz 2008, Kodešová et al. 2015). The list of available dye tracers is long and the suitability of a specific dye is essentially determined by the research question and the particular experimental constraints.

Brilliant Blue (BB) is a popular dye tracer in soil science due to its non-toxicity, the mobility, the bright blue color and the non-conservative adsorptive behavior (Morris et al. 2008). The physical and chemical performance of BB was investigated by Flury and Flühler (1995) and Kasteel et al. (2002) in different soils.

Morris et al. (2008) found that sorption of BB is not fully reversible and suggest that BB is not suitable for all forms of dye tracing in soils. Adsorption of BB to clay colloids substantially increases with an increasing clay content and decreasing pH-values. Likewise, an elevated ionic strength of the background solution leads to higher sorption coefficients of BB (Germán-Heins and Flury 2000). Janssen and Lennartz (2008) found marked amounts of BB solute shifting by preferential flow in paddy rice fields in China, while Chyba et al. (2013) state that soil compaction significantly affects the infiltration of BB in the topsoil.

Titanium(IV) oxide—also known as Titanium dioxide—is a bright white pigment widely used for coloring and varnish and as a food dye. It is not soluble in water and most organic solvents. A broad range of particle sizes is available for different applications. Titanium(IV) oxide (TiO_2) was firstly used by Liu & Lennartz (2015) to visualize preferential colloid pathways in dark colored peat soils. However, TiO_2 is recently more in focus of environmental and health sciences due to its potential as hazardous nanoparticle (Long et al. 2006, Weir et al. 2012, Frazier et al. 2014). TiO_2 particles are available in different sizes. It can be assumed that a narrow TiO_2 particle size distribution with a mean of 0.3 µm is a good representation of naturally occurring soil colloids of that size.

Although the in-situ visualization of soil pore distribution is redeemed by high-end laboratory techniques like X-ray computer tomography (Rogasik et al. 1999, Cnudde et al. 2006) field studies can be a useful tool for understanding soil physical processes at the field and pedon scale. Furthermore, there are limitations of laboratory techniques when it comes to the detection of active pore space in a soil sample. Active pore space in this context denotes the pore volume that is available for convective transport processes for the compound of consideration. Thus, dye tracer studies still appear to be an appropriate method revealing transport mechanisms under field conditions.

The aim of this study was to visualize the colloid transport in three different mineral soils used for crop production along a gradient of increasing clay content in North-Eastern Germany. In addition, we wanted to uncover differences in transport patterns between real solutions (Brilliant Blue) and suspensions (Titanium(IV) oxide) by analyzing stained soil profiles.

Based on literature studies we hypothesize: (i) Both tracers follow preferential pathways in the soil, (ii) the penetration depth of the tracer in the soil profile is a function soil texture, (iii) Titanium(IV) oxide is suitable for the visualization of colloid transport in mineral soils and exhibits a behavior that compares to the mobility of natural occurring soil colloids.

Studies using TiO_2 as a dye tracer in mineral soils are not available. We believe that the higher clay content causes temporal resistant singular biogene macropores that can transport the TiO_2 suspension through the soil, while in loose-bedded soils, earthworm holes are not persistent and soil macropores only allow very limited access of colloidal TiO_2.

6.2 Material and methods

6.2.1 Study region

Table 6-1: *Physical characteristics of the soils at the study sites.*

Site	Depth [m]	Clay (≤ 2 µm) [%]	Silt (2-63 µm) [%]	Sand (63–2000 µm) [%]	Stones [%]	Micro pores (≤ 0.2 µm) [Vol-%]	Meso pores (0.2–50 µm) [Vol-%]	Macro pores (> 50 µm) [Vol-%]	Bulk density [g cm^{-3}]	Organic matter content [%]	Soil colour (Munsell)
S	0.00–0.30	7.6	48.5	43.6	0.3	7.60±1.77	24.90±4.29	13.50±2.10	1.44±0.32	2.0 – 4.0	10YR 3/3
	0.30–0.42	8.4	47.4	43.8	0.4	7.60±0.09	20.70±0.49	12.40±0.97	1.57±0.02	2.0 – 4.0	10YR 3/4
	0.42–1.00	15.7	35.2	48.8	0.3	11.50±0.13	18.25±0.99	3.50±0.58	1.77±0.02	<1.0	10YR 5/3
C	0.00–0.28	6.1	44.9	48.7	0.3	8.10±0.10	21.60±1.0	8.40±0.90	1.64±0.02	2.0 – 4.0	10YR 3/3
	0.28–1.00	12.6	39.3	47.8	0.3	10.38±0.10	15.90±0.40	7.83±0.20	1.75±0.01	<1.0	10YR 4/6
R	0.00–0.35	0.3	1.8	89.8	8.1	6.40±0.00	24.0±0.83	8.20±0.30	1.63±0.00	1.0 – 2.0	10YR 4/2
	0.35–1.00	0.0	0.5	99.5	0.0	0.90±0.00	34.10±0.45	12.5±1.59	1.39±0.03	0.0	2.5 Y 5/4

The study region was a pleistocene lowland landscape located 10 km southeast of the city of Rostock in the federal state Mecklenburg-West Pomerania in north-eastern Germany. The landscape is dominated by light hillslopes (average slope class 0–4%, maximum slope class 8–32%) on a ground moraine formed in the Weichselian sequence. The climate is characterized by a gradient from atlantic to continental with an annual precipitation of 660 mm and a mean annual temperature of 9.1°C (German Weather Service, normal period 1981–2010).

We conducted the dye tracer experiments on three different soils along a clay content gradient (Table 6-1). The soil types were a Stagnosol (Aqualf, site S), a Cambisol (Ochrept, site C), and a Regosol (Entisol, site R) according to the Food and Agriculture Organization of the United Nations (FAO 1998 - USDA taxonomy in brackets (Soil Survey Staff 1999)). These soil types are typical for the lowlands in north-eastern Germany formed on Pleistocene glacial till. The A horizon had a thickness of 0.3 m at the sites C and R. Deep ploughing in a five-year cycle at site S have caused the formation of a secondary A horizon.

The study sites S and C are intensively-used agricultural acreages with sugar beet in 2015, the site R is a one year abandoned field with dry grassland vegetation.

6.2.2 Experimental design

We conducted dye tracer experiments with Brilliant Blue (BB) and Titanium(IV) oxide (TiO_2, supplier: Cristal Global; product name: Tiona AT-1; average particle size 0.3 µm with 75% of the particles being in the range of 0.2–0.4 µm; information supplied by Cristal Global). A metal collar sized 0.7 m × 0.7 m was carefully inserted into the soil (0.03 m depths). 24.5 l (50 mm) of water with a BB concentration of 4 g l^{-1} (as suggested by Flury et al. (1994)) or a concentration of 10 g l^{-1} TiO_2 (as suggested by Liu and Lennartz (2015)), were slowly poured out of a PVC canister onto a plastic sheet that covered the soil within each collar. The plastic sheet was then carefully (slowly from one side to the other within 5 to 10 sec) removed to ensure uniform flooding conditions. Twenty-four hours later, eight vertical soil profiles with a spacing of 0.1 m were prepared successively by slide-wise cutting the soil with a spade at each experimental site and photographed. The soil pit was 2 m wide and 1m deep in order to allow photographing of both (BB and TiO_2) infiltration domains. The photo-documented area of each soil profile was 0.49 m^2 (0.7 m × 0.7 m) for each dye tracer. In total, 48 soil profiles (3 sites × 8 profiles × 2 dye tracers) were prepared and processed; 24 profiles with BB and 24 with TiO_2.

In order to determine the standard soil physical properties of the experimental sites, disturbed and undisturbed soil samples were taken horizon-wise. Undisturbed samples were collected using 5 stainless steel cylinders of approximately 250 cm^3 in volume (7.1 cm in diameter and 6.2 cm in length) at each horizon. Disturbed samples were taken according to a randomly distributed pattern over each horizon. Particle size distribution (<2 mm) was determined using a combined sieve and pipette method (DIN 18123). The water retention function was measured using ceramic suction plates (at pF 1.8 and 2.48, corresponding to 60 and 300 hPa) and a pressure membrane apparatus (at pF 4.2, corresponding to 15,000 hPa). The water retention curve allowed calculating various pore size classes:

macropores,	MaP: > 50 µm;	MaP = Total porosity – θ at 60 hPa
mesopores,	MeP: 50–0.2 µm;	MeP = θ at 60 hPa – θ at 15,000 hPa
micropores,	MiP: ≤ 0.2 µm);	MiP = θ at 15,000 hPa,

where θ is the volumetric water content (Vol. %).

6.2.3 Image processing and statistical analyses

All image processing was done using Photoshop CS6 (Adobe Systems Incorporated). Prior to processing of the photographs we applied a photogrammetric rectification. Then, the photographs were edited adjusting contrast and brightness. Finally, stained areas were isolated from unstained areas manually by visual inspection and the results were presented in a binary (black and white) image (Nobles et al. 2010).

The pixels of stained and unstained areas from each profile section were counted in squares of 0.05 × 0.05 m and pixel-wise per row in downward direction of the soil profile for further statistical analysis.

Since the dye coverages were not normally distributed, differences of stained areas between individual soil profiles were analyzed using a Mann-Whitney-U-test.

We calculated vertical and horizontal semi-variograms by means of tracer coverage. Vertical semi-variograms were calculated by using dye coverage mean values of the 8 excavated soil profiles at each site. Horizontal semi-variograms were calculated depth-wise by taking all values of the 8 profiles of one depth (10 cm increments) representing one horizontal plane perpendicular to the soil profile.

The empirical semi-variogram cloud was calculated by the following equation:

$$\gamma(h)=\frac{1}{2n(h)}\sum_{i=1}^{n(h)}\left[Z(x_i)-Z(x_j)\right]^2 \quad \text{(I)}$$

, where x_i and x_j are the locations of two measurement spots, *n(h)* is the set of all pairwise Euclidean distances and *Z* is the value of the stained area at the spatial locations x_i and x_j. The locations of the measurement spots were derived from the center of each 0.05×0.05 m square in the processed images.

We fitted linear and spherical semi-variogram models to the empirical semi-variogram cloud according to the following equations (spherical semi-variogram model):

$$\gamma(h)=c_0+c\cdot\left(\frac{3h}{2a}-\frac{h^3}{2a^3}\right),\ \text{for } 0<h\leq a \qquad \text{(IIa)}$$

$$\gamma(h)=c_0+c,\ \text{for } h>a \qquad \text{(IIb)}$$

, where *h* is the Euclidean distance, c_0 is the nugget, c_0+c is the sill, and *a* is the range of the semi-variogram. The theoretical semi-variogram models were validated by the minimized sum of squares.

The semi-variogram is a quantitative description of spatial patterns in the soil. It provides information on spatial dependencies of measured parameters, and is, thereby, a prerequisite for the justified interpolation and mapping of soil properties (Burgess and Webster 2006). Semi-variograms have rarely been used to describe spatial variability of soil dye patterns (Liu & Lennartz 2015). The semi-variogram allows to limit the spatial extent of auto-correlation, which is helpful in interpreting flow and transport domains in soils.

6.3 Results and discussion

6.3.1 Observed dye patterns

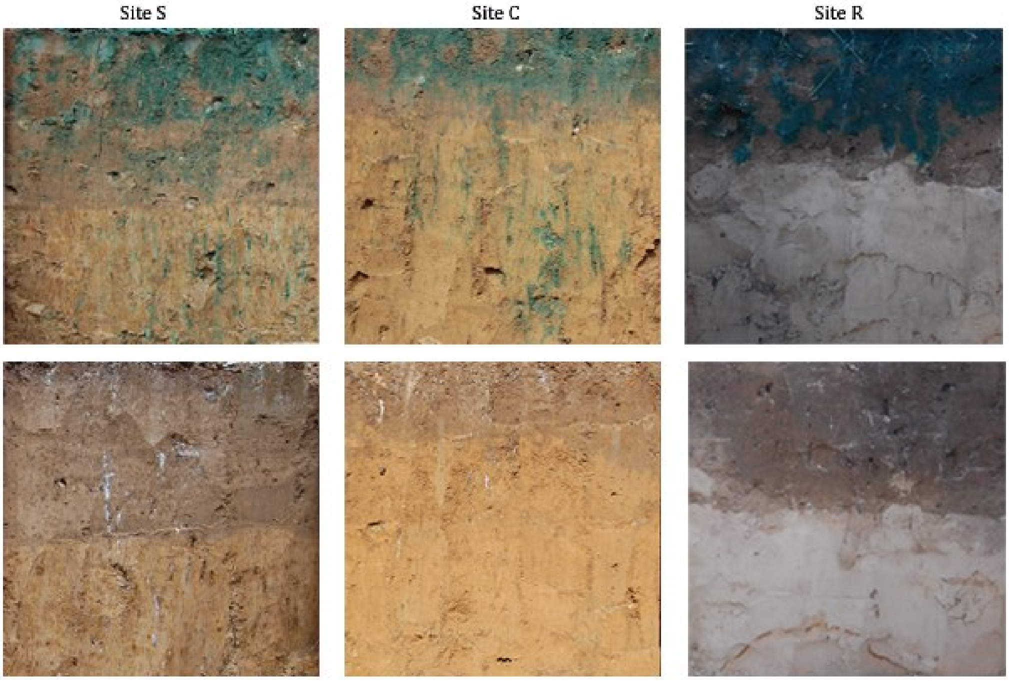

Figure 6-1: *Sample images of stained soil profiles. The upper row shows Brilliant Blue, while the lower row shows TiO_2.*

Profound differences in the relation of stained and unstained areas could be observed for BB and TiO_2 (Figure 6-1, Figure 6-4). The average BB-stained area, as calculated from eight soil profiles, was 0.14 m^2, 0.15 m^2, and 0.12 m^2 for the sites S, C and R, respectively, which corresponds to a relative coverage of 29%, 31%, and 24%.

For the upper soil horizon (0.3 m) we calculated mean BB-dye coverages of 0.12 m^2 (57%) for all three sites. The difference in dye coverage between topsoil (0–0.3 m) and subsoil (0.3–0.7 m) was significant for all three sites and all profiles ($p<0.001$). The stained area in the lower 0.4 m of the soil profiles was 0.02 m^2, 0.02 m^2, and 0.004 m^2 at the sites S, C and R, respectively, which corresponds to a relative coverage of 7%, 7%, and 1% (Figure 6-2).

Brilliant Blue passed the upper soil horizons in a broad front at all sites whereas the compacted subsoil with higher bulk densities restricted the transport of BB to preferential flow pathways. At sites S and C, subsoil related preferential transport pattern were evident. The macropore system consisted of earthworm burrows and root channels. However, at site R BB did not pass the A-horizon within 24 hours after tracer application. In contrast, BB reached the lower boundary (0.7 m) of all soil profiles at sites S and C.

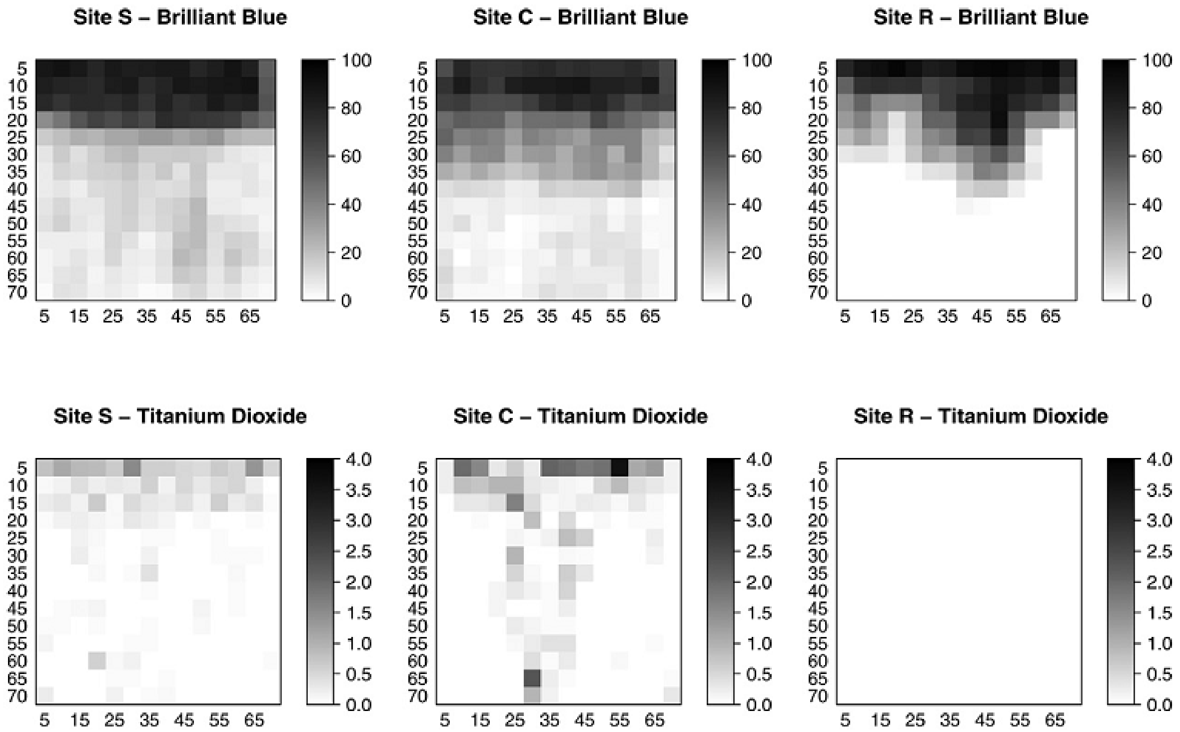

Figure 6-2: *Mean coverage (%) of dye tracer, as determined in 5 by 5 cm squares of all soil profiles per site (n = 8). note the differences in gray scaling for Brilliant Blue and Titanium Dioxide.*

The overall mean area covered by TiO_2 tracer was lower by the factor ten compared to BB with 0.005, 0.008 and 0.0 m² for the sites S, C and R, respectively which corresponds to a relative coverage of 1, 1 and 0% (Figure 6-1). At site R no tracer at all was found in the soil profiles. The upper soil horizons (0–0.3 m) were covered with TiO_2-dye on an area of $8.95 \cdot 10^{-4}$, $5.89 \cdot 10^{-4}$ m² at site S and C. In the subsoil (0.3–0.7 m) the mean coverage was $7.23 \cdot 10^{-4}$ and $4.59 \cdot 10^{-4}$ m² at sites S and C. This corresponds to relative coverages of less than 1%.

The dye photographs clearly demonstrate the differences in transport between TiO_2 and BB at site S and C. TiO_2 is exclusively transported through singular macropores; matrix transport is not visible (Figure 6-3). In contrast, BB is transported by matrix flow as indicated by the homogeneous coverage of the soil and at greater depths through the secondary pore system as originating from aggregation and biological activity (root and earthworm channels). This has also been observed by Nobles et al. (2010).

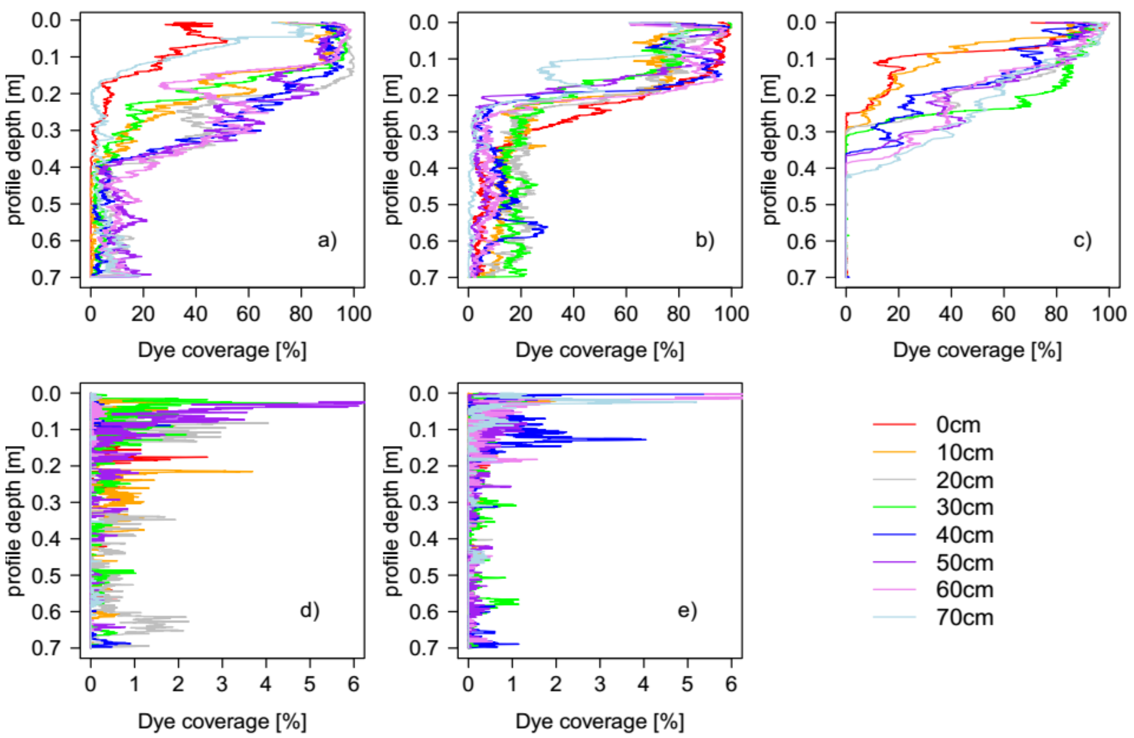

Figure 6-3: *Vertical dye coverages of each site and each tracer per soil profile with (a) site S (Brilliant Blue), (b) site C (Brilliant Blue), (c) site R (Brilliant Blue), (d) site S (TiO_2), and (e) site C (TiO_2). there is no graph for TiO_2 at site R, because no tracer was found in the soil profiles.*

Tillage of the upper soil horizon leads to a great proportion of highly accessible and equally distributed pores allowing the transport of water and BB which results in more or less homogeneously stained A-horizon (Yasuda et al. 2001). An increasing bulk density and clay content in the B-horizon facilitate structuring and formation of larger aggregates, which result in a more pronounced separation of the pore space in an inter- and intra-aggregate domain. As a consequence, a distinct pattern of preferential pathways establishes. In contrast to BB, TiO_2 is exclusively transported through singular macropores, e.g. earthworm channels, across the soil profile, also in the A-horizon. It was interesting to see that TiO_2 did not travel through large cracks as they origin from aggregation.

The results indicate that BB in contrast to TiO_2 is transported through aggregate interfaces (Figure 6-3c), root channels (Figure 6-1) and other macropores (Figure 6-1) of biological origin which confirms earlier observations (Nobles et al. 2004). Similarly, to the results from this study, Yasuda et al. (2001) observed that applying BB under ponding conditions, stains up to 100% of the upper part of a clay soil profile and follows preferential pathways in the subsoil. The authors estimated that only 10 to 20% of the cracks in the observed prismatic clay were active pore space and accessible for preferential transport. In more coarse-textured soils they observed fuzzy dye patterns and deduced dispersive transport mechanisms. Preferential flow of BB solution in compact clay and loam soils has also been shown by Hardie et al. (2011), Chyba et al. (2013) and Etana et al. (2013).

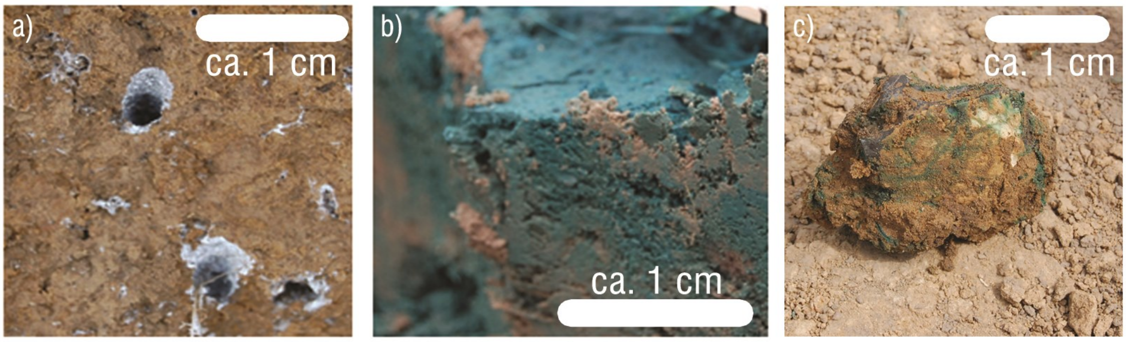

Figure 6-4: *Horizontal cut through soil profiles at site S. Figure (a) shows the transport of TiO_2 through earthworm channels (0.4 m depth), (b) shows matrix transport of Brilliant Blue (BB) in the topsoil (0.2 m depth), and (c) shows transport of BB through the interaggregate pore system.*

Dye tracer studies regarding TiO_2 are rare. Liu and Lennartz (2015) investigated the effect of applying TiO_2 as a tracer in degraded peat soils in north-eastern Germany. They found that TiO_2 is transported preferentially and, in contrast to Bromide as a conservative tracer and solute, has no or at least limited access to the fine pore system. It can be assumed that in our study BB behaved as a solute and was subjected to lateral transport by diffusion in addition to convective-dispersive mechanisms. Although diffusion in soils is in general lower as compared to a free solution, the entrance of BB into the fine pore system is possible and could be confirmed by the photo documentation (Figure 6-1, Figure 6-3c). In opposite, diffusion of TiO_2 is negligible and access to the fine pore system is hindered because of weight and size of the particles. We presume that with increasing colloid size of the tracer suspension the amount of active pore space decreases in the soil.

6.3.2 Spatial distribution of dye tracer in the soil profiles

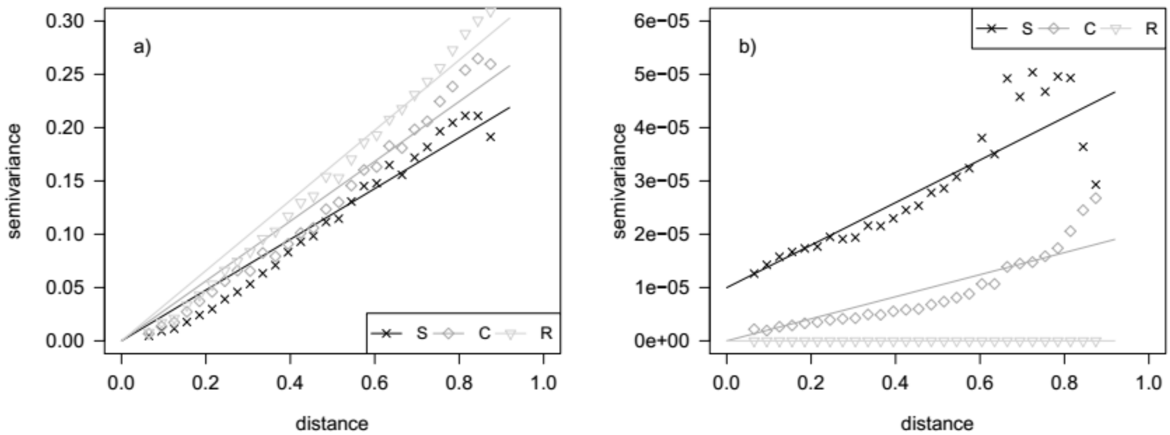

Figure 6-5: *Vertical empirical semivariogram clouds and fitted linear (Brilliant Blue, panel a) and Gaussian (TiO_2, panel b) semivarigram models for the three sites and both tracers.*

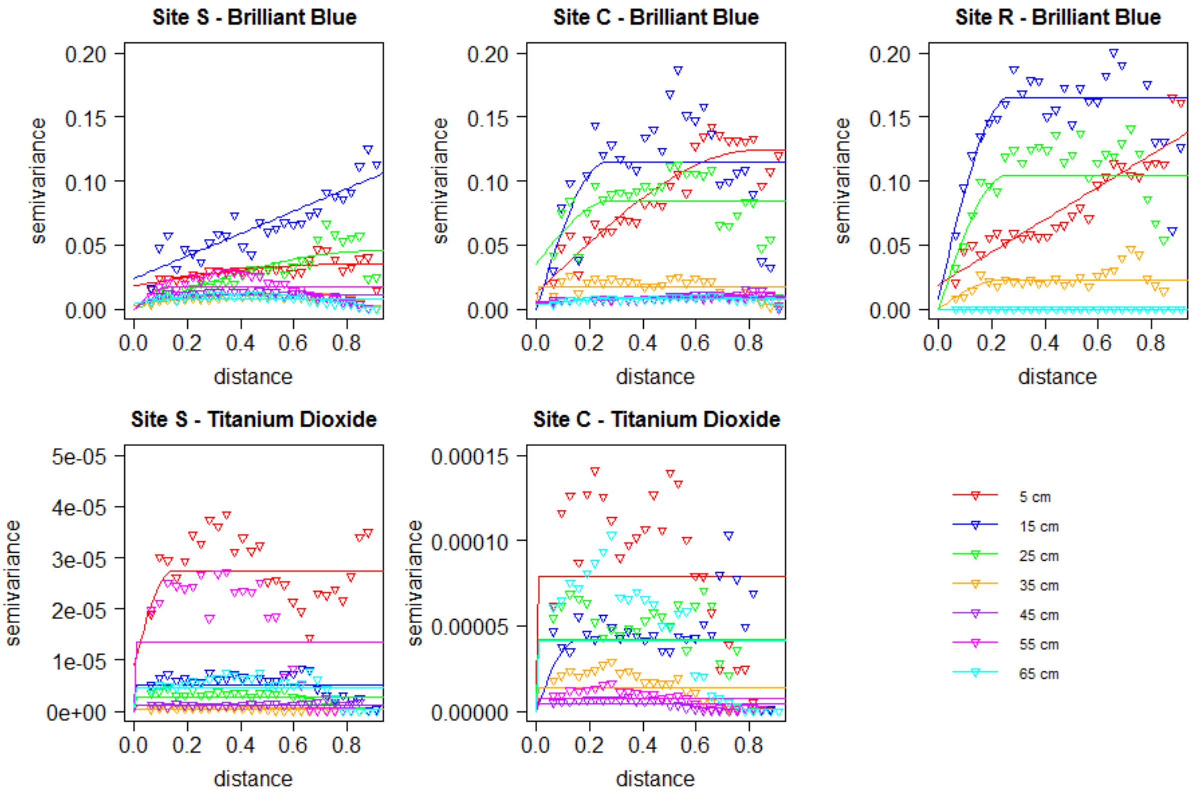

Figure 6-6: *Horizontal empirical semivariograms and fited spherical semivariogram models for different depths in 10 cm steps. note the varying y-axis.*

We calculated empirical semi-variograms and fitted theoretical linear and spherical models to the data to assess the spatial variability of the dye patterns. Vertical semi-variogram models indicate a strong spatial variability across all sites for both Brilliant Blue and TiO_2 (Figure 6-5). The semi-variograms do not reach a sill until the maximum distance. Zero nuggets were calculated for all three Brilliant Blue semi-variograms. This implies that the total stained area decreases with increasing depth even outreaching the observed profile depth. This can be attributed to preferential flow through the secondary pore system (Brilliant Blue) and through singular macropores (particle/colloid transport, Brilliant Blue) as it has often been observed in dye tracer studies (Nobles et al. 2010, Kasteel et al. 2005, Weiler & Flühler 2004, Liu & Lennartz 2015).

The semi-variograms for the horizontal plane indicate a smaller spatial variability compared to the vertical semi-variograms and show also a strong spatial dependence of dye coverage in the horizontal direction over short distances. This result suggests that individual and continuous pores such as well confined inter-aggregate spaces (BB) or bio-pores (BB+TiO_2) are the prime flux and particle transport domain rather than ‘flux fingers’, for instance. A sill was reached in the theoretical semi-variogram models at almost all horizontal cross sections for both BB and TiO_2 (Figure 6-6).

Yasuda et al. (2001) showed that the spatial dependence in the horizontal direction is larger than in vertical direction. This can be interpreted as a geostatistical expression of preferential flow through the soil profile. The effect of earthworm channels and root channels appears higher in vertical direction than in horizontal direction.

The low nuggets in the horizontal semi-variograms suggest that the spatial extent of the processes of vertical particle-facilitated transport can be mapped on the pedon scale.

6.3.3 Influence of soil texture on dye patterns

The results reveal a small but statistically significant positive relationship between the clay content and TiO_2 stained area for the topsoil and the subsoil ($R^2=0.24$, $p<0.05$ for topsoil and $R^2=0.2$, $p<0.05$ for subsoil, linear regression model). Furthermore, we found a significant relationship between dye coverage of TiO_2 and silt content ($R^2=0.29$, $p<0.05$ for topsoil and $R^2=0.26$, $p<0.05$ for subsoil, linear regression model). On the other hand, a combination of both clay and silt content gave no significant model. However, neither the pore size distribution, nor the content of sand have any effect on the stained area of the soil.

At site R we found a sandy soil with a lack of clay minerals and organic matter. Consequently, the soil particles are predominantly un-aggregated and loose; no soil structure forming a secondary pore system has developed. In opposite, at sites S and C an advanced pedogenesis with nuanced manifestation of soil horizons can be expected. This can also be seen in the formation of a solid soil structure, the higher bulk densities and the stable pore system.

We assume that higher clay and silt contents result in a more structured soil which leads to a pronounced secondary pore space and, hence, to a higher potential for the (preferential) transport of solutes and colloids. OM content, which was greater at site C and S as compared to site R, may also play an important role in the formation and stability of soil peds (Chaplot 2015). De Jonge et al. (2004) also found the clay content and the continuity of large macropores as an explanation for enhanced particle-facilitated transport.

Brilliant Blue is an extensively studied dye tracer, but studies on the influence of soil characteristics onto the obtained dye patterns are less frequent. Flury et al. (1994) found that structured soils were penetrated deeper by Brilliant Blue than unstructured soils which well reflects our results with structured soils at site S and C and the unstructured soil at site R.

We believe that the higher clay content causes temporal resistant singular biogene macropores that can transport the TiO_2 suspension through the soil, while in loose-bedded soils, earthworm holes are not persistent and soil macropores only allow very limited access of colloidal TiO_2.

6.3.4 Suitability of TiO_2 as a colloid dye tracer

Several studies on the transport of colloids are documented in the literature, whereby particle sizes in the range of 0.1–1.0 µm were considered, which was likewise the dominant range of TiO_2 particles as used in our study (Makris et al. (2006) – larger than 0.45 µm, VandeVoort et al. (2013) – smaller than 1 µm, Knappenberger et al. (2014) – 0.22 µm). Particle sizes of clay minerals and metal oxides are similar to the sizes of the TiO_2 particles presented here. Makris et al. (2006) stated that Iron hydroxides are an important fraction of potentially mobile soil colloids. We, thus, conclude that TiO_2 is a useful substance for the indication of potential pathways of colloids in soils. This assumption is supported by comparable densities of TiO_2 and different metal oxides. Cey et al. (2009), however, found that the colloid species do not influence transport to a greater degree than the flow system itself and concluded that even soluble dye tracers like BB are a reasonable surrogate for colloid distributions in the vadose zone. The comparison of TiO_2

and BB images, nonetheless, revealed that transport pathways of soluble and colloidal substances are not necessarily identical.

6.4 Summary and conclusion

We studied the visualization potential of particle facilitated transport by using Titanium(IV) oxide (TiO_2) as a tracer in mineral soils. The results revealed that: (i) both the solution (Brilliant Blue) as well as the suspension (TiO_2) follow preferential pathways; TiO_2 is, however, exclusively transported in singular macropores rather than along soil ped interfaces; (ii) there is a significant trend that greater clay and even silt contents cause a higher TiO_2 coverage of the soil profile indicating a more pronounced leaching potential for particles in structured soils (iii). Based on our findings and the observed differences in transport patterns between BB and TiO_2, we conclude that TiO_2 is suitable for the visualization of colloid pathways in the soil.

The observations made emphasize the importance of the active pore system in contrast to the overall pore space for preferential transport of colloids through soils. Up to date, the spatial distribution of particle pathways in the soil profile and its large spatial variability is not well understood and calls for further research. In a next step, dye tracing should be combined with a quantification of solute and particle transport across a flux plane to allow deriving quantitative indices from the stained soil profiles using TiO_2. Furthermore, since there are hints in the literature, different regimes of rainfall and initial soil moisture contents should be considered in particle tracer studies as those might influence colloid transport and mobilization.

Acknowledgements

We kindly acknowledge the help of our field workers Christian Möller, Robert Schmidtke and Stefan Kopperschmidt. We would likewise thank Dr. Andreas Bauwe and Evelyn Bolzmann for laboratory analysis regarding soil physical properties. The authors gratefully acknowledge the German Federal Ministry of Education and Research (BMBF) for funding the BonaRes project InnoSoilPhos (No. 031A558).

7 The use of field suction-plate lysimeters for the spatially-distributed assessment of phosphorous transport pathways on the pedon scale

Abstract

The transport of phosphorus (P) through the soil is not yet fully understood. Although the adsorption potential is large, a substantial amount of P may be leached through the soil by preferential flow.

We conducted an in-situ suction lysimter experiment with simulated strong rainfall events (40 mm precipitation every two hours, 480 mm total precipitation) in loamy soil in north-eastern Germany using potassium bromide (KBr) and potassium dihydrogen phosphate (KH_2PO_4) as tracer.

The breakthrough curves showed evidence for preferential transport of the dissolved Br at all 12 installed lysimeters and the mobilization potential of P in the soil. The spatial variation was large for Br, dissolved reactive phosphorus (DRP), and total phosphorus (TP), though most of the spatial variability could be attributed to lateral losses of water through the profile wall. There were no detectable changes in the DL-extractable soil P content before and after the experiment. Hence, there might have been problems with the solubility of the KH_2PO_4 and other methodological deficiencies.

A repetition of the experiment with an adjusted and improved methodology is necessary to understand the processes of preferential P—and the differences in the transport of DRP and TP—transport through loamy soils.

Keywords: *preferential flow, macropore flow, loamy soil, DRP, TP*

7.1 Introduction

Phosphorus (P) is an essential nutrient for crop production. However, P can, along with nitrogen (N), enhance the eutrophication of surface waters by amplifying algae bloom production.

It has often been shown that surface runoff is a major contributor to surface-water contamination by P. However, the vertical transport of phosphorus is nowadays in the limelight of research since it has frequently been shown that internal erosion processes may be the major pathway of P losses from agricultural fields (Makris et al. 2006, King et al. 2015b, Williams et al. 2016). Although surface runoff shows a more consistent response to discharge, the total annual loads transported through the soil to tile drainages are greater due to a greater total flow volume (Algoazany et al. 2007).

Different transport processes occur under a variety of tillage systems. It has been reported that event-based P concentrations in drainage water may be higher in a no-tillage field due to the stratification and persistence of macropores (Williams et al. 2016). But the texture may also regulate the leaching of P from soils. A German lysimeter study found that high P losses occurred in a sandy soil while leaching rates from a sandy loam were low (Godlinski et al. 2008). However, the potential of soil-bound P leaching to surface waters via internal erosion might be substantial. It was shown that the potential of colloid mobilization is the highest for soils with a clay content of 12% and 18% (Kjaergaard et al. 2004).

The experimental investigation of internal erosion in soils implies large uncertainties regarding the boundary conditions of the experimental setup. A sophisticated experimental approach on a smaller spatial scale with defined boundary conditions is the one with lysimeters. The first lysimeter ever installed was in 1875 (Hedrick & Sturtevant 1919). Nowadays, lysimeters are a standard method for the quantification of actual evapotranspiration and nutrient loss under different plants and crops, and a variety of soil types. Nonetheless, spatial patterns of solute transport cannot be quantified with standard lysimeters. Hence, grid lysimeters have been developed, and have found a broad use in the investigation of solute leaching and preferential transport of nutrients and contaminants (Andreini & Steenhuis 1990, Schoen et al. 1999, Rooij & Stagnitti 2002). However, grid lysimeters still require soil monoliths, a long-term operation, and space for installation, and are, therefore, expensive.

A new and inexpensive in-situ approach for the detection of spatial patterns of contaminant or nutrient leaching in soils are suction lysimeters. These small PVC, glass, or ceramic plates can be easily installed into the soil to sample pore water from a given flow cross-section. There are two options for operation: (1) a continuous or discontinuous constant pressure is applied for pore water sampling, and (2) the applied pressure head is controlled by the actual tension (soil-water content) of the soil. Suction-plate lysimeters have already found a broad application (Ciglasch et al. 2005, Cey 2013). The limitation of suction-plate lysimeters is the short timescales these are used for (Ciglasch et al. 2005)). Thus, they can cover only a small range of possible precipitation events (Ciglasch et al. 2005, Tindall & Friedel 2016). There are limitations and uncertainties in the boundary conditions (e.g. lateral movement of water) too, which are general problems in field experiments.

However, there is strong evidence that P is transported most prominently through the soil by preferential flow (Poirier et al. 2012, Williams et al. 2016). Although surface runoff is a well investigated pathway for P transport to surface waters, it is confirmed that, originating from the topsoil, P can be transported to tile drains, and, hence, to surface waters, via preferential flow (Poirier et al. 2012).

Based on the results of the study presented in chapter 4, the aim of our study was to find evidence for the preferential transport of total P (TP, includes particle-bound fraction of P) through an agriculturally used loamy soil at high precipitation rates by using suction-controlled field lysimeters. We hypothesize that even in strong rainfall, a large amount of P is bound to the topsoil. However, we expected that a substantial portion of the applied P would be transported as particle-bound P (TP) to the subsoil by preferential flow. We also expected a perceptible spatial variation of the estimated P loads at each lysimeter.

7.2 Material and methods

7.2.1 Study site

We used Site C (soil type Cambisol) for the suction lysimeter experiment, which was conducted in November 2016. The study site is comprehensively presented in chapter 2.1 and 5. At the time of the experiment, the agricultural field was covered with *Phacelia tanacetofolia* BENTH., *Trifolium repens* L., and *Brassica napus* L.

The soil showed a high proportion of clay and silt (Table 7-1). The dry conditions of the study year led to a strong polyhedric structure with many persistent biopores (e.g. root and earthworm channels, see chapter 6).

Table 7-1: *Grain size distribution of the investigated soil. All data in percent, based on a single sample per horizon.*

	Coarse sand 0.63-2.00 mm	Middle sand 0.20-0.63 mm	Fine sand 0.063-0.20 mm	Coarse silt 0.02-0.063 mm	Middle silt 0.0063-0.02 mm	Fine silt 0.002-0.0063 mm	Clay <0.002 mm
Topsoil 0-0.40 m	3.10	19.99	37.69	12.39	8.31	5.89	12.63
Subsoil 0.40-0.60 m	2.55	19.37	36.76	9.55	7.57	5.66	18.54

7.2.2 Experimental setup and data gathering

A soil profile was trenched (2.50 m × 2.50 m × 1.1 m), with four 0.60 m-deep horizontal wells of 0.25 m × 0.25 m edge length dug into the profile wall (Figure 7-1). Three circular suction lysimeter plates (ecoTech—Environmental Monitoring Systems, Bonn, Germany) with a diameter of 0.075 m were placed on the upper wall of each well at a 0.01 m distance from each other. Each lysimeter plate was connected to a sample bottle. The bottles were collectively linked to a suction-controlled pump (UGT—Umwelt-Geräte-Technik, Müncheberg, Germany). The applied suction was controlled by the actual water retention measured by three tensiometers (Tensio152, UGT—

Umwelt-Geräte-Technik, Müncheberg, Germany) that were installed horizontally in the depth of the suction plates.

A 2.5 m × 1.0 m-area was irrigated manually by carefully applying 40 mm of precipitation (100 l) 10-liter-wise over 15 minutes every two hours using a watering can. Between the irrigation events, the sprinkling area was covered with a blanket to avoid evapotranspiration losses and natural precipitation. A total precipitation of 480 mm was applied on two consecutive days.

Simultaneously, we applied a conservative potassium bromide tracer (Br) (KBr, S3 Chemicals, Germany, 98–100%) with a concentration of 50 mg l^{-1} Br^- as suggested by Sinaj et al. (2002) and (Kang et al. 2011) (total Br application of 5,000 mg), and potassium dihydrogen phosphate (KH_2PO_4, Carl Roth, Germany, >99%) with a concentration of 0.66 g l^{-1} KH_2PO_4. This equals a total application of 50 kg ha^{-1} P.

Before and after the irrigation, we collected around 300 g soil samples. Five samples were taken every five centimeters up to a depth of 0.6 m. The pre-irrigation samples were taken 0.3 m away from the irrigation area while the post-irrigation samples were taken directly under the irrigation area. The soil samples were analyzed for plant-available P (DL-extractable P, (Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten e.V. 1991) and for organic content (loss on ignition, Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten e.V. 1991). Both analytical approaches were done in the lab by the Agricultural Analysis and Research Institute (LMS-LUFA).

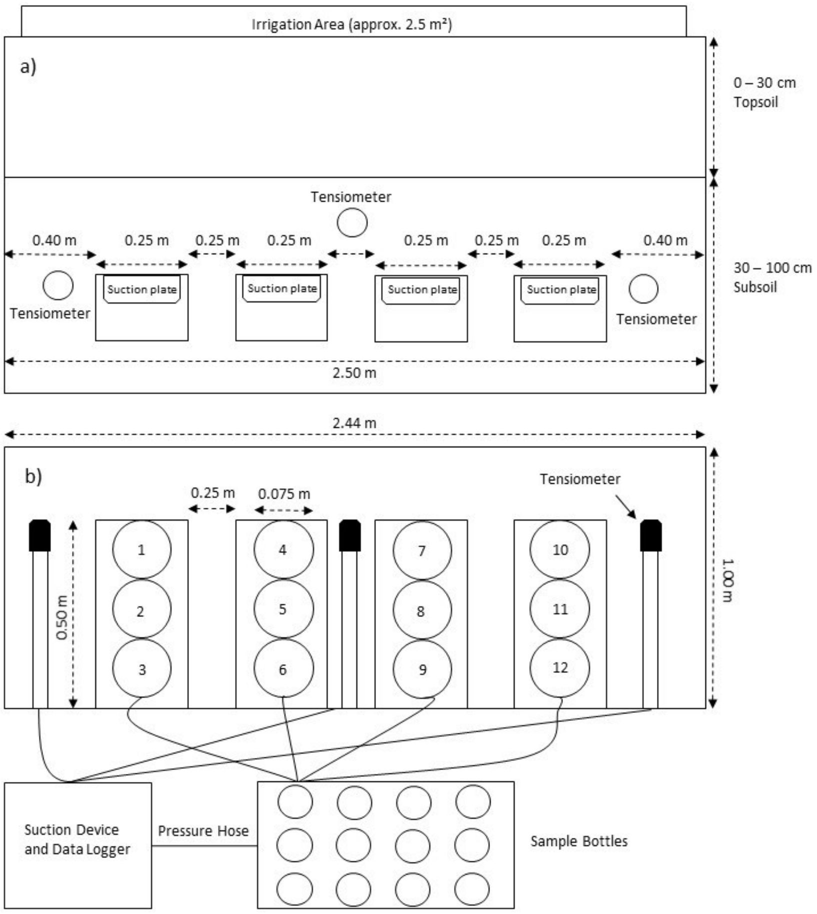

Figure 7-1: *Experimental setup with (a) cross-section of the soil profile, and (b) plan view of the setup at 0.60 m depth*

The collected pore-water samples were subdivided into two subsamples. One subsample was then immediately filtered in the field with a 0.45 µm cellulose acetate membrane filter. The filtered sample was subdivided into two subsamples for the investigation of Br and DRP. The samples were stored in the fridge for at least 10 hours after sampling. The concentrations of bromide were determined using ion chromatography (Metrohm AG, Herisau, Switzerland) after chemical suppression to reduce the self-conductivity of the sample (Bauwe et al. 2015). DRP concentrations were measured by dying them with ammonium heptamolybdate and analyzing them photometrically (Specord40, Analytic Jena). TP concentrations of the unfiltered samples were likewise measured photometrically after oxidation in alkaline medium in a microwave (CEM GmbH, Kamp-Lintfort).

7.2.3 Statistical Analyses

We used simple time-variation curves to visualize the temporal variability of Br, DRP, and TP concentrations. The concentrations were also plotted over the exchanged pore volume. We calculated the loads of each lysimeter plate by summarizing the product of concentration and sample volume at a given time. Unequally distributed sample groups were compared using a Mann-Whitney-U test.

The loads of Br and P were calculated as the product of the sample volume and the measured concentration.

7.3 Results and Discussion

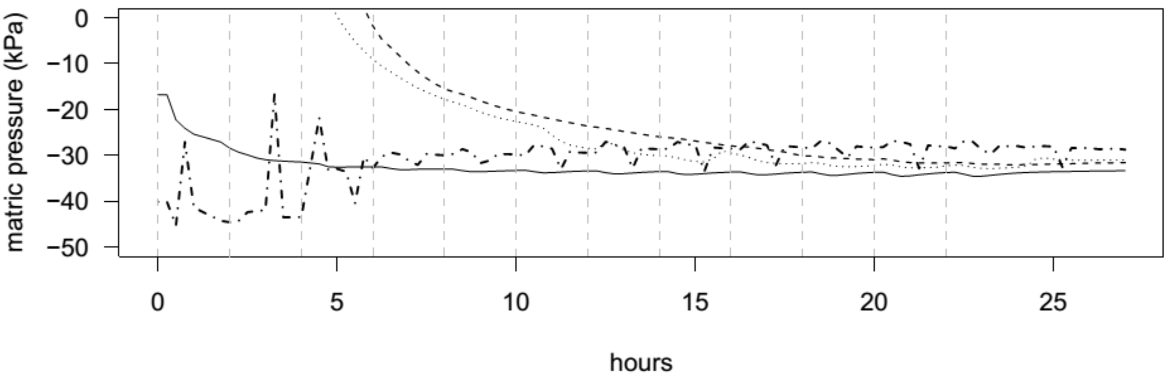

Figure 7-2: *The measured matric pressure at all three tensiometers (solid, dashed, and dotted lines), and the applied suction to the lysimeter plates (semicolon line). The vertical grey dashed lines represent the irrigation events.*

Although we simulated severe rainfall events, the first response of the two tensiometers took five hours (Figure 7-2). The logged measured suction at the tensiometers did not reflect the actual suction at the lysimeter plates. Positive values with the tensiometers can only occur if pore water is forced into the soil under pressure. We assumed that the low initial water content (-16 kPa) of the soil led to high pressure after the installation of the tensiometers using a soil-water suspension. This positive pressure was not released within 24 hours. Hence, we had to apply an almost constant pressure of about -300 hPa. The regularly occurring drops in the suction were caused by the opening of the sample bottles.

The patterns of the bromide concentrations in the filtered pore water were admirably homogenous (Figure 7-3). After an early peak, three to five hours after the initial irrigation event, the concentrations decreased markedly with a prolonged tailing over all the observed lysimeter plates. In all, we recovered 30.91 mg of the applied bromide, which corresponds to a recovery rate of 0.062%. Converted to an application area equal to the strained lysimeter area, we achieved a recovery rate of 29.2%. Bromide leaching patterns, with early peaks in Br concentrations, have been observed earlier in a field lysimeter study (Sinaj et al. 2002).

The observed patterns of DRP and TP appeared somehow random (Figure 7-3). We did not detect a concentration peak or the tailing of the breakthrough curves. Earlier studies did not confirm these patterns. A zero-tension lysimeter experiment showed early peaks of TP and a strong correlation to the flow rate (Messing et al. 2015). Only 0.08% and 0.07% of the applied 12.5 g P was recovered by the lysimeters in terms of DRP and TP. This equals $2.12 \cdot 10^{-3}$ g and $1.89 \cdot 10^{-3}$ g respectively.

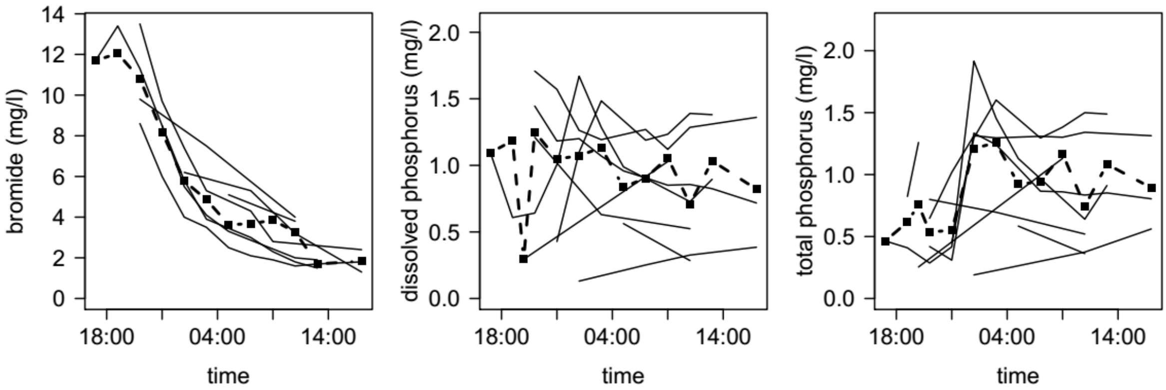

Figure 7-3: *Time-variation curves for bromide, dissolved reactive phosphorus, total phosphorus at each lysimeter (fine solid lines), and mean concentration for all lysimeters (bold, dashed line). Please note the different y-axis for bromide.*

Lab experiments with soil columns have often showed that bromide concentrations peak within the exchange of one pore volume of soil water. The early peaks in the exchanged pore volume in all the lysimeter plates in the first half (Figure 7-4) are strong indicators of preferential flow (Seyfried & Rao 1987, Gharabaghi et al. 2015). However, we expected a higher variability in the occurrence of preferential flow in the soil (see chapter 6).

The patterns of DRP and TP showed a higher variability (Figure 7-4) than Br. However, we noticed that the concentrations of DRP and TP were not significantly different ($p>0.1$, Mann-Whitney-U-test), and surprisingly, collinear. At some points, the DRP concentrations were even larger than the measured TP concentrations. This error can be attributed to laboratory errors as damages in the filter material, polluted chemicals, or errors in the aliquots. We could not delete these errors in time; so we had to incorporate them into this chapter.

However, the strong collinearity and the resemblance of DRP and TP seem to reveal that we could not cover singular macropores by the suction plates, and the observed transport patterns are pathways for solutes only. Although this explanation is reasonable, some problems may also have occurred in the membrane of the suction plates. Although pretests by Ecotech showed that all the plates were working properly, we assumed that either the applied suction was too low to extract the colloids and clay particles within the pore water or the membrane got occluded with clay minerals during our experiment.

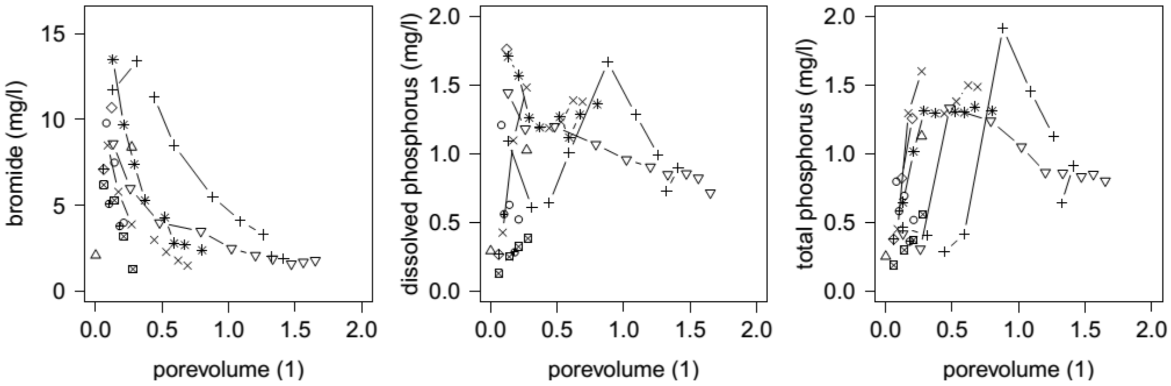

Figure 7-4: *Bromide, dissolved reactive phosphorus, and total phosphorus in relation to the exchanged pore volume. Please note the different y-axis for bromide.*

There are at least three reasons for the disappearance of solutes in soils: runoff, plant uptake, and preferential flow (Caron et al. 1996). Plant uptake might be negligible, since the duration of our experiment was only three days. However, the rates of Br uptake might differ under different crop types in one growing season. Although maize could take up 8.1% of the applied Br (Tilahun et al. 2006), potato plants were responsible for a 53% disappearance of Br (Kung 1990). The losses through surface runoff may also be negligible. The hill slope at our experimental plot was low (less than 2%), and the installed wooden collar likewise reduced surface runoff. We assume that most of the losses in our experiment were caused by preferential and lateral flow. As shown in chapter 6, we could clearly demonstrate the presence of preferential pathways for solute and colloid transport in the loamy soils at our study site.

Surprisingly, the soil P content in the topsoil and subsoil did not change significantly during the experiment (Mann-Whitney-U test, $p>0.1$, Figure 7-5 left panel). The DL-extractable P content is classified as soil content class C according to the recommendations of the VD-LUFA (see Table 5-4, Kerschberger et al. 1997). Class C with soil P contents of 4.5 to 9.0 mg P/100 mg soil is the intended target value. Hence, conservation fertilizer management is recommended. However, the observed pattern, with higher soil P contents in the topsoil and lower contents in the subsoil, has been observed at other sites, too (Dong et al. 2012). Severe decreases with increasing soil depths have also been reported for the topsoil only (Owens et al. 2008, Dong et al. 2012). We assume that the correlation of organic matter content and DL-extractable P (Figure 7-5 right panel, linear model, $r^2=0.91$, $p<0.001$) reflect the adsorption potential of loamy soils rich in organic matter. The low soil P contents of the subsoil show that P, after organic or inorganic fertilizer application, is not transported by matrix flow in deeper layers. We assume that a substantial part of the P is bound to organic compounds and re-mobilized by plant uptake. However, another noticeable fraction of the applied P might bypass the soil matrix via preferential flow (Fuchs et al. 2009).

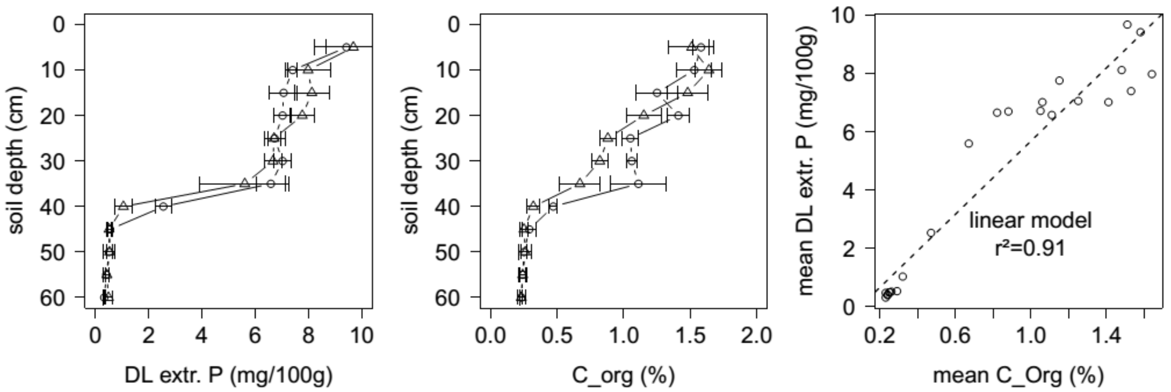

Figure 7-5: *Left and middle: DL-extractable P and the content of organic carbon in relation to soil depths before (circles) and after (triangles) the experiment. No significant changes were detected ($p>0.1$, Mann-Whitney-U test). Right: Relationship of mean contents of organic carbon and DL-extractable phosphorus ($r^2=0.91$, $p<0.001$, linear regression model).*

However, by repeating parts of the experiment in the laboratory, we recognized that a considerable portion of the applied K_2HPO_4 did not dissolve in the irrigation water because of the low temperatures in the field. This idea is also supported by the fact that the soil P contents did not change significantly during the experiment. Thus, we expect that the observed P transport patterns are the result of re-mobilized and leached dissolved reactive P by repeated severe rainfall.

Table 7-2: *Total loads (mg) of bromide, dissolved reactive phosphorus, and total phosphorus in each lysimeter.*

	Lysimeter Number											
	1	2	3	4	5	6	7	8	9	10	11	12
Bromide	1.64	0.92	0.00	10.60	2.76	1.36	5.92	1.17	0.00	5.21	0.46	0.88
DRP	0.19	0.12	0.00	1.63	0.86	0.22	1.80	0.08	0.00	1.16	0.02	0.09
TP	0.15	0.12	0.00	1.50	0.95	0.21	1.65	0.10	0.00	1.00	0.02	0.09

The spatial variation of the overall loads was large between all lysimeters (Figure 7-6) for Br, DRP, and TP. We detected a gradient from the furthermost point in the well to the profile wall with the highest concentrations at the furthermost point for Br, DRP, and TP. Although the concentrations measured at each lysimeter were quite homogeneous (Figure 7-3)—especially in the case of Br—the loads reveal a marked variability. We assume that this can be attributed to the differences in the sampled water volume. A noticeable portion of the applied water close to the profile wall might have been lost through lateral flow through the profile wall before it reached the depth of the lysimeters.

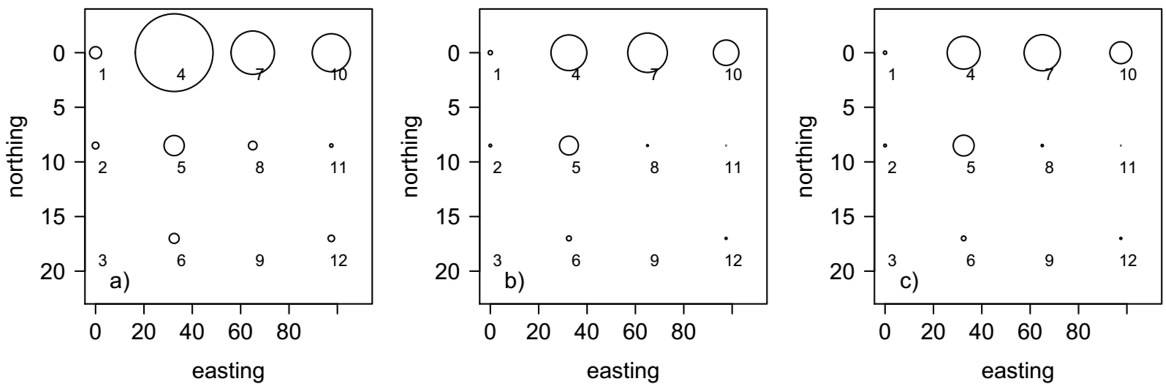

Figure 7-6: *Location plots of the lysimeters. The size of the circles is proportional to a) the loads of bromide, b) the loads of dissolved reactive phosphorus, and c) the loads of total phosphorus; b) and c) are super-elevated for better visualization.*

7.4 Conclusion

Although we detected some severe difficulties and weaknesses in the experimental setup and procedure, we learned that the potential for P leaching from agricultural soils may be large. The concentrations in the pore water samples exceed the concentrations measured in the tile drains at the same site (chapter 5) up to factor four. There were no changes in the P content of the soil during our experiment. Thus, we assume that the groundwater may be strongly P-laden though there is much P adsorbed into clay minerals and organic matter in the topsoil.

A repetition of the experiment will deliver more information on the preferential transport of DRP and TP after fertilizer application. However, the newly acquired knowledge will implicate some changes in the experimental setup.

i. Installation of the tensiometers prior to the experiment followed by a saturation and a drying phase of the soil prior to the experiment
ii. Preparation of a tracer solute in the lab with an ultrasonic bath
iii. Deeper wells to install the lysimeters deeper into the profile wall (or maybe the use of just two lysimeters per profile well (as described by Ciglasch et al. 2005)

More research is needed to understand the small-scale spatial and temporal variability of P loss and the quantification of P loss through preferential flow after rainfall events and at baseflow.

Acknowledgements

I kindly acknowledge the help of our field workers Robert Müller and Stefan Kopperschmidt. We would likewise thank Evelyn Bolzmann and Maria Holzkamm for laboratory analysis. The author gratefully acknowledges the German Federal Ministry of Education and Research (BMBF) for funding the BonaRes project InnoSoilPhos (No. 031A558).

8 Synthesis and Outlook

8.1 Current developments of the SWAT model regarding tile drainage and P modeling

Eco-hydrological modeling with SWAT has developed tremendously since the publication of the article presented in chapter 3. Nowadays, efforts are being made for the plausible quantification of flow pathways. Complex hydrological models like the Soil Water Assessment Tool (SWAT) distinguish the overall runoff of a certain stream into defined flow compartments. The flow compartments calculated in the SWAT model are surface runoff, lateral flow, groundwater discharge/baseflow, and the tile drainage discharge. Remarkable emphasis is given to the realistic estimation of surface runoff and drainage discharge.

Although some problems cropped up with the estimation of different flow pathways (Chapter 3, discussions section) in our model setup, we could clearly show that drainage discharge contributed markedly to the overall discharge of the sub-basin streams of the Warnow river basin. Furthermore, we found a strong positive relationship (r^2=0.69 and 0.71 for validation and calibration period respectively) of drainage discharge and the drained area. The overall variation of the tile drainage contribution was large (0.3 to 31.9%). However, there is evidence that the SWAT model can estimate realistic flow pathways. In a Danish watershed, the tile drainage discharge contributed 37% to the overall streamflow whereas baseflow, lateral flow, and surface runoff added another 45%, 3%, and 15% respectively (Lu et al. 2015). Furthermore, the quality of modeling the tile drainage discharge was large, with Nash-Sutcliffe efficiencies greater than 0.6 for calibration and validation period using the SWAT model (Lu et al. 2016). A high contribution of drainage discharge to the overall runoff was also found in the north-western German catchment area (Pfannerstill et al. 2014). The authors developed a multi-storage groundwater concept for the SWAT model which introduces both a fast and a slow groundwater flow component. The combination of this concept with the newly-established P routines seems reasonable since groundwater may have been an overlooked contributor to riverine P concentrations (see below).

The input of sediment-bound P to rivers via surface runoff is well studied. However, the literature and our study presented in chapter 5 clearly showed the relevance of sediment and dissolved nutrient (i.e. phosphorus) transport within the soil through internal erosion processes. Although the SWAT model has no tile-drainage P routine (Radcliffe et al. 2015) and was not specifically developed to model P losses from tile-drained agricultural fields (Kleinman et al. 2015b), SWAT was extensively used to model P loads in rivers on the watershed scale, including a tile-drainage flow component. However, no studies on the tile drainage P transport from agricultural fields have been published yet. The implementation of a functional tile-drainage P routine to the SWAT model is, therefore, a crucial future task since N and pesticide losses have already been modeled in tile-drained watersheds (Du et al. 2006, Moriasi et al. 2013).

Watershed scale modeling will become more and more important. Authorities and stakeholders frequently ask scientists to deliver guidelines and strategies for land-use management and the mitigation of elevated nutrient losses. This request may increase in the future, and large-scale eco-hydrological models represent a suitable tool. Nevertheless, the SWAT model is a valuable tool to understand the hydrology of agriculturally used lowland watersheds.

8.2 The relevance of event-based phosphorus transport in the eutrophication risk of surface waters

The presented studies have shown that peak flow events play an important role in the release of P across all the observed spatial scales. In chapter 6 and chapter 7, we observed the direct effects of the preferential flow to the transport of solutes on the plot scale. Chapter 6 revealed that even particles may be potentially transported by preferential flow to the subsoil. However, chapter 4 exposed that these effects are also detectable on a larger spatial scale (3,000 km^2). Our studies indicate that peak flow events have the potential to leach large amounts of solutes and particle-bound nutrients (e.g. DRP and TP) from agriculturally used areas. This is in contrast to the findings of earlier scientific contributions that emphasized the importance of surface runoff for P leaching (Nash et al. 2015, Bhadha et al. 2016). Our results are, nonetheless, supported by findings from a watershed study which revealed a hydrological control of inter-annual variability of P release to rivers (Zhang et al. 2016).

Recently, the impact of artificial subsurface drainage and internal soil erosion on riverine P loads has been more in the focus of research. A strong rainfall event of 64 mm h^{-1} leads to large increases in DRP and TP in runoff concentrations immediately after manure application on sandy loam (Eighball et al. 2002). However, 45 minutes later, the concentrations decreased to the pre-manure level. A second similar rainfall event—applied a day later—did not show likewise increases in DRP concentrations. Nevertheless, the potential of DRP losses after rainfall following organic or mineral fertilizer application is large (Eighball et al. 2002, Hahn et al. 2012, Williams et al. 2016).

Although problems occurred in the execution of our suction lysimeter experiment, we found evidence of preferential transport of solutes in the investigated loamy soil. Additionally, there is a potential for the leaching of particulate phosphorus which was revealed by the dye-tracer experiment using Titanium(IV) oxide. Due to the distribution of P in the soil, it can be assumed that most colloid-bound P (i.e. particulate P) in drains comes from the topsoil (Laubel et al. 1999, Chapman et al. 2001). A case study on the effect of rainfall events on the transfer of particulate P (PP) and DRP also showed that the concentrations of PP and DRP were the highest in the initial drainage flow. A large proportion of the investigated drainage flows on agricultural land shows high amounts of PP, which indicates a high contribution of preferential rather than matrix flow (King et al. 2015b).

It should be noted that only the results of the tilled soils were presented here. The conditions on no-till soil can be rather different. No-till soils develop a stable and persistent structure of biogene macropores in which preferential transport of particulate P can occur (Williams et al. 2016). From this, we can conclude that grasslands, in which tillage is only infrequently applied, are even more vulnerable to (particulate) P leaching than acre (Stamm et al. 1998, Hooda et al. 1999).

The relevance of a preferential flow for P leaching implies that a large fraction of the totally transported P is transported during short events. In our regional study (chapter 5), we found 15% to 77% of the DRP loads and 49% to 68% of the total seasonal loads transported to streams in just a few severe rainfall and discharge events. The large contribution of single or multiple rainfall events to the annual or seasonal loads is confirmed by other studies (Tiemeyer et al. 2009, Tomer et al. 2016).

Only high-frequency measurements will give detailed process-based insights into the relationship between rainfall and phosphorus concentrations in drainage/stream effluent and management measures (e.g. tillage or manure/fertilizer application) (Rozemeijer et al. 2016). For example, high-frequency measurements allowed the detection of different pathways of P release, which could be assigned to the relationship of DRP concentrations and discharge (Bowes et al. 2015). Although the authors found that the contribution of sewage treatment effluent is dominant in the investigated watershed, they could demonstrate that at high flow events, tile drainages and re-mobilized bed sediment are additional substantial sources of riverine P.

8.3 Sediments and phosphorus pools in catchments

Sediments in rivers are highly variable in hydro-physical and chemical properties, depending on the origin of the sediment. For instance, they may be strongly laden with particle-bound P. A study in three different watersheds (USA, Britain, and China) showed that the potential of re-mobilization in rivers is large (Powers et al. 2016). The authors stated that human-dominated river basins undergo a prolonged P-accumulation phase. The accumulated P continues being mobilized a long time after the inputs decline. A comprehensive review mentioned stream banks as "a net source of sediment and phosphorus to streams and rivers" (Fox et al. 2016). It was concluded that the dynamic interactions between the different P-pools (e.g. soil and sediment) have to be understood. However, the authors observed a large uncertainty in the reviewed studies. The observed portion of sediment P contributing to the total P loads of the receiving waters ranged from 6% to 93%. However, even with similar hydrology, geomorphology, and land use, there is a large uncertainty in the estimation of streambank P contributions because of watershed-specific variability in streambank erodibility and streambank P concentrations (Purvis et al. 2016). For instance, we observed hints of a rapid sedimentation even at high discharge events (chapter 5). We assume that the hydraulic properties of a stream (roughness, streambed properties and plant cover) play an important role in sedimentation or re-mobilization.

Furthermore, there is evidence that the runoff concentrations of P are strongly influenced by the initial soil P content (Sharpley 1995, Hahn et al. 2012). In this context, the loss of P has been found to be more sensitive to soil P content than to the application of manure (Hahn et al. 2012). However, even groundwater was mentioned as a substantial source of P to rivers and streams. It is affected by human activities and may exceed ecologically significant thresholds (Holman et al. 2008).

We assumed that only a full budget of P-pools in the watershed will give detailed insights into the main processes of P release into the receiving waters at peak flow events. The considered pools should be soil P, groundwater P, bed sediment P, and riverine P. Further research is needed on the interaction of these pools.

8.4 The effect of spatial scale on the assessment of phosphorus losses

The consideration of spatial scales is crucial for the assessment of freshwater hydrology and water quality. Many studies have focused on the plot and field scale where tile drainage discharge was not related to the catchment scale runoff (Turtola & Paajanen 1995). Tile drainage and the following drainage ditch are spatially closely related. However, the behavior of P transport is unique on both scales (see chapter 5).

The effect of tile drainage on P transport has been discussed earlier. Many soil properties, and land use and management strategies affect the amount of P that is released by tile drainage. In chapter 5, we could clearly show that tile drainage is a serious contributor to the transport of particle-bound P to surface waters with TP concentrations three times higher than DRP concentrations. The overall contribution of the events to the seasonal DRP and TP export was 48% and 50% respectively.

The variable behavior of drainage ditches as a sink or source of available P have been observed by Smith et al. (2005). There was a lower potential for P retention in the sediment with increasing drainage area (i.e. downstream), which was attributed to an increase in particle size and decrease in organic matter content downstream (Smith et al. 2005). Although we would expect lower particle sizes and higher organic matter content downstream, the authors state that, in that particular case, the low flow velocity and low energy to transport particles in the ditches (i.e. stagnant waters) was responsible for this phenomenon. However, there are also findings that revealed a downstream mobilization of P (Nausch et al. 2017, Fox et al. 2016). The authors observed an increase in TP concentrations in the drainage effluent and the adjoining measurement stations downstream (e.g. with increasing drainage area), and deduced the influence of livestock farms and human settlements. In contrast, in our streaming system, we observed a net sedimentation and no significant increases of DRP and TP concentrations with increasing drainage area. The TP:DRP ratios decreased with increasing catchment size, indicating sedimentation processes. However, a re-mobilization of sediments in larger streams has been observed frequently (Grundtner et al. 2014, Fox et al. 2016), (Purvis et al. 2016). Thus, we emphasize that the remobilization of bed sediment may also be a key factor for future P research.

It has been found that upstream land use may have a more influential effect on larger streams while local land use may be more important in smaller rivers (Buck et al. 2004). In chapter 5, we could clearly prove the effect of spatial scales on P transport in surface waters, despite the non-daily temporal resolution of the data. The marked decrease of P release per hectare indicates that measurements at just one spatial scale could strongly bias the results and the detectable processes of measurement campaigns and high-frequency measurements at multiple spatial scales will give insights into spatially distributed processes.

Although the detection of the drivers of P release at the watershed scale may be challenging, in chapter 4, we could demonstrate that the transport of TP is event-driven while the transport of DRP follows a baseflow component. These findings are supported by our local study at the tile drainage scale (chapter 5), which clearly showed the event-based release of TP through tile drains. The watershed scale is, in fact, interesting to assess in terms of risk assessment for receiving coastal waters. However, as stated earlier, process research demands a variety of smaller spatial scales from the soil profile to the sub-basin scale. It can be concluded that the detailed knowledge of watershed characteristics, land use, topography, morphology, and sediment characteristics is needed to assess the fate of P in agricultural catchments.

We conclude that the monitoring concepts should be sensitive to spatial scales. This idea is supported by (Buck et al. 2004), who stated that land use is more influential in larger streams. The knowledge of the spatial variability in the P-pools in a watershed, particularly, the soil P-pool and the bed sediment pool, will be helpful in nutrient management (Liu et al. 2016). However, since we showed that event-based P transport is a marked contributor to the overall release of P into surface water, we assume that a higher temporal resolution should be considered in the monitoring of river nutrient status.

8.5 The future of P research: Facing eutrophication and phosphorus scarcity—Management strategies to improve freshwater quality in rivers and streams and the re-use of phosphorus resources

The concentrations of DRP and TP in the Warnow River and its tributary streams decreased significantly between 1990 and 2010 (see chapter 4). However, the concentrations are sometimes still elevated in terms of the intended target values for a good water quality (Länderarbeitsgemeinschaft Wasser 1998). We need a comprehensive and detailed understanding of all the processes involved in the leaching of P from agricultural soils to effectively mitigate P loss and increase the P-use efficiency.

On the one hand, as explained extensively in chapter 1.3.7 and 1.3.9, excessive loss of P to surface waters by tile drains is a critical driver of freshwater eutrophication, as well as the eutrophication of the receiving coastal waters. Therefore, a removal of the dissolved and particulate P from drainage effluent and rivers and streams is a crucial task to obtain and restore a good ecological status of surface waters. For instance, P losses from drainage discharge might be reduced by managed drainage. Managed drainage is characterized by a marked reduction of the annual drainage discharge. It was observed that this measure can reduce the DRP loss in drainage discharge up to 80% (Nash et al. 2015). However, further research is needed on this. Rozemeijer et al. (2016) stated that the positive effect of controlled drainage on tile-drainage P losses may be counteracted by higher groundwater tables in the field, and a higher contribution of shallow groundwater N and P, and surface runoff to surface waters.

On the other hand, the use of soluble mineral fertilizers from mined phosphate taken from only a few places worldwide has led to a geographical imbalance in P distribution in agricultural landscapes compared to natural ecosystems (George et al. 2016). The need for improved technologies to reduce P demand and P loss from agricultural lands, as well as the development of sustainable and economically utilizable P recovery from surface waters and sediments, arise as a result of year-long mismanagement and the expected depletion of the Earth's phosphate-natural P resources. There is an ongoing debate about the definite point of P exhaustion. The size of the resources is uncertain but practically finite (Reijnders 2014). Many references see peak phosphorus—the point of the global maximum P mining rate, in accordance to the term "peak oil"—coming within the next 15 to 30 years (Cordell et al. 2009, Soil Association 2010, Walan 2013). Thus, a reduction of P inputs in the agricultural sector is indispensable to provide food security to future generations.

Although the demand for a broad P reduction in rivers and streams is reported frequently, several watershed scale studies indicate the importance of considering the lag time between installing P reduction measures and the actual improvement of water quality (Zhang et al. 2016).

The measures to achieve these goals are removal techniques (e.g. filter materials) and the recovery of P for reuse. These techniques are frequently studied and investigated. A general idea is to use the P stored in the effluent, sludge, and sludge ashes of sewage treatment works operating with P precipitation (Desmidt et al. 2014). This recovered material can be used as a primary and sustainable resource for fertilizer production (de-Bashan & Bashan 2004, Shepherd et al. 2016).

Feasible measures to clear drain waters from P are constructed wetlands. Constructed wetlands are artificial ponds, buffer strips, or wetlands that retain the tile drainage water before draining these into the receiving surface waters. The cleaning performance of the constructed wetlands is highly controlled by the residence time of the water in the wetland (Reinhardt et al. 2005). The authors showed that up to 50% of the incoming DRP load is retained when the residence time exceeds seven days. A comprehensive review of the effect of the different types of constructed wetlands is at hand (Land et al. 2016).

A third option for the extraction of P from drainage or drainage ditch water are bioreactors or other methods of using filter materials to adsorb P. Woodchips can be used to adsorb significant amounts of P from artificial subsurface drainage (Hua et al. 2016). Although woodchips have the ability to sustain de-nitrification and clean drainage water from nitrate, their ability to adsorb P is large. A study revealed that 71% of the TP from agricultural water was removed by a woodchip filter system (Choudhury et al. 2016). However the quality of the filter materials is about to change. Fe-hydroxides and Seashell filter materials showed a larger retention rates with lower mobilization rates at all observed flow rates (Canga et al. 2016). Of course, other filter materials, such as biochar, are available, which also have a large P-sorption capacity (Kholoma et al. 2016). However, being more extensive at this point would be beyond the scope of this study.

Astonishingly, attempts have been made to decrease riverine P loads by adding managed nitrate to surface waters. The advances in this method were recently reviewed (Beutel et al. 2016). It was reported that adding nitrate to P-laden waters could significantly reduce the total P and chlorophyll content. The nitrate has to be placed at the boundary of water and sediment to enhance de-nitrification. Other preconditions for this method can be found in (Beutel et al. 2016).

Cordell et al. (2011) posited that no single solution will achieve a P-secure future. The authors stated that besides an improved P-use efficiency, there is a need for a maximum recovery and reuse from all current waste streams throughout the food production and consumption systems.

The need for P research to mitigate coastal and freshwater eutrophication has often been propagated (Ansari & Gill 2014, van Wijnen et al. 2015, Dodds & Smith 2016). A strong emphasis is given to iterative application of P fate and transport, coupled with the demonstration of tradeoffs to local stakeholders (Kleinman et al. 2015). It has also been stated that a holistic approach is needed for combating eutrophication, including other nutrient and pollutant controls than P and physical river restoration (Jarvie et al. 2013).

Not to be scoffed at is the future contribution of climate change to the export of P. As we could clearly demonstrate in all our studies, quick flow events and preferential flow are major pathways of P to surface waters. It is highly likely that with the current knowledge of climate change, we can expect an increase in the number of severe rainfall events (Palmer & Räisänen 2002, Zebisch et al. 2005).

A further key question is the interaction of nitrogen with P in runoff and in the river. It has been found that elevated N increases P uptake by sediment and microbial biomass, and that climate change may also have a recognizable effect on it (McDowell et al. 2017).

However, my personal research follows a process-based approach, which is owed to the lower concentrations of P in the observed watershed and, thus, the low mitigation and recovery potential. However, we could clearly demonstrate that agricultural drainage has a large impact on the measured river streamflow. The evaluation of long-term data showed that this (fast) flow component contributes largely to the overall TP load in the Warnow river basin. Furthermore, we could visualize the potential of preferential flow for particulate P loss, which might play an important role in soil internal erosion of particle-bound P to tile drains and, hence, to the receiving waters. Unfortunately, due to technical problems, our lysimeter study did not give clear evidence of the large potential that preferential flow has for the transport of TP through the soil. Based on our findings and some new interesting findings from the literature, future research should focus on the riverbed sediment. Long-term re-mobilization of river sediments to surface waters in strongly industrialized and human-formed watersheds has been shown by (Powers et al. 2016)), and recently attested by (Purvis et al. 2016). The dynamic interaction among the different landscape P-pools is, thus, of considerable scientific interest (Fox et al. 2016).

The spatio-temporal dynamics of the interactions between the P-pools of soil, sediments (Fox et al. 2016), groundwater, and surface water are not yet fully understood. The variety of P-pools and their contribution to the overall loads of P in the rivers, in terms of DRP and TP, might be, therefore, an interesting approach in future P research. Even groundwater may contribute largely to surface-water eutrophication, particularly in lowland catchments (Holman et al. 2008), since lowland catchments have high groundwater tables and high fluxes of groundwater to receiving waters. In the context of spatial and temporal effects, Zhang et al. (2016) emphasized the importance of long-term river monitoring on the watershed scale.

The future of P research should emphasize on mitigation strategies, removal and recovery techniques, and the reduction of societal P inputs in areas where P concentrations in rivers and P stocks in the soils are high. Many national and international research projects focus on P in environmental cycles, on both fundamental research and socio-economical evaluation. To name only a few, these are the projects that my research is associated with:

i. InnoSoilPhos—Innovative Solutions to Sustainable Soil Phosphorus Management

   Funded by the Federal Ministry of Education and Research, Germany
   Focus on a variety of spatial scales

ii. NuReDrain (Nutrients Removal and Recovery from Drainage Water)

   Funded by Interreg—North Sea Region
   Focus on P reduction and recovery techniques using different filter materials

P is in the focus of interest of all natural sciences, displayed by the development of the Leibniz ScienceCampus Phosphorus Research at the University of Rostock. The ScienceCampus was founded to find solutions to the challenges of limited P availability, improper use of P inventories of soils, and the environmental impacts. At the time of the completion of this thesis, 26 research projects were recorded at the ScienceCampus. Additional information about projects and the partners of the campus can be found on their webpage (https://wissenschaftscampus-rostock.de/research/projects.html).

A large interdisciplinary research initiative on the global scale is The Global Phosphorus Research Initiative (GPRI). The GPRI is a collaboration of independent scientists and research institutes in Europe, North America, and Australia. Detailed information on ongoing projects, recent publications, and the aim of the GPRI can be found on their webpage (phosphorusfutures.net). The GPRI has a stronger focus on P scarcity and the need of P for the production of food.

9 References

Abbaspour KC, Vejdani M, Haghighat S (Hrsg) (2007) SWAT-CUP Calibration and Uncertainty Programs for SWAT. Society of Australia and New Zealand.

Abbott CL, Leeds-Harrison PB (1998) Research priorities for agricutlural drainage in developing countries; TDR Project R6879, Report OD/TN92. Cranfield University. http://books.hrwallingford.co.uk/acatalog/od_downloads/odtn92.pdf. last checked: 17. August 2016.

Adesemoye AO, Torbert HA, Kloepper JW (2009) Plant growth-promoting rhizobacteria allow reduced application rates of chemical fertilizers. Microbial Ecology 58:921–929.

Algoazany AS, Kalita PK, Czapar GF, Mitchell JK (2007) Phosphorus transport through subsurface drainage and surface runoff from a flat watershed in east central Illinois, USA. Journal of Environmental Quality 36:681–693.

Andersen JH, Carstensen J, Conley DJ, Dromph K, Fleming-Lehtinen V, Gustafsson BG, Josefson AB, Norkko A, Villnas A, Murray C (2017) Long-term temporal and spatial trends in eutrophication status of the Baltic Sea. Biological Reviews of the Cambridge Philosophical Society 92:135–149.

Andreini MS, Steenhuis TS (1990) Preferential paths of flow under conventional and conservation tillage. Geoderma 46:85–102.

Ansari AA, Gill SS (Hrsg) (2014) Eutrophication; Causes, consequences and control. Springer Science+Business Media, Dordrecht.

Arheimer B, Lidén R (2000) Nitrogen and phosphorus concentrations from agricultural catchments—influence of spatial and temporal variables. Journal of Hydrology:140–159.

Arnold JG, Moriasi DN, Gassmann PW, Abbaspour KC, White MJ, Srinivasan R, Santhi C, Harmel RD, van Griensven A, van Liew MW, Kannan N, Jha MK (2012) SWAT: Model use, calibration and validation; Model Use, Calibration, and Validation. Transactions of the ASABE 55:1491–1508.

Arnold JG, Srinivasan R, Muttiah RS, Williams JR (1998) Large area hydrologic modeling and assessment part I: Model development. Journal of the American Water Resources Association 34:73–89

Arnold JG, Srinivasan R, Muttiah RS, Williams JR (1998) Large are hydrologic modelling and assessment partI: Model development. Journal of the American Water Resources Association 34:73.

Awotwi A., Kumi, M., Jansson PE, Yeboah F, Nti IK (2015) Predicting Hydrological Response to Climate Change in the White Volta Catchment, West Africa. Journal of Earth Science & Climatic Change 6.

Bahnwart M, Hübener T, Schubert H (1999) Downstream changes in phytoplankton composition and biomass in a lowland river-lake system (Warnow River, Germany). Hydrobiologia:99–111.

Bacu V, Mihon D, Rodila D, Stefanut T, Gorgan D (2011) Grid based architectural components for SWAT model calibration 2011 International Conference on High Performance Computing & Simulation. IEEE, S 193–199.

Baker DB, Richards RP, Loftus TT, Kramer JW (2004) A new flashiness index: Characteristics and applications to midwestern rivers and streams. Journal of the American Water Resources Association 40:503–522.

Balemi T, Negisho K (2012) management of soil phosphorus and plant adaptation mechanisms to phosphorus stress for sustainable crop production: a review. Journal of Plant Nutrition and Soil Science 12:547–561.

Bates TR, Lynch JP (2000) Plant Growth and Phosphorus Accumulation of Wild Type and Two Root Hair Mutants of Arabidopsis thaliana (Brassicaceae). American Journal of Botany 87:958.

Bauwe A, Tiemeyer B, Kahle P, Lennartz B (2015) Classifying hydrological events to quantify their impact on nitrate leaching across three spatial scales. Journal of Hydrology 531:589–601.

Behrendt H, Bachor A (1998) Point and diffuse load of nutrients to the Baltic Sea by river basins of North East Germany (Mecklenburg-Vorpommern). Water Science and Technology 38:147–155

Beutel MW, Duvil R, Cubas FJ, Matthews DA, Wilhelm FM, Grizzard TJ, Austin D, Horne AJ, Gebremariam S (2016) A review of managed nitrate addition to enhance surface water quality. Critical Reviews in Environmental Science and Technology 99:1–28.

Bhadha JH, Lang TA, Daroub SH (2016) Influence of suspended particulates on phosphorus loading exported from farm drainage during a storm event in the Everglades Agricultural Area. Journal of Soils and Sediments.

Blann KL, Anderson JL, Sands GR, Vondracek B (2009) Effects of Agricultural Drainage on Aquatic Ecosystems; A Review. Critical Reviews in Environmental Science and Technology 39:909–1001.

Bonsdorff E, Blomqvist EM, Mattila J, Norkko A (1997) Coastal eutrophication: Causes, consequences and perspectives in the Archipelago areas of the northern Baltic Sea. Estuarine, Coastal and Shelf Science:63–72.

Borah DK, Bera M (2004) Watershed-Scale Hydrologic and Nonpoint-Source Pollution Models; Review of Applications. Transactions of the ASAE 47:789–803.

Bowes MJ, House WA, Hodgkinson RA, Leach DV (2005) Phosphorus-discharge hysteresis during storm events along a river catchment: the River Swale, UK. Water Research 39:751–762.

Bowes MJ, Jarvie HP, Halliday SJ, Skeffington RA, Wade AJ, Loewenthal M, Gozzard E, Newman JR, Palmer-Felgate EJ (2015) Characterising phosphorus and nitrate inputs to a rural river using high-frequency concentration-flow relationships. Science of The Total Environment 511:608–620.

Bowes MJ, Jarvie HP, Naden PS, Old GH, Scarlett PM, Roberts C, Armstrong LK, Harman SA, Wickham HD, Collins AL (2014) Identifying priorities for nutrient mitigation using river concentration–flow relationships; The Thames basin, UK. Journal of Hydrology 517:1–12.

Bowes MJ, Smith JT, Jarvie HP, Neal C (2008) Modelling of phosphorus inputs to rivers from diffuse and point sources. Science of The Total Environment 395:125–138.

Bowes MJ, Smith JT, Jarvie HP, Neal C, Barden R (2009) Changes in point and diffuse source phosphorus inputs to the River Frome (Dorset, UK) from 1966 to 2006. Science of The Total Environment 407:1954–1966.

Buck O, Niyogi DK, Townsend CR (2004) Scale-dependence of land use effects on water quality of streams in agricultural catchments. Environmental Pollution 130:287–299.

Burgess, T. M., Webster, R. (1980) Optimal interpolation and isarithmetic mapping of soil properties. Journal of Soil Science 31:333–341.

Cambardella CA, Karlen DL (1999) Spatial Analysis of Soil Fertility Parameters. Precision Agriculture:5–14.

Canga E, Heckrath GJ, Kjaergaard C (2016) Agricultural Drainage Filters. II. Phosphorus Retention and Release at Different Flow Rates. Water, Air, & Soil Pollution 227:1143.

Caron J, Banton O, Angers DA, Villeneuve JP (1996) Preferential bromide transport through a clay loam under alfalfa and corn. Geoderma 69:175–191.

Carpenter SR (2005) Eutrophication of aquatic ecosystems: Bistability and soil phosphorus. Proceedings of the National Academy of Sciences of the United States of America 102:10002–10005.

Cey EE (2013) Sampling Escherichia coli and Total Coliforms using Stainless Steel Suction Lysimeters. Vadose Zone Journal 12.

Cey EE, Rudolph DL, Passmore J (2009) Influence of macroporosity on preferential solute and colloid transport in unsaturated field soils. Journal of Contaminant Hydrology 107:45–57.

Chaplot V, Cooper M (2015) Soil aggregate stability to predict organic carbon outputs from soils. Geoderma 243-244:205–213.

Chapman AS, Foster IDL, Lees JA, Hodgkinson RA, Jackson RH (2001) Particulate phosphorus transport by sub-surface drainage from agricultural land in the UK. Environmental significance at the catchment and national scale. Science of The Total Environment:95–102.

Childers DL, Corman J, Edwards M, Elser JJ (2011) Sustainability Challenges of Phosphorus and Food; Solutions from Closing the Human Phosphorus Cycle. BioScience 61:117–124.

Chislock MF, Doster E, Zitomer RA, Wilson AE (2013) Eutrophication: Causes, Consequences, and Controls in Aquatic Ecosystems. Nature Education Knowledge 4:10.

Choudhury T, Robertson WD, Finnigan DS (2016) Suspended Sediment and Phosphorus Removal in a Woodchip Filter System Treating Agricultural Wash Water. Journal of Environmental Quality 45:796–802.

Christianson LE, Harmel RD, Smith D, Williams MR, King K (2016) Assessment and Synthesis of 50 Years of Published Drainage Phosphorus Losses. Journal of Environmental Quality 45:1467–1477.

Chyba J, Kroulik M, Lev J, Kumhála F (2013) Influence of soil cultivation and farm machinery passes on water preferential flow using brilliant blue dye tracer. Agronomy Research 11:25–30.

Ciglasch H, Amelung W, Totrakool S, Kaupenjohann M (2005) Water flow patterns and pesticide fluxes in an upland soil in northern Thailand. European Journal of Soil Science 0:050912034650046.

Cisse L, Mrabet T (2004) World Phosphate Production; Overview and Prospects. Phosphorus Research Bulletin 15:21–25.

Cnudde V, Masschaele B, Dierick M, Vlassenbroeck J, van Hoorebeke L, Jacobs P (2006) Recent progress in X-ray CT as a geosciences tool. Applied Geochemistry 21:826–832.

Collick AS, Fuka DR, Kleinman PJA, Buda AR, Weld JL, White MJ, Veith TL, Bryant RB, Bolster CH, Easton ZM (2015) Predicting phosphorus dynamics in complex terrains using a variable source area hydrology model. Hydrological Processes 29:588–601.

Corazza EJ, Brossard M, Muraoka T, Filho, Mauricio Antonio Coelho (2003) Spatial variability of soil phosphorous of a low productivity Brachiaria brizantha pasture. Scientia Agricola 60:559–564.

Cordell D, Drangert J, White S (2009) The story of phosphorus; Global food security and food for thought. Global Environmental Change 19:292–305.

Cordell D, Rosemarin A, Schroder JJ, Smit AL (2011) Towards global phosphorus security: a systems framework for phosphorus recovery and reuse options. Chemosphere 84:747–758.

Dąbrowska J, Lejcuś K, Kuśnierz M, Czamara A, Kamińska J, Lejcuś I (2016) Phosphate dynamics in the drinking water catchment area of the Dobromierz Reservoir. Desalination and Water Treatment:25600–25609.

Daloğlu I, Cho KH, Scavia D (2012) Evaluating causes of trends in long-term dissolved reactive phosphorus loads to Lake Erie. Environmental Science & Technology 46:10660–10666.

Daniel EB, Camp JV, Leboeuf EJ et al. (2011) Watershed modeling and its applications: a State-of-the-Art review. The Open Hydrology Journal 5:26–50

Daniel TC, Sharpley AN, Edwards DR, Wedepohl R, Lemunyon JL (1994) Minimizing surface water eutrophication from agriculture by phosphorous management. Journal of Soil and Water Conservation 49:30–38.

Daniel TC, Sharpley AN, Lemunyon JL (1998) Agricultural Phosphorus and Eutrophication; A Symposium Overview. Journal of Environmental Quality 27:251–257.

de Jonge LW, Moldrup P, Rubæk GH, Schelde K, Djurhuus J (2004) Particle Leaching and Particle-Facilitated Transport of Phosphorus at Field Scale. Vadose Zone Journal 3:462–470.

de-Bashan LE, Bashan Y (2004) Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003). Water Research 38:4222–4246.

Desmidt E, Ghyselbrecht K, Zhang Y, Pinoy L, van der Bruggen B, Verstraete W, Rabaey K, Meesschaert B (2014) Global Phosphorus Scarcity and Full-Scale P-Recovery Techniques; A Review. Critical Reviews in Environmental Science and Technology 45:336–384.

Deutsches Institut für Normung. 2004. DIN EN ISO (2004) Water quality Determination of phosphorus – Ammonium molybdate spectrometric method (ISO:6878:2004; German version EN ISO 6878:2004 Deutsches Institut für Normung, Berlin, Germany.

Deutsches Institut für Normung. 2005. DIN EN ISO (2005) Water quality – Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) – Part1: Method of flow injection analysis (FIA) (ISO 15681-1:2003); German version EN ISO 15681:2004 Deutsches Institu für Normung, Berlin, Germany.

Deutsches Institut fur Normung. 2011. Soil, investigation and testing—Determination of grain-size distribution. DIN 18123. (In German.) Deutsches Institut fur Normung, Berlin, Germany.

Di Luzio M, Arnold JG, Srinivasan R (2005) Effect of GIS data quality on small watershed stream flow and sediment simulations. Hydrological Processes 19:629-650.

Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy as amended by Decision 2455/2001/EC and Directives 2008/32/EC, 2008/105/EC and 2009/31/EC.

Djodjic F, Ulén B, Bergström L (2000) Temporal and spatial variations of phosphorous losses and drainage in a structured clay soil. Water Research 34:1687–1695.

DLR (2003) CORINE Land Cover Vectordata CLC2000. German Aerospace Center, Cologne

Dodd RJ, Sharpley AN (2015) Recognizing the role of soil organic phosphorus in soil fertility and water quality. Resources, Conservation and Recycling 105:282–293.

Dodds W, Smith V (2016) Nitrogen, phosphorus, and eutrophication in streams. Inland Waters 6:155–164.

Dong SK, Wen L, Li YY, Wang XX, Zhu L, Li XY (2012) Soil-Quality Effects of Grassland Degradation and Restoration on the Qinghai-Tibetan Plateau. Soil Science Society of America Journal 76:2256.

Du B, Arnold JG, Saleh A, Jaynes DB (2005) Development and application of SWAT to landscapes with tiles and potholes. Transactions of the ASAE 48:1121–1133

Du B, Saleh A, Jaynes DB, Arnold JG (2006) Evaluation of SWAT in simulating nitrate nitrogen and atrazine fates in a watershed with tiles and potholes. Transactions of the ASABE 49:949–959.

Edixhoven JD, Gupta J, Savenije HHG (2014) Recent revisions of phosphate rock reserves and resources; A critique. Earth System Dynamics 5:491–507.

Eighball B, Gilley JE, Baltensperger DD, Blumenthal JM (2002) Long-Term Manure and Fertilizer Application Effects on Phosphorus and Nitrogen in Runoff. Transactions of the ASAE 45:687–694.

Ekholm P (1998) Algal-available phosphorus originating from agriculture and municipalities. Monographs of the Boreal Environment Research No. 11, Helsinki.

Ekholm P, Rankinen K, Rita H, Räike A, Sjöblom H, Raateland A, Vesikko L, Cano Bernal JE, Taskinen A (2015) Phosphorus and nitrogen fluxes carried by 21 Finnish agricultural rivers in 1985-2006. Environmental Monitoring and Assessment 187:216.

Ellis BK, Craft JA, Stanford JA (2015) Long-term atmospheric deposition of nitrogen, phosphorus and sulfate in a large oligotrophic lake. PeerJ 3:e841.

Etana A, Larsbo M, Keller T, Arvidsson J, Schjønning P, Forkman J, Jarvis N (2013) Persistent subsoil compaction and its effects on preferential flow patterns in a loamy till soil. Geoderma 192:430–436.

Federolf C, Westerschulte M, Olfs H, Broll G, Trautz D (2016) Enhanced nutrient use efficiencies from liquid manure by positioned injection in maize cropping in northwest Germany. European Journal of Agronomy 75:130–138.

Ficklin DL, Luo Y, Luedeling E, Zhang M (2009) Climate change sensitivity assessment of a highly agricultural watershed using SWAT. Journal of Hydrology 374:16–29.

Flury M, Flühler H (1995) Tracer Characteristics of Brilliant Blue FCF. Soil Science Society of America Journal 59:22–27.

Flury M, Flühler H, Jury WA, Leuenberger J (1994) Susceptibility of soils to preferential flow of water: A field study. Water Resources Research 30:1945–1954.

Food and Agriculture Organization of the United Nations (2008) Current world fertilizer trends and outlook to 2011/12. FAO. Last checked: 30. Januar 2017.

Fox GA, Purvis RA, Penn CJ (2016) Streambanks: A net source of sediment and phosphorus to streams and rivers. Journal of Environmental Quality 181:602–614.

Foy RH, Smith RV, Jordan C, Lennox D (1995) Upward trend in soulble phosphorus loadings to Lough Neagh despite phosphorus reduction at sewage treatment works. Water Research 29:1051–1063.

Francesconi W, Srinivasan R, Pérez-Miñana E, Willcock SP, Quintero M (2016) Using the Soil and Water Assessment Tool (SWAT) to model ecosystem services; A systematic review. Journal of Hydrology 535:625–636.

Frazier TP, Burklew CE, Zhang B (2014) Titanium dioxide nanoparticles affect the growth and microRNA expression of tobacco (Nicotiana tabacum). Functional & Integrative Genomics 14:75–83.

Freitas JR de, Banerjee MR, Germida JJ (1997) Phosphate-solubilizing rhizobacteria enhance the growth and yield but not phosphorus uptake of canola (Brassica napus L.). Biology and Fertility of Soils 24:358–364.

Fuchs JW, Fox GA, Storm DE, Penn CJ, Brown GO (2009) Subsurface transport of phosphorus in riparian floodplains: influence of preferential flow paths. Journal of Environmental Quality 38:473–484.

Gächter R, Ngathia JM, Stamm C (1998) Transport of Phosphate from Soil to Surface Waters by Preferential Flow. Environmental Science & Technology 32:1865–1869.

Gassman PW, Reyes MR, Green CH, Arnold JG (2007) The Soil and Water Assessment Tool: historical development, applications, and future research directions. Transactions of the ASABE 50:1211–1250

Gelbrecht J, Lengsfeld H, Pöthig R, Opitz D (2005) Temporal and spatial variation of phosphorus input, retention and loss in a small catchment of NE Germany. Journal of Hydrology 304:151–165.

Gentry LE, David MB, Royer TV, Mitchell CA, Starks KM (2007) Phosphorus transport pathways to streams in tile-drained agricultural watersheds. Journal of Environmental Quality 36:408–415.

Geohring LD, McHugh OV, Walter MT, Steenhuis TS, Akhtar MS, Walter MF (2001) Phosphorus Transport Into Subsurface Drains By Macropores After Manure Applications: Implications for Best Manure Management Practices. Soil Science 166:896–909.

George TS, Hinsinger P, Turner BL (2016) Phosphorus in soils and plants – facing phosphorus scarcity. Plant and Soil 401:1–6.

Germán-Heins J, Flury M (2000) Sorption of Brilliant Blue FCF in soils as affected by pH and ionic strength. Geoderma:87–101.

Gharabaghi B, Safadoust A, Mahboubi AA, Mosaddeghi MR, Unc A, Ahrens B, Sayyad G (2015) Temperature effect on the transport of bromide and E. coli NAR in saturated soils. Journal of Hydrology 522:418–427.

Godlinski F, Reiche E, Lennartz B, Meissner R (2008) Simulation of phosphorus losses from lysimeters. Journal of Plant Nutrition and Soil Science 171:621–633.

Gonzales AL, Nonner J, Heijkers J, Uhlenbrook S (2009) Comparison of different base flow separation methods in a lowland catchment. Hydrology and Earth System Sciences 13:2055–2068

Gottselig N, Bol R, Nischwitz V, Vereecken H, Amelung W, Klumpp E (2014) Distribution of Phosphorus-Containing Fine Colloids and Nanoparticles in Stream Water of a Forest Catchment. Vadose Zone Journal 13:0.

Grabowski RC, Gurnell AM (2016) Diagnosing problems of fine sediment delivery and transfer in a lowland catchment. Aquatic Sciences 78:95–106.

Grant R, Laubel A, Kronvang B, Andersen HE, Svendsen LM, Fuglsang A (1996) Loss of dissolved and particulate phosphorus from arable catchments by subsurface drainage. Water Research 30:2633–2642.

Grant R, Laubel A, Kronvang B, Andersen HE, Svendsen LM, Fuglsang A (1996) Loss of dissolved and particulate phosphorus from arable catchments by subsurface drainage. Water Research 30:2633–2642.

Green CH, Tomer MD, Di Luzio M, Arnold JG (2006) Hydrologic evaluation of the Soil and Water Assessment Tool for a large tile-drained watershed in Iowa. Transactions of the ASABE 49:413–422

Green HG, Tomer MD, Di Luzio M, Arnold JG (2006) Hydrologic evaluation of the Soil and Water Asessment Tool for a large tile-drained watershed in Iowa. Transactions of the ASABE 49:413–422.

Griensven AV, Meixner T, Grunwald S, Bishop T, Diluzio M, Srinivasan R (2001) A global sensitivity analysis tool for the parameters of multi-variable catchment models. Journal of Hydrology 324:10–23

Grimvall A, Stålnacke P, Tonderski A (2000) Time scales of nutrient losses from land to sea — a European perspective. Ecological Engineering:363–371.

Grundtner A, Gupta S, Bloom P (2014) River bank materials as a source and as carriers of phosphorus to lake pepin. Journal of Environmental Quality 43:1991–2001.

Grunwald S, Corstanje R, Weinrich BE, Reddy KR (2006) Spatial patterns of labile forms of phosphorus in a subtropical wetland. Journal of Environmental Quality 35:378–389.

Hahn C, Prasuhn V, Stamm C, Schulin R (2012) Phosphorus losses in runoff from manured grassland of different soil P status at two rainfall intensities. Agriculture, Ecosystems & Environment 153:65–74.

Hardie MA, Cotching WE, Doyle RB, Holz G, Lisson S, Mattern K (2011) Effect of antecedent soil moisture on preferential flow in a texture-contrast soil. Journal of Hydrology 398:191–201.

Harrison-Atlas D, Theobald DM, Goldstein JH (2016) A systematic review of approaches to quantify hydrologic ecosystem services to inform decision-making. International Journal of Biodiversity Science, Ecosystem Services & Management 12:160–171.

Heathwaite L, Haygarth PM, Matthews R, Preedy N, Butler P (2005) Evaluating Colloidal Phosphorus Delivery to Surface Waters from Diffuse Agricultural Sources. Journal of Environmental Quality:287–298.

Hedrick UP, Sturtevant EL (1919) Sturtevant's notes on edible plants / Edited by U.P. Hedrick. J.B. Lyon, Albany.

Heilmann E, Leinweber P, Ollesch G, Meißner R (2005) Spatial variability of sequentially extracted P fractions in a silty loam. Journal of Plant Nutrition and Soil Science 168:307–315.

Hirsch RM, Slack JR, Smith RA (1982) Techniques of Trend Analysis for Monthly Water Quality Data. Water Resources Research 18:107–121.

Hirt U, Meyer BC, Hammann T (2005) Proportions of subsurface drainages in large areas—methodological study in the Middle Mulde catchment (Germany). Journal of Plant Nutrition and Soil Science 168:375–385.

Holman IP, Whelan MJ, Howden NJK, Bellamy PH, Willby NJ, Rivas-Casado M, McConvey P (2008) Phosphorus in groundwater-an overlooked contributor to eutrophication? Hydrological Processes 22:5121–5127.

Holvoet K, Griensven AV, Seuntjens P, Vanrolleghem P (2005) Sensitivity analysis for hydrology and pesticide supply towards the river in SWAT. Physics and Chemistry of the Earth 30:518–526

Hooda PS, Moynagh M, Svoboda IF, Edwards AC, Anderson HA, Sym G (1999) Phosphorus Loss in Drainflow from Intensively Managed Grassland Soils. Journal of Environmental Quality 28:1235–1242.

Hörmann G, Köplin N, Cai Q, Fohrer N (2009) Using a simple model as a tool to parameterise the SWAT model of the Xiangxi river in China. Quaternary International 208:116–120

Hua G, Salo MW, Schmit CG, Hay CH (2016) Nitrate and phosphate removal from agricultural subsurface drainage using laboratory woodchip bioreactors and recycled steel byproduct filters. Water Research 102:180–189.

Illmer P, Schinner F (1992) Solubilization of inorganic phosphates by microorganisms isolated from forest soils. Soil Biology and Biochemistry 24:389–395.

IUSS Working Group WRB. 2015. World reference base for soil resources 2014, update 2015: International soil classification system for naming soils and creating legends for soil maps. World Soil Resour. Rep. 106. FAO, Rome.

Jacobsen OH, Moldrup P, Larsen C, Konnerup L, Petersen L (1997) Particle transport in macropores of undisturbed soil columns. Journal of Hydrology 196:185–203.

Janssen M, Lennartz B (2008) Characterization of Preferential Flow Pathways through Paddy Bunds with Dye Tracer Tests. Soil Science Society of America Journal 72:1756–1766.

Jarvie HP, Neal C, Withers PJ (2006) Sewage-effluent phosphorus; A greater risk to river eutrophication than agricultural phosphorus? Science of The Total Environment 360:246–253.

Jarvie HP, Sharpley AN, Withers PJA, Scott JT, Haggard BE, Neal C (2013) Phosphorus Mitigation to Control River Eutrophication; Murky Waters, Inconvenient Truths, and “Postnormal” Science. Journal of Environmental Quality 42:295.

Jiang X, Bol R, Willbold S, Vereecken H, Klumpp E (2015) Speciation and distribution of P associated with Fe and Al oxides in aggregate-sized fraction of an arable soil. Biogeosciences 12:6443–6452.

Johnes P, Moss B, Phillips G (1996) The determination of total nitrogen and total phosphorus concentrations in freshwaters from land use, stock headage and population data: testing of a model for use in conservation and water quality management. Freshwater Biology:451–473.

Jordan P, Melland AR, Mellander P, Shortle G, Wall D (2012) The seasonality of phosphorus transfers from land to water: implications for trophic impacts and policy evaluation. Science of The Total Environment 434:101–109.

Juang K, Liou D, Lee D (2002) Site-Specific Phosphorus Application Based on the Kriging Fertilizer-Phosphorus Availability Index of Soils. Journal of Environmental Quality 31:1248.

Kang J, Amoozegar A, Hesterberg D, Osmond DL (2011) Phosphorus leaching in a sandy soil as affected by organic and inorganic fertilizer sources. Geoderma 161:194–201.

Kasteel R, Burkhardt M, Giesa S, Vereecken H (2005) Characterization of Field Tracer Transport Using High-Resolution Images. Vadose Zone Journal 4:101–111.

Kasteel R, Vogel H, Roth K (2002) Effect of non-linear adsorption on the transport behaviour of Brilliant Blue in a field soil. European Journal of Soil Science:231–240.

Kerschberger M, Hege LU, Jungk A (09/1997) Phosphordüngung nach Bodenuntersuchung und Pflanzenbedarf. Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten. Last checked: 22. November 2016.

Kholoma E, Renman G, Renman A (2016) Phosphorus removal from wastewater by field-scale fortified filter beds during a one-year study. Environmental technology 37:2953–2963.

Kiesel J, Fohrer N, Schmalz B, White MJ (2010) Incorporating landscape depressions and tile drainages of a northern German lowland catchment into a semi-distributed model. Hydrological Processes 24:1472–1486.

King KW, Williams MR, Fausey NR (2015a) Contributions of systematic tile drainage to watershed-scale phosphorus transport. Journal of Environmental Quality 44:486–494.

King KW, Williams MR, Macrae ML, Fausey NR, Frankenberger J, Smith DR, Kleinman PJA, Brown LC (2015b) Phosphorus transport in agricultural subsurface drainage: A review. Journal of Environmental Quality 44:467–485.

Kjaergaard C, Moldrup P, Jonge LW de, Jacobsen OH (2004) Colloid Mobilization and Transport in Undisturbed Soil Columns. II. The Role of Colloid Dispersibility and Preferential Flow. Vadose Zone Journal 3:424–433.

Kladivko EJ, Grochulska J, Turco RF, Van Scoyoc GE, Eigel JD (1999) Pesticide and nitrate transport into subsurface tile drains of different spacings. Journal of Environmental Quality 28:997–1004

Klaus VH, Boch S, Boeddinghaus RS, Hölzel N, Kandeler E, Marhan S, Oelmann Y, Prati D, Regan KM, Schmitt B, Sorkau E, Kleinebecker T (2016) Temporal and small-scale spatial variation in grassland productivity, biomass quality, and nutrient limitation. Plant Ecology 217:843–856.

Kleeberg A, Schlungbaum G (1993) In situ phosphorus release experiments in the Warnow River (Mecklenburg, northern Germany) Proceedings of the Third International Workshop on Phosphorus in Sediments, S 263–274.

Kleinman PJA, Sharpley AN, Withers PJA, Bergstrom L, Johnson LT, Doody DG (2015) Implementing agricultural phosphorus science and management to combat eutrophication. Ambio 44:S297-S310.

Kleinman PJA, Smith DR, Bolster CH, Easton ZM (2015b) Phosphorus fate, management, and modeling in artificially drained systems. Journal of Environmental Quality 44:460–466.

Knappenberger T, Flury M, Mattson ED, Harsh JB (2014) Does water content or flow rate control colloid transport in unsaturated porous media? Environmental Science & Technology 48:3791–3799.

Koch S, Bauwe A, Lennartz B (2013) Application of the SWAT Model for a Tile-Drained Lowland Catchment in North-Eastern Germany on Subbasin Scale. Water Resources Management 27:791–805.

Kozar B, Lawrence R, Long DS (2002) Soil phosphorus and potassium mapping using a spatial correlation model incorporating terrain slope gradient. Precision Agriculture:407–417.

Kronvang B, Audet J, Baattrup-Pedersen A, Jensen HS, Larsen SE (2012) Phosphorus Load to Surface Water from Bank Erosion in a Danish Lowland River Basin. Journal of Environmental Quality 41:304.

Kronvang B, Rubaek GH, Heckrath G (2009) International phosphorus workshop: diffuse phosphorus loss to surface water bodies--risk assessment, mitigation options, and ecological effects in river basins. Journal of Environmental Quality 38:1924–1929.

Kronvang B, Vagstad N, Behrendt H, Bogestrand J, Larsen SE (2007) Phosphorus losses at the catchment scale within Europe: an overview. Soil Use and Management:104–116.

Kuchenbuch RO, Buczko U (2011) Re-visiting potassium- and phosphate-fertilizer responses in field experiments and soil-test interpretations by means of data mining. Journal of Plant Nutrition and Soil Science 174:171–185.

Kumar S, Merwade V (2009) Impact of watershed subdivision and soil data resolution on SWAT model calibration and parameter uncertainty. Journal of the American Water Resources Association 45:1179–1196

Kung KS (1990) Influence of Plant Uptake on the Performance of Bromide Tracer 54:975–979.

Lagzdins A, Jansons V, Sudars R, Abramenko K (2012) Scale issues for assessment of nutrient leaching from agricultural land in Latvia. Hydrology Research 43:383.

Lam QD, Schmalz B, Fohrer N (2010) Modelling point and diffuse source pollution of nitrate in a rural lowland catchment using the SWAT model. Agricultural Water Management 97:317–325.

Land M, Granéli W, Grimvall A, Hoffmann CC, Mitsch WJ, Tonderski KS, Verhoeven JTA (2016) How effective are created or restored freshwater wetlands for nitrogen and phosphorus removal?; A systematic review. Environmental Evidence 5:126.

Länderarbeitsgemeinschaft Wasser (1998) Beurteilung der Wasserbeschaffenheit von Fließgewässern in der Bundesrepublik Deutschland; Chemische Gewässergüteklassifikation. Last checked: 25. November 2016.

Landesamt für Umwelt, Naturschutz und Geologie (2005) Beiträge zum Bodenschutz in Mecklenburg-Vorpommern. Böden in Mecklenburg-Vorpommern. Abriss ihrer Entstehung, Verbreitung und Nutzung. 2. Aufl. Landesamt für Umwelt, Naturschutz und Geologie. Güstrow.

Landesamt für Umwelt, Naturschutz und Geologie (LUNG) (2007) BÜK 500, Bodenübersichtskarte 1:500,000. State Agency for the Environment, Nature Conservation and Geology of Mecklenburg-West Pomerania (LUNG), Güstrow

Landesamt für Umwelt, Naturschutz und Geologie (LUNG) (2010) BÜK 200, Bodenübersichtskarte 1:200,000. State Agency for the Environment, Nature Conservation and Geology of Mecklenburg-West Pomerania (LUNG), Güstrow

Landesamt für Umwelt, Naturschutz und Geologie (2016) personal communication.

Laubel A, Jacobsen OH, Kronvang B, Grant R, Andersen HE (1999) Subsurface Drainage Loss of Particles and Phosphorus from Field Plot Experiments and a Tile-Drained Catchment. Journal of Environmental Quality 28:576.

Lennartz B, Michaelsen J, Widmoser P, Wichtmann W (1999) Time Variance Analysis of Preferential Solute Movement at a Tile-Drained Field Site. Soil Science Society of America Journal 63:39–47.

Leopold U, Heuvelink GB, Tiktak A, Finke PA, Schoumans OF (2006) Accounting for change of support in spatial accuracy assessment of modelled soil mineral phosphorous concentration. Geoderma 130:368–386.

Liu H, Lennartz B (2015) Visualization of Flow Pathways in Degraded Peat Soils Using Titanium Dioxide. Soil Science Society of America Journal 79:757–765.

Liu R, Xu F, Yu W, Shi J, Zhang P, Shen Z (2016) Analysis of field-scale spatial correlations and variations of soil nutrients using geostatistics. Environmental Monitoring and Assessment 188:126.

Long TC, Saleh N, Tilton RD, Lowry GV, Veronesi B (2006) Titanium Dioxide (P25) Produces Reactive Oxygen Species in Immortalized Brain Microglia (BV2); Implications for Nanoparticle Neurotoxicity. Environmental Science & Technology 40:4346–4352.

Lu S, Andersen HE, Thodsen H, Rubæk GH, Trolle D (2016) Extended SWAT model for dissolved reactive phosphorus transport in tile-drained fields and catchments. Agricultural Water Management 175:78–90.

Lu S, Kronvang B, Audet J, Trolle D, Andersen HE, Thodsen H, van Griensven A (2015) Modelling sediment and total phosphorus export from a lowland catchment; Comparing sediment routing methods. Hydrological Processes 29:280–294.

LVA M-V (2000) DEM25, Digital Elevation Model grid size 25 × 25 m. Land survey office Mecklenburg-West Pomerania, Schwerin.

Macrae ML, English MC, Schiff SL, Stone M (2007) Intra-annual variability in the contribution of tile drains to basin discharge and phosphorus export in a first-order agricultural catchment. Agricultural Water Management 92:171–182.

Makris KC, Grove JH, Matocha CJ (2006) Colloid-mediated vertical phosphorus transport in a waste-amended soil. Geoderma 136:174–183.

McDowell RW, Elkin KR, Kleinman PJA (2017) Temperature and Nitrogen Effects on Phosphorus Uptake by Agricultural Stream-Bed Sediments. Journal of Environmental Quality 46:295–301.

McDowell RW, Sharpley AN (2001) Approximating Phosphorus Release from Soils to Surface Runoff and Subsurface Drainage. Journal of Environmental Quality 30:508–520.

McGechan MB, Lewis DR (2002) Transport of Particulate and Colloid-sorbed Contaminants through Soil,Part 1: General Principles. Biosystems Engineering 83:255–273.

Mehl D, Hoffmann TG, Steinhäuser A (2010) Ermittlung von Art und Intensität künstlicher Entwässerung von landwirtschaftlichen Nutzflächen in Mecklenburg-Vorpommern. biota – Institut für ökologische Forschung und Planung GmbH. Last checked: 06. Juni 2017.

Mellander P, Jordan P, Shore M, Melland AR, Shortle G (2015) Flow paths and phosphorus transfer pathways in two agricultural streams with contrasting flow controls. Hydrological Processes 29:3504–3518.

Messing I, Wesström I, Joel A, Strock J (2015) In Situ Method for Measuring Water Fluxes, Sediment, and Phosphorus at High Drip Infiltrometer Intensities in the Upper Half Meter of a Tilled Clay Soil. Communications in Soil Science and Plant Analysis 46:2139–2151.

Minaudo C, Meybeck M, Moatar F, Gassama N, Curie F (2015) Eutrophication mitigation in rivers; 30 years of trends in spatial and seasonal patterns of biogeochemistry of the Loire River (1980–2012). Biogeosciences 12:2549–2563.

Ministerium für Landwirtschaft, Umwelt und Verbraucherschutz Mecklenburg-Vorpommern (11/2011) Konzept zur Minderung der diffusen Nährstoffeinträge aus der Landwirtschaft in die Oberflächengewässer und in das Grundwasser. Last checked: 13. Dezember 2016.

Mohrholz V, Naumann M, Nausch G, Krüger S, Gräwe U (2015) Fresh oxygen for the Baltic Sea — An exceptional saline inflow after a decade of stagnation. Journal of Marine Systems 148:152–166.

Moriasi DN, Gowda PH, Arnold JG, Mulla DJ, Ale S, Steiner JL (2013) Modeling the impact of nitrogen fertilizer application and tile drain configuration on nitrate leaching using SWAT. Agricultural Water Management 130:36–43.

Morris C, Mooney SJ, Young SD (2008) Sorption and desorption characteristics of the dye tracer, Brilliant Blue FCF, in sandy and clay soils. Geoderma 146:434–438.

Müller J, Toev T, Heisters M, Teller J, Moore KL, Hause G, Dinesh DC, Burstenbinder K, Abel S (2015) Iron-dependent callose deposition adjusts root meristem maintenance to phosphate availability. Developmental Cell 33:216–230.

Nash JE, Sutcliffe JV (1970) River flow forecasting through conceptual models. Part I - A discussion of principles. Journal of Hydrology 10:282–290

Nash PR, Nelson KA, Motavalli PP, Nathan M, Dudenhoeffer C (2015) Reducing phosphorus loss in tile water with managed drainage in a claypan soil. Journal of Environmental Quality 44:585–593.

Nathan RJ, McMahon TA (1990) Evaluation of automated techniques for base flow and recession analyses. Water Resources Research 26:1465–1473.

Nausch M, Woelk J, Kahle P, Nausch G, Leipe T, Lennartz B (2017) Phosphorus fractions in discharges from artificially drained lowland catchments (Warnow River, Baltic Sea). Agricultural Water Management 187:77–87.

Neitsch SL, Arnold JG, Kiniry JR, Williams JR (2005) Soil and Water Assessment Tool: Theoretical documentation. Temple, Texas

Neset TS, Cordell D (2012) Global phosphorus scarcity; Identifying synergies for a sustainable future. Journal of the Science of Food and Agriculture 92:2–6.

Nkebiwe PM, Weinmann M, Bar-Tal A, Müller T (2016) Fertilizer placement to improve crop nutrient acquisition and yield; A review and meta-analysis. Field Crops Research 196:389–401.

Nobles MM, Wilding LP, Lin HS (2010) Flow pathways of bromide and Brilliant Blue FCF tracers in caliche soils. Journal of Hydrology 393:114–122.

Nobles MM, Wilding LP, McInnes KJ (2004) Pathways of dye tracer movement through structured soils on a macroscopic scale. Soil Science 169:229–242.

Northcott W, Cooke RA, Walker SE, Mitchell JK, Hirschi MC (2002) Modelling flow on a tile-drained watershed using a GIS integrated DRAINMOD. Transactions of the ASAE, ASAE Annual International Meeting, Chicago, Illinois, 1–11

Olivera F, Valenzuela M, Srinivasan R et al. (2006) Arcgis-SWAT: A geodata model and GIS interface for SWAT. Journal of the American Water Resources Association 85:909–309

Ott C, Rechberger H (2012) The European phosphorus balance. Resources, Conservation and Recycling 60:159–172.

Outram FN, Lloyd CEM, Jonczyk J, Benskin CMH, Grant F, Perks MT, Deasy C, Burke SP, Collins AL, Freer J, Haygarth PM, Hiscock KM, Johnes PJ, Lovett AL (2014) High-frequency monitoring of nitrogen and phosphorus response in three rural catchments to the end of the 2011–2012 drought in England. Hydrology and Earth System Sciences 18:3429–3448.

Owens PN, Deeks LK, Wood GA, Betson MJ, Lord EI, Davison PS (2008) Variations in the depth distribution of phosphorus in soil profiles and implications for model-based catchment-scale predictions of phosphorus delivery to surface waters. Journal of Hydrology 350:317–328.

Page T, Haygarth PM, Beven KJ, Joynes A, Butler T, Keeler C, Freer J, Owens PN, Wood GA (2005) Spatial variability of soil phosphorus in relation to the topographic index and critical source areas: sampling for assessing risk to water quality. Journal of Environmental Quality 34:2263–2277.

Pfannerstill M, Guse B, Fohrer N (2014) A multi-storage groundwater concept for the SWAT model to emphasize nonlinear groundwater dynamics in lowland catchments. Hydrological Processes 28:5599–5612.

Poirier S, Whalen JK, Michaud AR (2012) Bioavailable Phosphorus in Fine-Sized Sediments Transported from Agricultural Fields. Soil Science Society of America Journal 76:258.

Powers SM, Bruulsema TW, Burt TP, Chan NI, Elser JJ, Haygarth PM, Howden NJK, Jarvie HP, Lyu Y, Peterson HM, Sharpley AN, Shen J, Worrall F, Zhang F (2016) Long-term accumulation and transport of anthropogenic phosphorus in three river basins. Nature Geoscience 9:353–356.

Purvis RA, Fox GA, Penn CJ, Storm DE, Parnell A (2016) Estimating Streambank Phosphorus Loads at the Watershed Scale with Uncertainty Analysis Approach. Journal of Hydrologic Engineering 21:4016028.

Qi H, Qi Z (2016) Simulating phosphorus loss to subsurface tile drainage flow; A review. Environmental Reviews:1–13.

R Core Team (2015). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/.

Rubæk GH, Kristensen K, Olesen SE, Østergaard HS, Heckrath G (2013) Phosphorus accumulation and spatial distribution in agricultural soils in Denmark. Geoderma 209-210:241–250.

Radcliffe DE, Reid DK, Blombäck K, Bolster CH, Collick AS, Easton ZM, Francesconi W, Fuka DR, Johnsson H, King KW, Larsbo M, Youssef MA, Mulkey AS, Nelson NO, Persson K, Ramirez-Avila JJ, Schmieder F, Smith DR (2015) Applicability of models to predict phosphorus losses in drained fields: A review. Journal of Environmental Quality 44:614–628.

Rahman MM, Thompson JR, Flower RJ (2016) An enhanced SWAT wetland module to quantify hydraulic interactions between riparian depressional wetlands, rivers and aquifers. Environmental Modelling & Software 84:263–289.

Räike A, Pietiläinen O, Rekolainen S, Kauppila P, Pitkänen H, Niemi J, Raateland A, Vuorenmaa J (2003) Trends of phosphorus, nitrogen and chlorophyll a concentrations in Finnish rivers and lakes in 1975–2000. Science of The Total Environment 310:47–59.

Refsgaard JC, Storm B (1995) MIKE SHE. In: Singh VP, ed. Computer models of watershed hydrology. Highlands Ranch, Water Research Publications, Colorado

Reijnders L (2014) Phosphorus resources, their depletion and conservation, a review. Resources, Conservation and Recycling 93:32–49.

Reinhardt M, Gachter R, Wehrli B, Muller B (2005) Phosphorus retention in small constructed wetlands treating agricultural drainage water. Journal of Environmental Quality 34:1251–1259.

Richter D (1995) Ergebnisse methodischer Untersuchungen zur Korrektur des systematischen Niederschlagsmeßfehlers des Hellman-Niederschlagsmessers. Berichte des Deutschen Wetterdienstes 194, Selbstverlag, Offenbach

Roberts TL (2009) The Role of Fertilizer in Growing the World's Food. Better Crops:12–15.

Rogasik H, Crawford JW, Wendroth O, Young IM, Joschko M, Ritz K (1999) Discrimination of Soil Phases by Dual Energy X-ray Tomography. Soil Science Society of America Journal 63:741.

Roger A, Libohova Z, Rossier N, Joost S, Maltas A, Frossard E, Sinaj S (2014) Spatial variability of soil phosphorus in the Fribourg canton, Switzerland. Geoderma 217-218:26–36.

Romanowicz AA, Vanclooster M, Rounsevell M, La Junesse I (2005) Sensitivity of the SWAT model to the soil and land use data parametrisation: A case study in the Thyle catchment, Belgium. Ecological Modelling 187:27–39

Rooij GH de, Stagnitti F (2002) Spatial and temporal distribution of solute leaching in heterogeneous soils: analysis and application to multisampler lysimeter data. Journal of Contaminant Hydrology:329–346.

Rozemeijer JC, Visser A, Borren W, Winegram M, van der Velde Y, Klein J, Broers HP (2016) High-frequency monitoring of water fluxes and nutrient loads to assess the effects of controlled drainage on water storage and nutrient transport. Hydrology and Earth System Sciences 20:347–358.

Ryther JH, Dunstan WM (1971) Nitrogen, Phosphorus, and Eutrophication in the Coastal Marine Environment. Science 171:1008–1013.

Santhi C, Kannan N, Arnold JG, Di Luzio M (2008) Spatial calibration and temporal validation of flow for regional scale hydrologic modeling. Journal of the American Water Resources Association 44:829–846

Schachtman DP (1998) Phosphorus Uptake by Plants; From Soil to Cell. Plant Physiology 116:447–453.

Schmalz B, Fohrer N (2009) Comparing model sensitivities of different landscapes using the ecohydrological SWAT model. Advances in Geosciences 21:91–98.

Schmalz B, Tavares F, Fohrer N (2008) Modelling hydrological processes in mesoscale lowland river basins with SWAT—capabilities and challenges. Hydrological Sciences Journal 53:989–1000.

Schoen R, Gaudet J, Bariac T (1999) Preferential flow and solute transport in a large lysimeter, under controlled boundary conditions. Journal of Hydrology 215:70–81.

Selig U, Baudler H, Krech M, Nausch G (2006) Nutrient accumulation and nutrient retention in coastal waters – 30 years investigation in the Darss-Zingst Bodden chain. Acta hydrochimica et hydrobiologica 34:9–19.

Seyfried MS, Rao PSC (1987) Solute Transport in Undisturbed Columns of an Aggregated Tropical Soil; Preferential Flow Effects1. Soil Science Society of America Journal 51:1434.

Sharma SB, Sayyed RZ, Trivedi MH, Gobi TA (2013) Phosphate solubilizing microbes: sustainable approach for managing phosphorus deficiency in agricultural soils. SpringerPlus 2:587.

Sharpley AN (1995) Dependence of Runoff Phosphorus on Extractable Soil Phosphorus. Journal of Environmental Quality:920–926.

Sharpley AN, Bergström L, Aronsson H, Bechmann M, Bolster CH, Börling K, Djodjic F, Jarvie HP, Schoumans OF, Stamm C, Tonderski KS, Ulén B, Uusitalo R, Withers PJA (2015) Future agriculture with minimized phosphorus losses to waters: Research needs and direction. Ambio 44 Suppl 2:163–179.

Sharpley AN, Chapra SC, Wedepohl R, Sims JT, Daniel TC, Reddy KR (1994) Managing agricultural Phosphorous for protection of surface waters: Issues and Options. Journal of Environmental Quality 23:437–451.

Sharpley AN, Jarvie HP, Buda AR, May L, Spears B, Kleinman PJA (2013) Phosphorus legacy: overcoming the effects of past management practices to mitigate future water quality impairment. Journal of Environmental Quality 42:1308–1326.

Sharpley AN, Kleinman PJA, McDowell R, Gitau M, Bryant RB (2002) Modeling Phosphorus Transport in Agricultural Watersheds: Processes and Possibilities. Journal of Soil and Water Conservation 57:425–439.

Sharpley AN, Syers JK (1979) Phosphorus inputs into a stream draining an agricultural watershed. Water, Air, and Soil Pollution 11:417–428.

Shepherd JG, Sohi SP, Heal KV (2016) Optimising the recovery and re-use of phosphorus from wastewater effluent for sustainable fertiliser development. Water Research 94:155–165.

Shrestha NK, Shakti PC, Gurung P (2010) Calibration and validation of SWAT model for low lying watersheds: a case study on the Kliene Nete watershed, Belgium. Hydro Nepal 6:47–51

Simard RR, Beauchemin S, Haygarth PM (2000) Potential for preferential pathways of phophorous transport. Journal of Environmental Quality 29:97–105.

Sims JT, Simard RR, Joern BC (1998) Phosphorus Loss in Agricultural Drainage: Historical Perspective and Current Research. Journal of Environmental Quality:277–293.

Sinaj S, Stamm C, Toor GS, Condron LM, Hendry T, Di HJ, Cameron KC, Frossard E (2002) Phosphorus Exchangeability and Leaching Losses from Two Grassland Soils. Journal of Environmental Quality 31:319–330.

Skaggs RW (1978) A water management model for shallow water table soils. University of North Carolina, Water Resource Research Institute, Technical Report 134

Skaggs RW, Brevé MA, Gilliam JW (1994) Hydrologic and water quality impacts of agricultural drainage. Critical Reviews in Environmental Science and Technology 24:1–32.

Skaggs RW, van Schilfgaarde J, Bartels JM, Hatfield JL, Volenec JJ, Bigham JM (1999) Agricultural drainage. American Society of Agronomy, Inc.; Crop Science Society of America, Inc.; Soil Science Society of America, Inc, Madison, Wisconsin, USA.

Skorbilowicz M, Ofman P (2014) Seasonal changes of nitrogen and phosphorus concentration in Suprasl River. Journal of Ecological Engineering 15:26–31.

Smith DR, Haggard BE, Warnemuende EA, Huang C (2005) Sediment phosphorus dynamics for three tile fed drainage ditches in Northeast Indiana. Agricultural Water Management 71:19–32.

Smith DR, King KW, Johnson L, Francesconi W, Richards P, Baker D, Sharpley AN (2015) Surface runoff and tile drainage transport of phosphorus in the midwestern United States. Journal of Environmental Quality 44:495–502.

Soil Association (2010) A rock and a hard place; Peak phosphorus and the threat to our food security. Last checked: 16. Mai 2017.

Soil Survey Staff. 1999. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. 2nd ed. USDA–NRCS Agric. U.S. Gov. Print. Office, Washington, DC.

Sophocleous M (2002) Interactions between groundwater and surface water; The state of the science. Hydrogeology Journal 10:52–67.

Stålnacke P, Grimvall A, Sundblad K, Tonderski A (1998) Estimation of riverine loads of nitrogen and phosphorus to the Baltic Sea, 1970-1993. Environmental Monitoring and Assessment:173–200.

Stålnacke P, Pengerud A, Vassiljev A, Smedberg E, Mörth C, Hägg HE, Humborg C, Andersen HE (2015) Nitrogen surface water retention in the Baltic Sea drainage basin. Hydrology and Earth System Sciences:981–996.

Stamm C, Flühler H, Gächter R, Leuenberger J, Wunderli H (1998) Preferential Transport of Phosphorus in Drained Grassland Soils. Journal of Environmental Quality 27:515–522.

Starks PJ, Moriasi DN (2009) Spatial Resolution Effect of Precipitation Data on SWAT Calibration and Performance; Implications for CEAP. Transactions of the ASABE 52:1171–1180.

Stepanauskas R, Jörgensen NOG, Eigaard OR, Zvikas A, Tranvik LJ, Leonardson L (2002) Summer inputs of riverine nutrients to the Baltic Sea: Bioavailability and eutrophication relevance. Ecosystems 72:579–597.

Strokal M, Yang H, Zhang Y, Kroeze C, Li L, Luan S, Wang H, Yang S, Zhang Y (2014) Increasing eutrophication in the coastal seas of China from 1970 to 2050. Marine Pollution Bulletin 85:123–140.

Succow M (Hrsg) (2001) Landschaftsökologische Moorkunde; Mit 136 Tabellen. Schweizerbart, Stuttgart.

Tetzlaff B, Kuhr P, Vereecken H, Wendland F (2009) Aerial photograph-based delineation of artificially drained areas as a basis for water balance and phosphorus modelling in large river basins. Physics and Chemistry of the Earth 34:552–564.

Tetzlaff B, Kuhr P, Wendland F (Hrsg) (2010) National inventory of artificially drained lands in Germany; XVIIth World Congress of the International Commission of Agricultural and Biosystems Engineering (CIGR). Canadian Society for Bioengineering (CSBE/SCGAB).

Thampi SG, Raneesh KY (2010) Influence of scale on SWAT model calibration for streamflow in a river basin in the humid tropics. Water Resources Management 24:4567–4578

Thomas Z, Abbott BW, Troccaz O, Baudry J, Pinay G (2016) Proximate and ultimate controls on carbon and nutrient dynamics of small agricultural catchments. Biogeosciences 13:1863–1875.

Tiemeyer B, Kahle P, Lennartz B (2006) Nutrient losses from artificially drained catchments in North-Eastern Germany at different scales. Agricultural Water Management 85:47–57.

Tiemeyer B, Kahle P, Lennartz B (2009) Phosphorus losses from an artificially drained rural lowland catchment in North-Eastern Germany. Agricultural Water Management 96:677–690.

Tiemeyer B, Kahle P, Lennartz B (2010) Designing Monitoring Programs for Artificially Drained Catchments. Vadose Zone Journal 9:14.

Tiemeyer B, Lennartz B, Kahle P (2008) Analysing nitrate losses from an artificially drained lowland catchment (North-Eastern Germany) with a mixing model. Agriculture, Ecosystems and Environment 123:125–136

Tilahun K, Botha JF, Bennie AT (2006) Bromide movement and uptake under bare and cropped soil conditions at Dire Dawa, Ethiopia. South African Journal of Plant and Soil 23:1–6.

Tindall J, Friedel MJ (2016) Transport of Atrazine Versus Bromide and δO18 in Sand. Water, Air, and Soil Pollution 227.

Tipping E, Benham S, Boyle JF, Crow P, Davies J, Fischer U, Guyatt H, Helliwell R, Jackson-Blake L, Lawlor AJ, Monteith DT, Rowe EC, Toberman H (2014) Atmospheric deposition of phosphorus to land and freshwater. Environmental Science. Processes & Impacts 16:1608–1617.

Tomer MD, Meek DW, Jaynes DB, Hatfield JL (2003) Evaluation of nitrate nitrogen fluxes from a tile-drained watershed in Central Iowa. Journal of Environmental Quality 32:642–653

Tomer MD, Moorman TB, Kovar JL, Cole KJ, Nichols DJ (2016) Eleven years of runoff and phosphorus losses from two fields with and without manure application, Iowa, USA. Agricultural Water Management 168:104–111.

Turtola E, Paajanen A (1995) Influence of improved subsurface drainage on phosphorus losses and nitrogen leaching from a heavy clay soil. Agricultural Water Management 28:295–310.

Ulén B, Stenberg M, Wesström I (2016) Use of a flashiness index to predict phosphorus losses from subsurface drains on a Swedish farm with clay soils. Journal of Hydrology 533:581–590.

Ulén B, Wesström I, Johansson G, Forsberg LS (2014) Recession of phosphorus and nitrogen concentrations in tile drainage water after high poultry manure applications in two consecutive years. Agricultural Water Management 146:208–217.

van der Perk M, Klutman WAJ, Li C, Owens PN, Deeks LK, Haygarth PM (2007) The effect of land use on phosphorus content of streambed sediment in the Taw catchment, UK. Geophysical Research Abstracts.

van der Perk M, Owens PN, Deeks LK, Rawlins BG (2006) Streambed Sediment Geochemical Controls on In-Stream Phosphorus Concentrations during Baseflow. Water, Air, & Soil Pollution: Focus 6:443–451.

van Dijk KC, Lesschen JP, Oenema O (2016) Phosphorus flows and balances of the European Union Member States. Science of The Total Environment 542:1078–1093.

van Vuuren DP, Bouwman AF, Beusen A (2010) Phosphorus demand for the 1970–2100 period; A scenario analysis of resource depletion. Global Environmental Change 20:428–439.

van Wijnen J, Ivens WP, Kroeze C, Löhr AJ (2015) Coastal eutrophication in Europe caused by production of energy crops. Science of The Total Environment 511:101–111.

VandeVoort AR, Livi KJ, Arai Y (2013) Reaction conditions control soil colloid facilitated phosphorus release in agricultural Ultisols. Geoderma 206:101–111.

Vaughan RE, Needelman BA, Kleinman PJA, Allen AL (2007) Spatial variation of soil phosphorus within a drainage ditch network. Journal of Environmental Quality 36:1096–1104.

VDLUFA (1991) Das VDLUFA Methodenbuch; Band I - Die Untersuchung von Böden, Speyer.

Vigerstol KL, Aukema JE (2011) A comparison of tools for modeling freshwater ecosystem services. Journal of Environmental Management 92:2403–2409.

Walan P (2013/5) Modeling of Peak Phosphorus; A Study of Bottlenecks and Implications for Future Production, Uppsala, Sweden.

Wang Y, Zhang X, Huang C (2009) Spatial variability of soil total nitrogen and soil total phosphorus under different land uses in a small watershed on the Loess Plateau, China. Geoderma 150:141–149.

Weiler M, Flühler H (2004) Inferring flow types from dye patterns in macroporous soils. Geoderma 120:137–153.

Weir A, Westerhoff P, Fabricius L, Hristovski K, Goetz N von (2012) Titanium dioxide nanoparticles in food and personal care products. Environmental Science & Technology 46:2242–2250.

Werner W, Olfs HW, Auerswald K, Isermann K (1991) Stickstoff- und Phosphoreintrag in Oberflächengewässer über "diffuse Quellen". In: Hamm A (ed) Studie über Wirkungen und Qualitätsziele von Nährstoffen in Fließgewässern, Academia Verlag, Sankt Augustin, pp. 665–764

Whiteside MC (1983) The mythical concept of eutrophication. Hydrobiologia:107–111.

Williams MR, King KW, Ford W, Buda AR, Kennedy CD (2016) Effect of tillage on macropore flow and phosphorus transport to tile drains. Water Resources Research 52:2868–2882.

Winter TC (2001) The concept of hydrologic landscapes. Journal of the American Water Resources Association 37:335–349.

Xie H, Chen L, Shen Z (2015) Assessment of Agricultural Best Management Practices Using Models; Current Issues and Future Perspectives. Water 7:1088–1108.

Xu ZX, Pang JP, Liu CM, Li JY (2009) Assessment of runoff and sediment yield in the Miyun Reservoir catchment by using SWAT model. Hydrological Processes 23:3619–3630

Yasuda H, Berndtsson R, Persson H, Bahri A, Takuma K (2001) Characterizing preferential transport during flood irrigation of a heavy clay soil using the dye Vitasyn Blau. Geoderma 100:49–66.

Zajíček A, Kvítek T, Kaplická M et al. (2011) Drainage water temperature as a basis for verifying drainage runoff composition on slopes. Hydrological Processes 25:3204-3215

Zhang Q, Ball WP, Moyer DL (2016) Decadal-scale export of nitrogen, phosphorus, and sediment from the Susquehanna River basin, USA: Analysis and synthesis of temporal and spatial patterns. Science of The Total Environment 563-564:1016–1029.

Zhang TQ, Tan CS, Zheng ZM, Drury CF (2015) Tile drainage phosphorus loss with long-term consistent cropping systems and fertilization. Journal of Environmental Quality 44:503–511.

Zhang X, Srinivasan R, Liew MV (2008) Multi-Site calibration of the SWAT model for hydrologic modeling. Transactions of the ASABE 51:2039-2049

Zimmer D, Kahle P, Baum C (2016) Loss of soil phosphorus by tile drains during storm events. Agricultural Water Management 167:21–28.

10 Appendix

Curriculum vitae

Personal

Name:	Stefan Koch
Date of birth:	27.05.1985
Place of birth:	Rostock
Citizenship:	German
Marital status:	unmarried, no children

Academic and occupational

since 05/2015	Research assistant at the University of Rostock, Faculty for Agricultural and Environmental Sciences, Chair for Soil Physics in the BMBF project “InnoSoilPhos”
04/2011 – 07/2015	Research assistant at the University of Rostock, Faculty for Agricultural and Environmental Sciences, Chair for Landscape Ecology and Site Evaluation in the BMBF project „COMTESS“
2007 – 2011	Studential research assistant at the Chair for Geodetics and Geo-Informatics and the chair for Soil Physics and Resources Conservation at the University of Rostock, Faculty for Agricultural and Environmental Sciences
since 2005	Freelancer in graphic design and photography

Educational

10/2008 – 04/2011	Academic studies in Land Cultivation and Environmental Protection (M. Sc.), Faculty for Agriculture and Environmental Sciences, University of Rostock, Germany. Master thesis: „Hydrological modelling of the Warnow River“
10/2005 – 04/2008	Academic studies in Land Cultivation and Environmental Protection (M. Sc.), Faculty for Agriculture and Environmental Sciences, University of Rostock, Germany. Bachelor thesis: „Untersuchung des Stofftransportes in einem degradierten Niedermoor mittels Tracerversuch“
09/2004 – 07/2005	Civil Service in the inpatient care at the Clinic and Polyclinic Radiotherapy of Rostock University
1995 – 2004	Secondary school „Käthe Kollwitz“ in Rostock, graduated with A-level
1991 – 1995	Primary school „Uns Lierkasten“ in Rostock

Publication record

Peer-reviewed articles

Koch, Stefan; Kahle, P.; Lennartz, B. (2017): Long-term phosphorus dynamics in an agricultural watershed in North-Eastern Germany. In: *Ambio*. Submitted in November 2016, currently under review.

Koch, Stefan; Kahle, P.; Lennartz, B. (2016): Visualization of colloid transport pathways using Titanium(IV) oxide as a tracer. In: *Journal of Environmental Quality* 45, 2053–2059.

Koch, Stefan; Jurasinski, G.; Koebsch, F.; Koch, M.; Glatzel, S. (2014): Spatial variability of annual estimates of methane emissions in a phragmites australis (cav.) trin. ex steud. dominated restored coastal brackish fen. *Wetlands* 34(3), 593-602.

Koch, Stefan; Bauwe, A.; Lennartz, B. (2013): Application of the SWAT Model for a Tile-Drained Lowland Catchment in North-Eastern Germany on Subbasin Scale. In: *Water Resources. Management* 27 (3), 791–805.

Abstracts/poster presentations/oral presentations

Kahle, Petra; Bauwe, A.; Koch, S.; Lennartz, B. (2017): P-Export patterns from artificially drained agricultural land. *Poster presentation.* 11th Baltic Sea Science Congress. Rostock. 12.16.06.2017

Koch, Stefan; Kahle, P.; Lennartz B. (2016) Phosphorus dynamics in agricultural used lowland catchments in NE-Germany. *Poster presentation.* IPW 8, Rostock 12.-16.09.2016

Koch, Stefan; Kahle, P.; Lennartz B. (2016) Visualization of colloid transport pathways in mineral soils. IPW 8, *Poster presentation.* Rostock 12.-16.09.2016

Koch, Stefan; Kahle, P.; Lennartz, B. (2015): Visualization of colloid transport pathways in mineral soils. *Poster presentation.* Sustain. Kiel. 22.-25.09.2015.

Koch, Stefan; Jurasinski, G.; Glatzel, S. (2014): Variability of methane emissions from coastal ecosystems in Northern Germany. *Oral presentation.* 7. Agrosnet Doktorandentag, Halle. 18.02.2014.

Koch, Stefan; Jurasinski, G.; Glatzel, S. (2014): Spatial variability of annual estimates of methane emissions in a phragmites australis (cav.) trin. ex steud. dominated restored coastal brackish fen. *Oral presentation.* EGU General Assembly Conference Abstracts 15, 2740.

Koch, Stefan; Witte, S.; Jurasinski, G. (2013): Variability of methane emissions from coastal ecosystems in Northern Germany. *Oral presentation.* BMBF status conference (A/B) 2013, Berlin. 18.-19.04.2013.

Koch, Stefan; Jurasinski, G.; Glatzel, S. (2013): Spatial variability of annual estimates of methane emissions in a phragmites australis (cav.) trin. ex steud. dominated restored coastal brackish fen. *Poster presentation.* BMBF status conference (A/B) 2013, Berlin. 18.-19.04.2013.

Theses

I Rationale and research objectives

- Besides nitrate (NO_3^-), phosphorus (P) in its mobile form (PO_4^{3-}) is the main contributor to the eutrophication of north-eastern German freshwaters and the Baltic Sea.
- Nonetheless, there is a lack of understanding of P-transport processes on a variety of spatial scales from the plot and the field to the catchment scale.
- Although awareness about environmental health is increasing, and so is the willingness of responsible resource use, there is still marked P leaching from agricultural areas in north-eastern Germany.
- Understanding the hydrology and the transport pathways of P to surface waters is crucial to deliver land use- and P-management guidelines for farmers and other stakeholders and authorities.
- This thesis aims to contribute to our understanding of P-transport pathways to surface waters in agriculturally used lowland catchments, particularly by answering the following questions: (i) How does artificial drainage affect the hydrology of the Warnow river basin and its contributing sub-basins, and the predictive power of an eco-hydrologic model? (ii) How does the spatial scale affect the detectable pathways of P transport to surface waters? (iii) Do certain events play a critical role in the release of P from agriculturally used areas? (iv) Can field scale processes be reproduced at the catchment scale?

II Methods

- A top-down approach was used to determine the P-transport pathways from the catchment to the field and the soil profile scale.
- The Soil and Water Assessment Tool (SWAT) model was used to determine the impact of artificial subsurface drainage to the catchment hydrology.
- Long-term data of dissolved reactive phosphorus (DRP) and total phosphorus (TP) (derived by the State Office of Environment, Nature Conservation, and Geology of Mecklenburg-West Pomerania, LUNG MV) were analyzed for temporal trends and detectable pathways of P transport at the catchment scale.
- DRP and TP concentrations were monitored in the hydrological season 2015/2016 at our field monitoring site. The impact of rainfall and discharge events was evaluated on three spatial scales (tile drain (4.2 ha), drainage ditch (179 ha), and a brook (1,550 ha)).
- A dye-tracer study was conducted using Brilliant Blue (BB, solution) and Titanium(IV) oxide (TiO_2, suspension), as tracers to visualize solute and particle transport through soils with different clay content.
- A suction lysimeter experiment was conducted to determine the preferential transport of bromide (Br^-), DRP, and TP.

III Main results

- The incorporation of artificial drainage into the setup of the SWAT model significantly improved the predictive power of the model.
- The riverine concentrations of P (DRP, TP) in the Warnow river basin decreased significantly between 1990 and 2010, which is most likely related to the installation of sewage treatment works in the 1990s. Nonetheless, the contribution of diffused sources of P to surface waters was high.
- DRP followed the base-flow signal while the TP followed a fast flow component, which seems most likely related to event-based drainage discharge.
- In the study season, five rainfall events contributed 15% to 77% and 49% to 68% of the total seasonal load of DRP and TP on the three observed spatial scales at our field site respectively.
- The contribution of tile drainage to the export of TP (e.g. particulate P) from agricultural fields is higher than that for larger spatial scales. The TP:DRP ratio decreases with increasing catchment area, which indicates sedimentation.
- The spatial variability of DL-extractable soil P on the field scale is high, and shows recurring patterns.
- The transport of solutes and particles is strongly affected by preferential flow in loamy and clay soils.
- Although the overall transport of colloids to deeper soil horizons is low, the potential of fast transport through singular macropores (e.g. earthworm channels)—through which colloids are exclusively transported—is large and increased with increasing clay or silt content.
- TiO_2 is a suitable dye tracer for the visualization of colloid transport in mineral soils.
- Bromide is transported preferentially through the investigated loamy soil while DRP and TP follow erratic transport patterns. The suction lysimeter test indicates a high potential of DRP being released into the groundwater through severe rainfall events.

IV Conclusion and Outlook

- Our studies indicate the importance of artificial tile drainage and rainfall events to the transport of P to surface waters on all the observed spatial scales.
- However, further research is needed on the interaction of different P pools (groundwater, soil, bed sediment, water). Particular focus should be given to the re-mobilization of bed sediments during discharge events, and the chemical and biological interaction with other nutrients (NO_3^-).
- High-frequency measurements on different scales, beginning with the tile drainage scales, will give insights into transport processes following management measures (e.g. manure application, ditch dredging, etc.).
- The integrated modeling of P and the impacts of land-use management strategies and climate change on the catchment scale will be a helpful future tool for the development of guidelines for authorities and stakeholders.
- The pollution of the Baltic Sea is still high. Since the concentrations of P observed in the larger rivers of the southern Baltic are typically small, we should extend our monitoring to smaller rivers and direct dischargers.

Acknowledgements

I've been working at the University of Rostock for six consecutive years now. These years were an exceptional experience. I had the pleasure to work at the Chair of Landscape Ecology and Site Evaluation and at the Chair of Soil Physics (formerly Soil Physics and Resources Conservation). The academic work has filled my life with joy and meaningful work. I met many new friends and great academic scholars.

I gratefully emphasize the efforts Prof. Dr. Bernd Lennartz put into my work as a Ph. D. student and in my education as a bachelor and master student at the University of Rostock. My Bachelor and Master theses were likewise supervised at the chair for soil physics. He always trusted in my skills and abilities and had a friendly ear whenever needed. I like to acknowledge the ideas, inspirations, great suggestions for improvements, target-aimed discussions and feedback he gave me throughout my time as a Ph. D. student. His enthusiasm helped me to stay focused and to finish the thesis in time.

I'm also grateful to Dr. Petra Kahle, research assistant at the Chair of Soil Physics. She was a great peer since I joined the work group. I will never want to do without any of our long discussions on P transport, our sampling station in Dummerstorf or the work in the lab and in the field again. She also significantly contributed to two manuscripts that are presented here.

Particular thanks go to Dr. Andreas Bauwe. He significantly contributed to one manuscript presented here. He is also great kindred spirit regarding the work with the Soil and Water Assessment tool that granted us not just one sleepless night.

Furthermore, I thank the whole work group of the Chair for Soil Physics for helping each other out through the scientific daily routine, administrative challenges and laboratory and field work.

Of course, a particular thanks belongs to my family. My parents always supported me and my private and occupational decisions and bore all my tempers. My brother was a great help in the process of finishing my thesis and is a great peer in Environmental Science and his criticism and ideas force me to improve and to progress.

My Girlfriend Claudia always supported all steps I made since we know each other. I would like to thank her for being my bastion of calm, my sandbag and my best friend.

As I stated in the beginning my scientific work life started at the chair for Landscape Ecology and Site Evaluation. I would like to thank my former colleagues and friends there for helping through the struggles of getting started in an academic career. Particular thanks go to Dr. Gerald Jurasinski, whose enthusiasm and cheerfulness in educating young Ph. D. students should be mandatory at Universities and a good example to other academic teachers.

Finally, I would like to draw attention and say thanks to all of my friends that make my life what it is. Without my friends and the fun I have in my private life, my occupational life would not be half as joyful and exciting as it is.

Eidesstattliche Erklärung

Hiermit erkläre ich durch eigenhändige Unterschrift, die vorliegende Dissertation selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet zu haben. Die aus den Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht. Die Dissertation ist in dieser Form noch keiner anderen Prüfungsbehörde vorgelegt worden.

Rostock, den 27.06.2017

Stefan Koch