Ministry of Environment of Denmark
Environmental Protection Agency

Modelling and mapping pesticide exposure risk at the catchment scale (MOMAPEST)

Pesticide Research
No. 221

Marts 2024

Publisher: The Danish Environmental Protection Agency

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ISBN: 978-87-7038-605-0

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Preface

The research project 'Modelling and mapping pesticide exposure risk at the catchment scale (MOMAPEST)' was carried out from 2017 to 2022 at Aarhus University, Department of Ecoscience, in cooperation with the Geological Survey of Denmark and Greenland, Department of Groundwater and Quaternary Geology Mapping.

The project was financially supported by the Danish Environmental Protection Agency's Pesticide Research Programme and the authors wish to acknowledge the Danish Environmental Protection Agency for funding the project (J.no. 2019-12571).

Sammenfatning og konklusion

Der er behov for modeller til at give realistiske vurderinger af pesticideksponering af overfladevand og grundvand på landskabsniveau. Komplekse, fuldt distribuerede modeller med store krav til inputdata har tidligere været forsøgt anvendt til at beskrive pesticidtransport i vandløb i Danmark uden tilfredsstillende resultat.

Formålet med projektet er at undersøge, om den semi-distribuerede model SWAT kan anvendes under danske forhold til at beregne og visualisere pesticideksponering af grundvand og overfladevand fra lille skala til landskabsniveau. SWAT er en frit tilgængelig, open source økohydrologisk oplandsmodel, som fleksibelt kan tilpasses de tilgængelige inputdata. SWAT er en holistisk model, som parallelt beskriver hydrologi, sediment-, næringsstof- og pesticiddynamik. Der er mulighed for at inddrage ikke-landbrugskilder til pesticideksponering, f.eks. frugt- og juletræsplantager og byområder. SWAT har været anvendt til at beskrive pesticiddynamik i en række studier i USA og Europa

I projektet videreudvikles og testes et modul til SWAT til beskrivelse af transport af opløste og partikelbundne pesticider gennem makroporer og drænrør. SWAT-modellen, udvidet med det nye modul, anvendes i en stor-skala opsætning på hele Fyn. På grundlag af modellens output udarbejdes detaljerede kort over risikoområder for pesticidtab og vandområder i risiko for pesticideksponering. Risikokort over pesticideksponering sammenlignes med de tilgængelige målinger af pesticidkoncentration i grundvand og overfladevand.

Den originale SWAT-model (revision 622) blev udvidet med et nyt modul, DrainPST, som muliggør simulering af præferentiel transport af vand, sediment og pesticider gennem makroporer til dræn og videre til overfladevand. SWAT-modellen udvidet med DrainPST og den originale SWAT-model blev begge opsat på det mindre, drænede opland Lillebæk. De to modellers evne til at simulere drænafstrømning, vandføring, sedimentransport samt pesticidkoncentration og -transport af tre pesticider (Bentazon, Propiconazol og Pirimicarb) blev vurderet og sammenlignet.

Både den originale SWAT-model og SWAT-modellen udvidet med DrainPST er i stand til at simulere vandføring i dræn og vandløb, hvor den udvidede SWAT-model præsterer bedst. Makroporemodulet betyder, at vandføringen gennem dræn stiger på bekostning af overfladisk og overfladenær afstrømning sammenlignet med den originale SWAT-model. Dette medfører en forbedret simulering af sedimenttransport i vandløbet. Simuleringen af pesticidtransport er ikke tilfredsstillende for nogen af modellerne baseret på et Nash-Sutcliffe Efficiency kriterium, men tilføjelsen af modulet DrainPST forbedrer dog i høj grad simuleringen med den udvidede model, specielt for Bentazon. SWAT-modellen udvidet med DrainPST beskriver for alle tre pesticider amplituden i målt transport, dvs. at på trods af at modellen fejler i simulering af den tidslige forekomst af pesticidhændelser, så kan modellen reproducere tilsvarende hændelser.

Sædskifter og pesticid-management (dosering og sprøjtetidspunkter) blev udviklet for fynske afgrøder baseret på data fra landovervågningsprogrammet i NOVANA, det nationale natur- og miljøovervågningsprogram, og suppleret af indberettede, landsdækkende sprøjtejournaldata. Managementdata blev inkluderet i en storskala SWAT-model for hele Fyn. En mindre delmodel omfattende tre hovedoplande på Fyn blev introduceret for at reducere simuleringstiden. Delmodellen blev kalibreret og valideret mod daglige vandføringsdata for de tre vandløb for perioden 2003 – 2017 med tilfredsstillende resultat. De kalibrerede parametre blev overført til modellen for hele Fyn og valideret mod daglige vandføringsdata for hele studieperioden 2006 – 2015 med tilfredsstillende resultat.

SWAT beregner kombinationer på daglig basis af aktuelt vejr, jordforhold, topografi og dyrkningspraksis inklusiv pesticidsprøjtninger. Modellen blev anvendt til at producere risikokort for hele Fyn over eksponering af overfladevand med pesticiderne Bentazon, Propiconazol og Pirimicarb. De simulerede gennemsnitskoncentrationer var lave, men modellen udpegede deloplande med relativt højere værdier. De simulerede daglige maksimumværdier var to til tre størrelsesordener større end gennemsnitsværdierne. Adskillige deloplande havde maksimum Bentazon-koncentrationer større end 0,5 µg/l og op til 3,4 µg/l. For Pirimicarb blev der ikke beregnet daglige koncentrationer større end 0.5 µg/l, og generelt var de beregnede maksimumkoncentrationer mellem 0,1 µg/l og 0,5 µg/l. Kun to deloplande havde Propiconazol-koncentrationer større end 0,1 µg/l, og ingen deloplande havde koncentrationer over 0,5 µg/l.

En økotoksikologisk vurdering af de beregnede vandløbskoncentrationer indikerer, at maksimumkoncentrationerne af specielt Pirimicarb og Propiconazol kan have skadelige effekter på vandløbsorganismer, mens gennemsnitskoncentrationerne er vurderet ikke at have nogen effekt.

En reel validering af de simulerede pesticidkoncentrationer var ikke mulig pga. de meget få pesticidmålinger i fynske vandløb. En sammenligning med pesticidmålinger fra alle danske vandløb indikerede, at modelresultaterne er i den rigtige størrelsesorden for alle tre undersøgte pesticider. Dette peger på, at trods den usikkerhed, der er knyttet til modelresultaterne, kan den udvidede SWAT-model være et nyttigt værktøj til at vurdere risiko for pesticideksponering af overfladevand på landskabsniveau, f.eks. i udarbejdelse af en strategisk moniteringskampagne.

SWAT simulerer ikke pesticidprocesser i grundvand. Detaljerede kort over potentiel nedvaskning af pesticider til grundvand blev produceret ved post-processering af SWAT-output på HRU-niveau. Modelresultaterne blev vurderet ved at sammenligne med pesticidmålinger i grundvand foretaget under NOVANA-delprogrammerne GRUMO og LOOP og suppleret af data fra vandværker.

Ud af de tre test-pesticider og deres nedbrydningsprodukter er kun Bentazon og 1,2,4-Triazol (nedbrydningsprodukt af bl.a. Propiconazol) fundet i grundvand på Fyn. Sammenligningen mellem målinger og simuleret potentiel nedvaskning af pesticid viste, at der ikke er nogen statistisk signifikant sammenhæng mellem påvist pesticid eller nedbrydningsprodukt i en grundvandsboring og modelsimuleret, potentiel nedvaskning indenfor en 1 km's radius fra boringen. Med hensyn til pesticideksponering af grundvand må det derfor konkluderes, at SWAT-modellen på det nuværende udviklingsstade ikke er velegnet som beslutningsstøtteværktøj.

Summary and conclusion

A quantitative description of the fate of pesticides in the terrestrial and aquatic environments is very complex. Models are needed to give realistic evaluations of pesticide exposure of streams and groundwater at the landscape level. Fully distributed models aiming at a physically and chemically correct simulation of local adsorption, degradation and transport in time and space have been tested in Denmark to describe transport of pesticides in streams in Denmark without satisfactory results.

The aim of this project is to test the ability of the semi-distributed SWAT model to quantify and visualize pesticide exposure of groundwater and surface water from small scale to landscape scale. SWAT is a freely available, open-source eco-hydrological catchment model that flexibly can be adapted to the available input data. SWAT is a holistic model describing synchronously hydrology, sediment-, nutrient-, and pesticide dynamics. Non-agricultural pesticide sources, e.g. orchards and plantations of Christmas trees, can be included. SWAT has been applied in several studies of pesticide dynamics in the USA and in Europe.

A new module for SWAT to describe the transport of dissolved and particulate bound pesticides via macropores to tile drains is further developed and tested in the project. Subsequently, the SWAT model extended with the new module is used to quantify and visualize pesticide exposure of streams and groundwater for the entire island of Fyn, Denmark. Risk maps of pesticide exposure are compared to available measurements of pesticide concentrations in streams and groundwater.

The original SWAT model (revision 622) was extended with a new module, DrainPST, enabling simulation of the processes of preferential transport of water, sediment and pesticide through soil macropores to tile drains and further to surface waters. The SWAT model extended with DrainPST and the original SWAT were both applied to a small tile drained catchment, Lillebæk, in Denmark. The simulation performance of tile drain flow, streamflow, sediment yield and occurrence of three types of pesticides (Bentazone, Propiconazole, Pirimicarb) by the two models were evaluated and compared.

Both the original SWAT and DrainPST are capable of simulating streamflow and tile drain flow with DrainPST performing slightly better. However, the added macropore module in DrainPST results in a higher drain flow mainly on the expense of surface flow and lateral surface flow compared to SWAT. This again results in an improved simulation of sediment delivery and transport in the stream. Although overall unacceptable based on Nash Sutcliffe Efficiency criteria, DrainPST greatly improves the simulations of pesticide transport, most notably for Bentazone compared to SWAT. The SWAT model extended with DrainPST captures for all three pesticides the amplitude in measured transport, i.e. in spite of failing to correctly simulate the timing of pesticide transport peaks, the model can reproduce similar events.

Pesticide management rotations for the crops in Fyn were developed from 2006-2015 based on the Danish national environmental LOOP monitoring program NOVANA. These pesticide management rotations were adapted to a large SWAT catchment scale model covering the entire Fyn, Denmark. A smaller inversion model was developed only including three main catchments in Fyn in order to reduce computation time. The inversion model was calibrated and validated using daily discharge data for every second year for respectively calibration and validation with acceptable performance. The calibrated parameters were transferred to the forward model covering the entire Fyn. The forward model was validated against daily discharge measurements for the entire study period with acceptable performance.

SWAT calculates combinations on a daily basis of actual weather, soil conditions, topography, and land management including timing of pesticide application. The forward model was used to produce maps of pesticide exposure for the entire Fyn for the pesticides Bentazone, Primicarb and Propiconazol. The simulated average concentrations were low, however the model pointed to specific sub-basins with relatively elevated values. The simulated daily maximum values are two to three orders of magnitude higher than the average values. For Bentazone, several sub-basins had concentrations above 0.5 µg/l and up to 3.4 µg/l. For Pirimicarb, no simulated maximum concentrations were above 0.5 µg/l and in general most of the simulated maximum concentrations were between 0.1 and 0.5 µg/l. For Propiconazol, only two sub-basins had concentrations above 0.1 µg/l and no sub-basins had concentrations above 0.5 µg/l.

An ecotoxicological evaluation of the simulated streams water concentrations indicate that the maximum levels of pesticides modelled for the MOMAPEST sub-basins, especially Pirimicarb and Propiconazole, may have detrimental effects on aquatic organisms, whereas the mean levels are all very low and not expected to have negative effects.

Scarcity of pesticide measurements in streams on Fyn hampered a proper validation of the modelling results. However, a comparison to all available pesticide measurements in Danish streams indicated that modelling results are in the right order of magnitude for all three test pesticides. Thus, despite the uncertainty surrounding model predictions, the extended SWAT model may be a useful tool for assessing the risk of pesticide exposure of surface waters at landscape level and used e.g. as a guide for setting up strategic monitoring campaigns.
Maps of potential leaching to groundwater were produced by post processing SWAT output at HRU level for the entire catchment as SWAT does not track pesticides in groundwater. The performance of SWAT was evaluated by comparing simulated pesticide leaching to groundwater to pesticide measurements in the dataset prepared annually for the NOVANA program, including the wells from the national groundwater monitoring network (GRUMO and LOOP) and the waterworks’ wells used for drinking water purposes.

From the selected pesticides and metabolites, only Bentazone and 1,2,4-triazole were detected in the groundwater at Fyn. There is no statistically significant spatial association between the simulated maximum pesticide leaching within 1km of the well and the detected pesticides (or degradation product) in groundwater at the larger scale (Fyn). Thus, it can be concluded that regarding groundwater, SWAT at its current development stage is not useful for decision-making or to inform policy on the risk of pesticides exposure.

1. Introduction

A quantitative description of the fate of pesticides in the terrestrial and aquatic environments is very complex. Fully distributed models aiming at a physically and chemically correct simulation of local adsorption, degradation and transport in time and space have been developed during more than 20 years. In Denmark, Styczen et al. (2004) developed a fully distributed model set-up for pesticide transport in two small catchments. These detailed models face, however, large challenges and so far, modelling of pesticide transport in Denmark has seen only little success at full catchment scale. One challenge is parameterization and calibration of these very complex models (e.g. degradation and sorption characteristics of pesticides, see also Köhne et al., 2009) since sufficient data for parameterization seldom are available at a high spatial resolution. This problem will only increase if these kind of models were to be used for larger areas in Denmark since high resolution input data on e.g. soil characteristics are non-existent in the required quality. In spite of great efforts, it has still not been possible to simulate pesticide transport for larger areas nation-wide at catchment scale satisfactorily. In the work of Styczen et al. (2004) it was concluded, based on a very comprehensive study using a fully distributed model in two intensively monitored small catchments, that lack of data for calibration/validation was a main obstacle for a successful model implementation. It should therefore be carefully considered whether this model approach is the optimal in order to obtain valid predictions at the catchment scale. It may be that a more pragmatic model approach would be more robust and provide more useful results especially at the larger scale in spite of a more simplistic description of physical and chemical processes.

Hypothesis
The SWAT model, extended with process-descriptions of pesticide transport through macropores and tile drains, is able to simulate the risk of pesticide exposure to ground water and surface water bodies at the national scale in Denmark.

1.1 Background

Several countries in Europe report that groundwater has concentrations of pesticides that exceed the quality standards (Eurostat 2018). The European Union states that water pollution are among the main challenges in the European countries and agriculture is considered as the greatest contributor to pesticides in European surface and groundwater (Eurostat 2018, Kristensen et al. 2018). In Denmark, the same trend is seen and more and more chemicals such as different pesticides are recently found in the drinking water (Miljøministeriet and Miljøstyrelsen 2021, Fiskeri 2020). However, the number of pesticides being analyzed for has also increased over the years. In 2019, the Danish Environmental Agency did the largest screening for pesticides in drinking water so far involving 263 wells being tested for 415 different pesticides (Fiskeri 2020). The normal monitoring of drinking water quality in Denmark includes testing for 40 different pesticides due to the high cost associated with monitoring of pesticides (Fiskeri 2020).

Pesticides in groundwater and surface waters are addressed by several directives in order to reduce the risks and impacts of pesticide use on human health and the environment (Eurostat 2018). Among these are the Pesticides Framework Directive (Directive 2009/128/EC) (European Parliament 2009), Environmental Quality Standards Directive (Directive 2008/105/EC) (European Parliament 2008), Drinking Water Directive (Directive 98/83/EC) (Council of the European Union 1998) and Groundwater Directive (Directive 2006/118/EC) (European Parliament 2006). The last three are under the Water Framework Directive (WFD) (2000/60/EC) (European Parliament 2000).

Environmentally hazardous substances have been included in The Danish Environmental Protection Agency's National Monitoring Program for the Aquatic Environment and Nature (NOVANA) since 2003. Monitoring of environmentally hazardous substances in groundwater has been included from the beginning of the National Groundwater-monitoring program GRUMO from 1989, which is a part of NOVANA (Miljøstyrelsen 2000, Nilsson et al. 2019a). The Danish monitoring program is divided into surveillance and operational monitoring according to the WFD (European Parliament 2000). At every revision of the Danish monitoring program adjustments have been made regarding to which hazardous substances should be included in the monitoring. If the previous monitoring has shown that a substance is not or largely not detected, or if it occurs for a long time at an unchanged concentration level, the substance is removed from the monitoring program (Nilsson et al. 2019a). Monitoring data are stored in Danish national databases. New substances are included in the monitoring for example if legal requirements are made for monitoring or if other results have shown that this substance is relevant. The adjustments which are made have always been made on the basis of the strategy for monitoring of environmentally hazardous substances in Denmark, which was developed and described in connection with the establishment of NOVANA 2011-2015 (Naturstyrelsen et al. 2011) and adjusted in connection with the organization of NOVANA 2017-21. Overall it means that the length of available time series varies for all pesticides in the Danish monitoring (Nilsson et al. 2019a). Pesticides in stream water are currently analyzed yearly at five surveillance stations and at 10 – 36 operational stations. Respectively 17 and 11 different pesticides are analyzed for at the two station types with a frequency of 4 – 12 samplings per year (Miljøstyrelsen, 2017b).

Quantitative assessment of the spatial-temporal distribution of pesticide occurrence and exposure in water bodies could benefit researchers and local stakeholders for understanding pesticide contamination status and potential ecological risks (Wang et al., 2019), and thus help foster science-informed agriculture management and pesticide mitigation strategies. While watershed monitoring is expensive and labor intensive, and short-term monitoring is difficult for addressing potential long-term exposure variability (Cheng et al., 2020), the application of process-based watershed-scale models, such as the Soil and Water Assessment Tool (SWAT) (Neitsch et al., 2011), the Hydrologic Simulation Program-Fortran (HSPF) (Bicknell et al., 1996; Laroche et al., 1996) and the Pesticide Root Zone Model-Riverine Water Quality model (Mullins et al., 1993; Parker et al., 2007), has become increasingly popular in obtaining quantitative information on pesticide exposure (Wang et al., 2019).

Several one-dimensional models, such as HYDRUS 1D (Šimůnek, Huang and van Genuchten 1998), MACRO (Jarvis 1991) and Daisy (Hansen et al. 2012) have been developed to simulate vertical pesticide transport in the soil as a function of physically based soil, water and pesticide transport algorithms, which are often much more detailed than corresponding routines used in catchment models. However, although the process description of pesticide transport is usually simplified compared with small-scale models, catchment models offer the capability of simulating overall complex physical, chemical, and biological interactions of multiple land uses and soils at the landscape level (Krysanova, Müller-Wohlfeil and Becker 1998). Thus, catchment models are essential tools for investigating pesticide fate and transport at the catchment scale, which cannot be accomplished with field-scale or one-dimensional models.

The Soil and Water Assessment Tool (SWAT) is a continuous time and spatially semi-distributed catchment model, in which hydrological processes and water quality are coupled with crop growth and agricultural management practices (Arnold et al., 1998). The major components of SWAT include hydrology, weather, erosion, nutrients and pesticide fate. SWAT considers surface runoff, percolation, lateral subsurface flow, flow through tile drains, groundwater return flow, evapotranspiration and channel transmission losses. Aarhus University has recently extended SWAT with a module describing the flow of water through macropores to tile drains (Lu et al., 2015). The current version of SWAT simulates pesticide movement and fate in the landscape by algorithms adapted from GLEAMS (Leonard, Knisel and Still 1987). In this setup, SWAT has been applied and evaluated for modeling pesticide transport for catchments in the United States (Luo et al., 2008, Luo and Zhang, 2009; Du et al., 2006; Vazquez-Amabile et al., 2006; Neitsch et al., 2002; Zhang & Zhang, 2011) and also in Europe (Boithias et al., 2011; Gevaert et al., 2008; Kannan et al., 2006; Fohrer et al., 2014). SWAT is recognized by the U.S. Environmental Protection Agency (EPA) and has been incorporated into the EPA's BASINS (Better Assessment Science Integrating Point and Non-point Sources).

SWAT divides a catchment into sub-catchments based on topography, each sub-catchment including one stream, comprised of a small tributary and a main channel, respectively. The spatial differentiation is flexible; the size of the sub-catchments is decided by the model user and depends on the desired level of detail in the model description. Within sub-catchments, SWAT aggregates unique combinations of land cover, soil, and management combinations into hydrologic response units or HRUs. This aggregation of HRUs, which dramatically speeds up model run time, is one of the main differences between the semi-distributed SWAT model and fully distributed models (e.g. MikeSHE). HRUs in the current SWAT model do not interact with each other, thus SWAT is currently not capable of simulating three-dimensional flow of groundwater (although ongoing work is coupling SWAT with the MODFLOW groundwater model, eventually resulting in a fully distributed model, Chung et al., 2011, Bailey et al., 2016; Molina-Navarro et al., 2019; Liu et al., 2020).

In the EU, the modelling approach of the Forum for the Coordination of pesticide fate models and their Use (FOCUS) is used to determine the worst case predicted environmental concentration (PEC) in surface waters and sediments. FOCUS uses mechanistic models to consider pesticide leaching via drainage (MACRO, Jarvis, 2015), surface runoff (PRZM-3, Carsel et al., 1998), and spray drift as well as fate and transport processes in the respective water bodies (TOXSWA, Adriaanse et al., 2009). However, it has been demonstrated that the FOCUS approach underestimates the measured field concentration of insecticides (Knäbel et al., 2012) and fungicides (Knäbel et al., 2014). The current version of SWAT uses some of the same methods as FOCUS, e.g. for simulating surface runoff and in-stream routing of pesticides, but needs extensions, however, to model pesticide transport through macropores and tile drains. An extension including pesticide transport to tile drains has been developed and preliminary results have been presented at the international SWAT conference (Lu et al., 2015), while the modelling of macropore flow and pesticide transport need further development and validation. The FOCUS approach includes a single field-surface water body system, thus contrary to SWAT it is not possible to simulate landscape processes including multiple land uses with multiple management practices and several sources of pesticides.

Aarhus University has developed a national SWAT model comprising six regional models with 761 sub-catchments and more than 40,000 HRUs, figure 1.1 (Thodsen et al., 2015; Lu et al., 2016). Agricultural management data was derived from the national register of fertilizer accounts (mandatory to fill out for every farmer), and the general agricultural register containing information on crop coverage. These data were combined to yield coherent data for crop distributions and fertilizer applications at the 'field-block' level for Denmark following the procedure in Børgesen et al. (2009). This data set was divided into a series of farm types and 5-year crop rotations (in total 84) including timing and application rates of fertilizers.

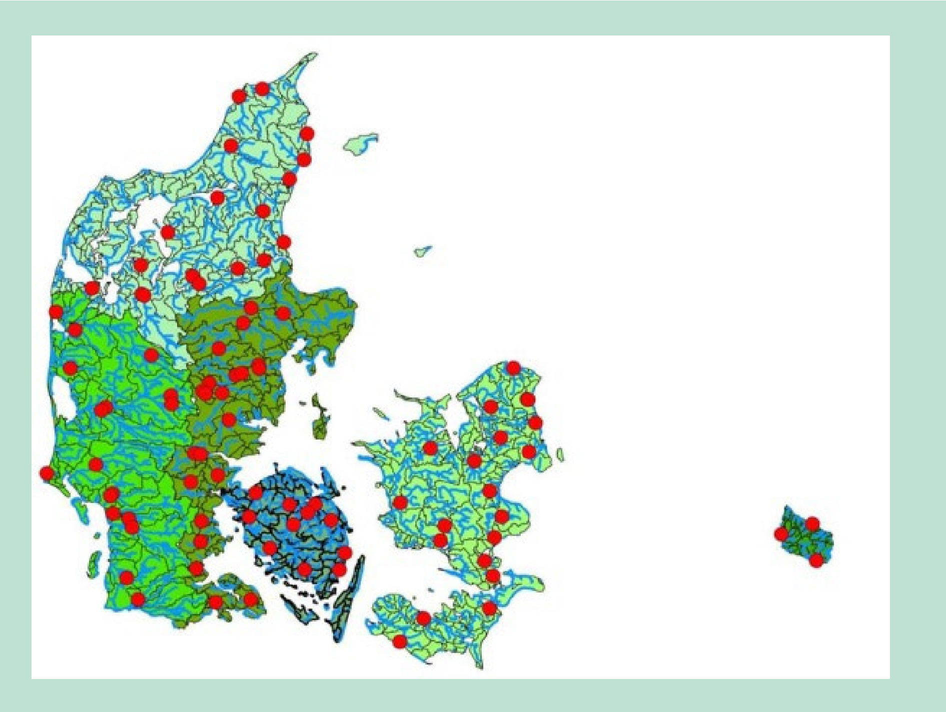

FIGURE 1.1. The national SWAT model divided into 6 regional models and 761 sub-catchments. Data from 91 gauging stations are used for model calibration.

A main advantage of SWAT is, apart from calculation speed, the ability to tailor the model application to the amount of data which is actually available. SWAT is run through an ArcGIS interface, and results can be presented as maps visualizing critical source areas and water bodies at risk of exposure to pesticides.

1.2 Aim

This project (*i*) develops and tests catchment scale modelling of pesticide degradation, adsorption and transport from land surfaces to ground water and surface waters under Danish conditions by expanding an existing SWAT catchment model setup, and (*ii*) demonstrates and visualizes the ability to do large catchment scale mapping of risk of pesticide exposure to ground water and surface water bodies.

1.3 Project implementation

The scientific and applied focus of this project is three-fold:

1. Further development of the macropore module (Lu et al., 2015) enabling SWAT to simulate pesticide transport via macropores and tile drains to surface waters.
2. Test of the ability of the extended SWAT model to simulate pesticide transport in stream water.
3. Demonstration and visualization of the extended SWAT model to map critical source areas and ground water and surface water bodies at risk of pesticide exposure in a large catchment scale application based on the national SWAT model.

1.4 Structure of the report

This report is divided into three main sections, where the completed activities and results are reported.
Section 1: Further development of the macropore module in SWAT.
Section 2: Test of the extended SWAT model in the small catchment Lillebæk and
Section 3: Risk assessment of pesticide exposure at large catchment scale.

2. Further development and test of the macropore module in SWAT

In this part we describe the development of an extension, DrainPST, for the SWAT model (revision 622) so that the processes of preferential transport of water, sediment and pesticide through soil macropores to tile drains and further to surface waters can be included. The DrainPST SWAT and the original SWAT were both applied to a small tile drained catchment, Lillebæk, in Denmark. The simulation performance of tile drain flow, streamflow, sediment yield and occurrence of three types of pesticides, Bentazone, Propiconazole, and Pirimicarb, by the two models were evaluated and compared. These three pesticides are selected because they represent a large range in characteristics

2.1 Materials and methods

2.1.1 Pesticide modelling in SWAT

In SWAT, the basin is divided into sub-basins according to a digital elevation model (DEM) and an optional user-input stream network, each sub-basin containing a section of main channel or a tributary of the river. Each sub-basin is further divided into Hydrologic Response Units (HRUs), which are unique combinations of land use, soil type, and surface slope, making up the smallest building blocks of the semi-distributed model (Liu et al., 2020), figure 2.1. In each HRU, water balance, crop growth, sediment erosion, the fate of nutrients, microorganisms and pesticides are modelled as lumped, i.e. calculated with disregard to geographic location, and then summed at sub-basin level and routed through the streams (Neitsch et al., 2011).

FIGURE 2.1. SWAT set up illustrating a riverbasin subdivided into a sub-basin which is further subdivided into Hydrologic Response Units defined by unique combinations of landuse, surface slope and soil type (after Zettam, 2018).

The pesticide modeling in SWAT can be grouped into three processes, which are pesticide fate at field scale (HRU level), pesticide transport at basin level and pesticide transport in streams. Pesticides are aerially applied (sprayed) to a HRU with some fraction partially intercepted by crop foliage and the rest reaching the soil surface. Pesticides in the soil environment are further distributed between interstitial water and soil particles, and experience degradation due to various physico-chemical processes (volatilization, photolysis, hydrolysis, and biolysis). SWAT employs a chromatographic module (King & McCarty, 1968) with a partition coefficient K_p to represent the phase distribution of pesticides. Pesticide dissolved in soil water can be transported to streams via surface runoff and lateral flow or leach out of the soil profile and finally reach the shallow aquifer (not further tracked by SWAT), while pesticides adsorbed to soil particles are transported with runoff via soil erosion. Upon delivery to the main channel, pesticides are transported with water flow in the channel and continue to partition into particulate and dissolved forms. The original algorithms in SWAT to simulate pesticide fate in fields, pesticide movement in the land phase, and pesticide in-stream processes were adapted from respectively GLEAMS (Leonard et al., 1987), EPIC (Williams, 1995), combined with a simple mass balance developed by Chapra (2008). SWAT calculates tile flow as a fraction of the soil water leaching out of the soil profile. Tile drainage occurs when the perched water table, which is the height of the water table above the impervious zone, rises above the depth at which the tile drains are installed. The specific equations and detailed description of the conceptual processes regarding pesticide and tile drainage simulation in SWAT can be found in (Wang et al., 2019) and the SWAT theory manual (Neitsch et al., 2011).

Based on the above mentioned fundamental mechanisms of pesticide and tile drainage modeling in the original SWAT, we developed two additional transport modules within DrainPST to refine pesticide modeling in tile-drained areas: a matrix transport module and a macropore transport module, which aim to simulate the transport of pesticides to tile drains through the soil matrix and soil macropores, respectively.

2.1.2 The matrix transport module in DrainPST

Solutes transported with tile drain flow are often calculated by summing the solute concentration in each soil layer multiplied by the tile drain flow from each soil layer (Brevé et al., 1997; Larsson & Jarvis, 1999). However, in the SWAT2012 model tile drain flow is derived for the whole soil profile and not separately for each soil layer. Hence, in our DrainPST module, tile drain flow (Q_{tile}) is partitioned among the soil layers situated between the perched shallow water table depth (SWT) and tile drain depth (DDRAIN) (Fig. 2.1). The contribution ratio of each soil layer ($fr_{tile,ly}$) to the tile drain flow is calculated from the layer thickness relative to the total height difference between SWT and DDRAIN ($Drain_{diff}$) (Fig. 2.1).

The amount of soluble pesticide transported via tile drain flow through the soil matrix to the tile drains (PST_{drain}) in each HRU is calculated as a sum of the tile drain flow multiplied by the solute pesticide concentration in each soil layer $C_{PST,ly}$ between SWT and DDRAIN:

$$PST_{drain} = \sum_{ly=top}^{bottom} fr_{tile,ly}\, Q_{tile} C_{PST,ly} \qquad (1)$$

Equations for calculating the concentration of solute pesticide of each layer can be found in the SWAT theory manual.

2.1.3 The macropore transport module in DrainPST

DrainPST can be switched on by a logical parameter (*ifast* = 1) in the input file, and the macropore flow at a given time step will then be calculated for all non-urban areas that are tile drained. Beven and Germann (1982) stated that macropore flow starts when the precipitation is higher than the soil matrix infiltration capacity. Therefore, in DrainPST, the net precipitation entering the soil profile should be higher than the critical soil matrix infiltration capacity (*Infil*) before the macropore flow starts. In order to calculate *Infil*, a new parameter, the depth of wet soil layers (DEP_WET), was defined. A new soil layer was created at DEP_WET, and *Infil* was calculated as the sum of the water needed to fill all the soil layers above DEP_WET (wet layers) to field capacity on a given time step:

$$Infil = \sum_{ly=1}^{wly}(FC_{ly} - SW_{ly}) \qquad (2)$$

where *Infil* is the critical soil matrix infiltration capacity (mm), *wly* is the number of wet layers, FC_{ly} is the field capacity of the soil layer (mm), and SW_{ly} is the soil water content in the soil layer (mm). Infiltration capacity was calculated with field capacity rather than saturation because when soil water reaches field capacity in SWAT, the excess water moves to the next soil layer.

In DrainPST, macropore flow is active when the following criteria are fulfilled: i) soil water content in each wet layer exceeds a threshold that is calculated as a percentage of saturated soil water ($fr \cdot SAT_{ly}$), where *fr* is the fraction of the saturated soil water content and SAT_{ly} is the saturated water content of the soil layer (mm); ii) the net precipitation entering the soil profile should be higher than *Infil*. Both DEP_WET and *fr* can be calibrated. In his review of macropore flow studies, Jarvis (2007) concluded that macropore flow mainly occurs when the soil water content in part of the soil profile is near saturation. Therefore, criteria (i) ensures that the soil water content in the wet layers is not too low for macropore flow to start. Criteria (ii) ensures that macropore flow starts only when net precipitation is higher than *Infil*.

Water entering the soil profile is then divided into macropore water and soil matrix water using the fraction *α* once the criteria is met, which is similar to the procedure by Larsson et al. (2007) and Tiemeyer et al. (2007). The amount of macropore flow on a given time step is calculated as:

$$Q_{macro} = \alpha \cdot Q_{sepday} \qquad (3)$$

where Q_{macro} is the amount of macropore flow in a given time step (mm), *α* is the fraction of the water entering the macropores in a given time step, and Q_{sepday} is the water entering the soil profile in a given time step (mm).

Studies indicate that more water enters the macropores and the macropore flow lasts longer when the soil water content is high (Gjettermann et al., 1997; Kung et al., 2000). Therefore, it was assumed that the fraction of macropore water (*α*) increase with relative soil moisture (θ) based on a Michaelis-Menten saturation approach, where K_{theta} is a half-saturation constant for the macropore flow fraction:

$$\alpha = \frac{\theta}{\theta + K_{theta}} \qquad (4)$$

The relative soil moisture (θ) of each soil layer was calculated as:

$$\theta_{ly} = \frac{SW_{ly}}{depth_{ly} \cdot sol\_por_{ly}} \qquad (5)$$

where θ_{ly} is the relative soil moisture in the soil layer, ranging from 0 to 1, SW_{ly} is the soil water content in the soil layer (mm), $depth_{ly}$ is thickness of the soil layer (mm), and sol_por_{ly} is the porosity of the soil layer. *α* can only take on values less than 1 and the minimum *α* in all wet layers was used in equation (4).

To ensure that not all water entering the soil profile goes to macropores (α = 1) during extreme precipitation events, water was reserved for the soil matrix. The amount of macropore flow on a given time step cannot exceed the maximum value ($Q_{macro,max}$), which was calculated as:

$$Q_{macro,max} = Q_{sepday} - Infil. \qquad (6)$$

Macropore flow is routed as a bypass flow: in tile drained HRUs, it enters the tile drains directly and does not interact with the soil matrix; in other HRUs, it enters the soil layer below the depth of DEP_WET. The amount of soluble pesticide transported via macropores to tile drains, PST_{macro}, were derived by the concentration of pesticide in the top 10 mm soil layer ($C_{PST,top}$) multiplied by the amount of macropore flow (Q_{macro}):

$$PST_{macro} = C_{PST,top} Q_{macro} \qquad (7)$$

The concentration of soluble pesticides in the surface layer is derived from a percolation coefficient (PERCOT), which controls the amount of pesticides removed from the surface layer in runoff relative to the amount available for matrix and macropore flow.

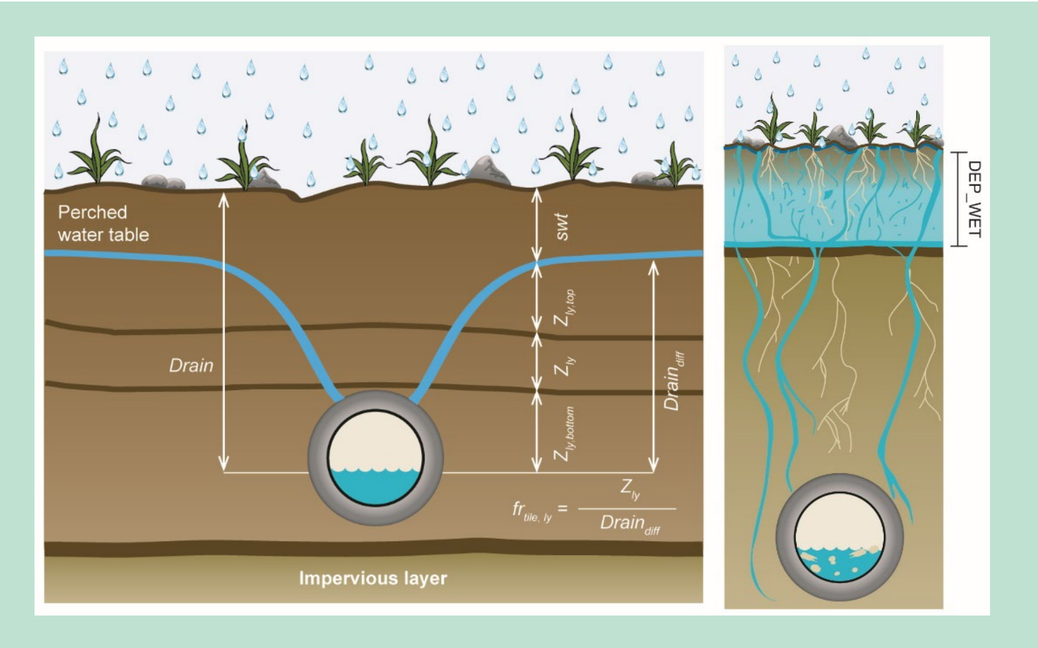

FIGURE 2.2. (left pane) Illustration of how soil layers between the shallow water table (swt) and the tile drain depth (DDRAIN) contribute to the tile drain flow (〖fr〗 _(tile,ly)); (right pane) macropore soil water, sediment and sediment bounded pesticide transport.

2.1.4 Sediment transport module

DranPST calculates sediment transported to the tile drains only for tile drained HRUs, this is calculated in two steps: first, a simple detachment in the top soil layer, and next a decrease of the concentration during transport to tile drains due to the filtering effect, similar to the processes in the MACRO model (Jarvis et al., 1999) adapted by Larsson et al. (2007). Jacobsen et al. (1997) calculated the sediment detachment with rainfall kinetic energy at the soil surface and reached equally good results. Jarvis et al. (1999) introduced an available sediment pool due to the limited supply of particles. Larsson et al. (2007) added crop cover and a management factor from the Universal Soil Loss Equation (USLE) to reduce detachment when plants cover the bare soil. In DrainPST, sediment detachment is calculated similar to Larsson et al. (2007) as:

$$D = K_d \cdot EI \cdot C_{usle} \cdot M_s$$

Where D is detached sediment at the top soil layer in a given time step (g m^{-2}), K_d is the soil erodibility factor (g J^{-1} mm^{-1}), C_{usle} is the USLE cover and management factor, EI is the rainfall erosion index (J mm m^{-2}), and M_s is the available sediment pool for detaching (g g^{-1}).

The available sediment pool M_s is reduced after detachment and replenished approaching to the maximum value. Replenishment was calculated as:

$$R_{sed} = k_r \cdot \left(1 - \frac{M_s}{M_{max}}\right)$$

Where R_{sed} is the replenishment to the available sediment pool (g g^{-1}), k_r is the replenish rate coefficient, and M_{max} is the maximum available sediment pool calculated from the soil clay content (Brubaker et al., 1992). Larsson et al. (2007) assumed that R_{sed} was the result of soil particle rearrangement such as tillage, freeze- and-thaw, wetting and drying, and earthworm activities. Studies indicate that tillage increases the sediment leaching to tile drain (Petersen et al., 2004; Schelde et al., 2006). Therefore, after each tillage operation, *Ms* recovers to half M_{max} if M_s is lower than half M_{max}.

The amount of detached sediment reaching the tile drain declines due to the filtering effect. The sediment concentration in macropore flow (C_{sed}) is calculated as:

$$C_{sed} = \frac{D}{Q_{macro}}$$

and the amount of sediment reaching the tile drains (Sed_{tile}) was calculated as:

$$Sed_{tile} = Q_{macrotile} \cdot C_{sed} \cdot e^{-filt \cdot depth_{ddrain}}$$

Where *filt* is a filtering coefficient (m^{-1}). Pesticides sorbed to sediments are transported along with the sediment. The amount of sorbed pesticides is derived as in the original SWAT code (described in detail in the theoretical documentation of SWAT), which employs an enrichment ratio, defined as the ratio of the concentration of sorbed pesticide transported with the sediment relative to the total concentration in the soil surface layer. The amount of sorbed pesticides is further influenced by a soil adsorption coefficient, which will differ between different types of pesticides.

The concentration of pesticide sorbed on sediment transported in macropores is assumed similar to the concentration of pesticide on sediment in the top 10 mm soil layer.

3. Test of the extended SWAT model

3.1 Study site and monitoring data

The Lillebæk catchment (55°6'14"-55°9'22"N, 10°41'13"-10°50'35"E) is located on the island of Fyn in Denmark and drains an area of about 3.53 km^2, comprising about 91% intensive agricultural land and 9% scattered settlements or natural landscapes (Hansen et al., 2013), Fig. 3.1a. During the study period of 1999 to 2010, the average annual precipitation in the Lillebæk catchment was 844 mm, and annual average daily maximum temperature was 12.3 °C, being highest in July with average daily maximum temperature of 22 ℃ and coldest in January (3.5 ℃). A gauging station is located at the outlet of the Lillebæk catchment, with continuous measurement of sediment yield and stream water level since 1989, water level converted into streamflow by the stage-discharge rating curve method. The high-streamflow periods occur in winter (December–February) with an average monthly flow of 0.063 m^3/s at the catchment outlet and low-flow periods occur in summer (June–August) (0.012 m^3/s).

The surface elevation of the catchment decreases from 50-60 meters above sea level in the west to a few meters above sea level along the coast in the east within 3 km (Fig. 3.1b). The catchment is situated in a young glacial landscape dominated by till soils. Geologically, like many other areas in Denmark, the stratigraphy of the catchment is heavily influenced by previous glacial periods (Flindt Jørgensen et al., 2016). Its near-surface geology consists of an upper layer of Quaternary deposits, of which the total thickness varies between 30 to 60 m, laying unconformable on Paleogene limestones and marls (Hansen et al., 2013). The Quaternary deposits consist of a layer of Weichselian-age clayey till that overlies a layer dominated by sand, which in turn overlies a layer of clayey till from the Saale glaciation (De Schepper et al., 2015). The upper layer of Quaternary deposits contains complex fracture and macropore networks that can create vertical preferential water flow and mass transport pathways between the surface and the underlying sand (De Schepper et al., 2015). Soils with loamy sand texture predominate the catchment (97%).

Tile drains have been installed in 22% of the agricultural fields at depths between 0.8 and 1.4 m with a horizontal spacing of around 20 m. Plastic tubes of 100 mm diameter were typically installed as drainage pipes in sandy loam soils. However, detailed information on tile drainage system was not available for the monitored tile-drained fields. Therefore, drainage depth and spacing were subject to calibration (Table 3.2), while the effective radius of the drainage tubes (RE) was set to 50 mm (Lu et al., 2016). TileDF1 and TileDF2 are two drain-flow monitored tile drained fields, which are both intensively cultivated and mainly fertilized with solid animal manure and slurry (Fig. 3.1c).

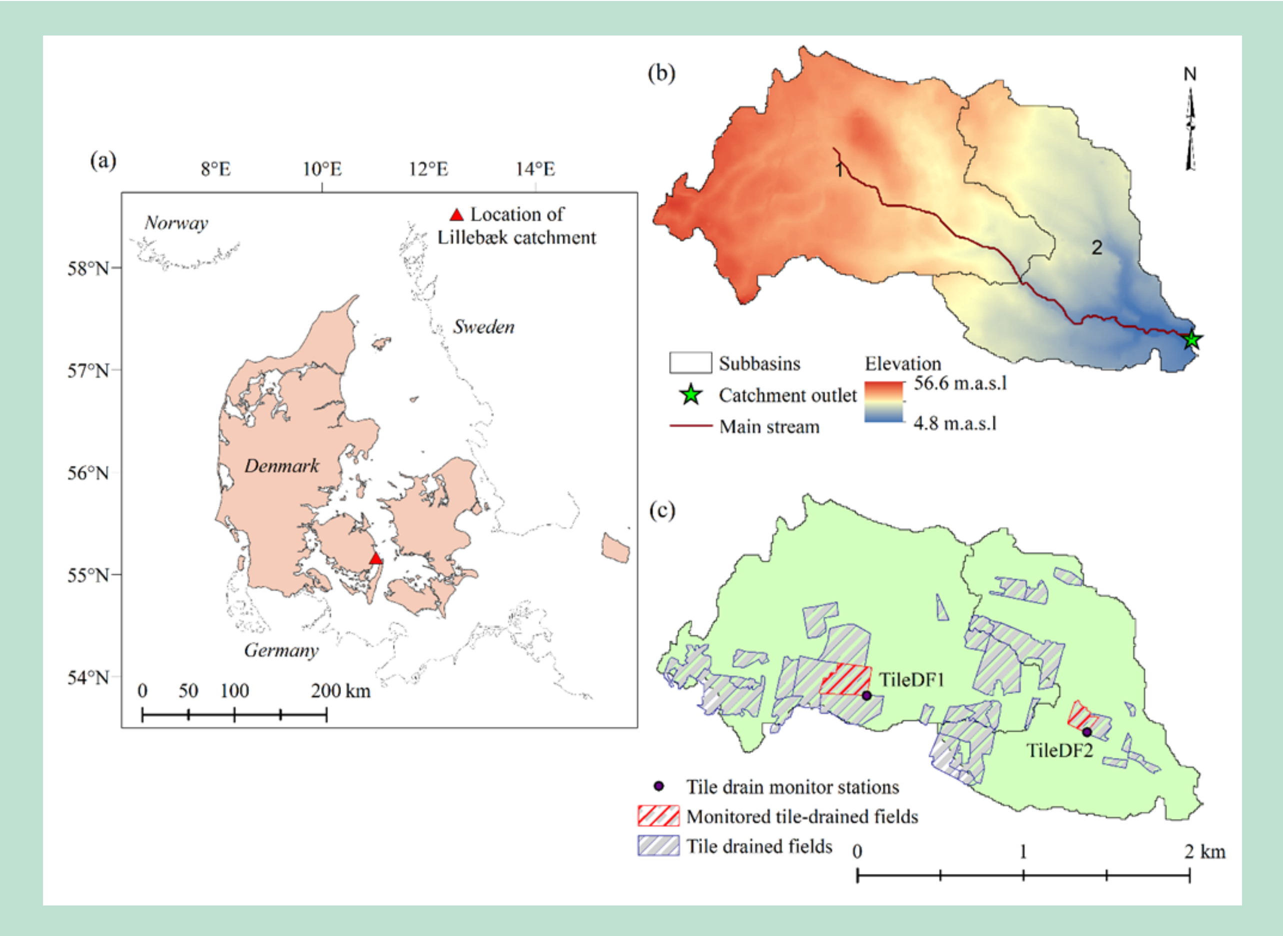

FIGURE 3.1. (a) Location of the Lillebæk catchment; (b) elevation map and subdivision of the Lillebæk catchment; (c) tile-drained areas and location of monitored tile drained fields.

3.2 Model set-up and calibration

We used the QSWAT 1.5 interface, which works with the latest SWAT Editor version 2012.12.19 and is integrated into a QGIS 2.8.1 interface. A DEM with a resolution of 16 m x 16 m resampled from a 1.6-m LiDAR DEM (KMS, 2010) (Knudsen and Olsen 2008) and a digital stream network were used for catchment delineation (Figure 3.1b), resulting in two sub-basins generated. We created a new land use map by combining a digital tile drain distribution map with the frequently-used land use map based on the Danish Area Information System so that the tile drained fields can be distinguished in the land use map. The new land use map and a three-layer national soil map of 250-m grid resolution (Greve et al., 2007) were used for HRU definition. Scattered settlements and nature areas were merged into agricultural land, to reduce the number of HRUs. Each monitored tile drained field (TileDF1 and TileDF2) was specified as a separate land use type for the Lillebæk catchment. The surface slope was divided into two classes: 0.0-8% and > 8%. The land use, soil layout and slope discretization resulted in 14 HRUs.

Climate data used in the model comprised the 10-km-grid national daily precipitation data corrected for rain gauge under-catch, 20-km-grid daily solar radiation and wind speed data, and station-based daily maximum and minimum temperature and relative humidity data during 1989-2010 from the Danish Meteorological Institute. Two types of 10-year crop rotations with different crop types, pesticides and manure/fertilizer application intensities, as well as dates of sowing, harvesting, and tillage collected from regional agricultural statistics in 2005 (Statistics Denmark, 2014) were assigned to the TileDF1 (owned by a dairy farm) and the remaining area of the catchment including TileDF2 (owned by a pig farm), respectively (Table 3.1). Data on pesticide application (dose and timing) was adapted from appendix 1. Section 4.2.3 further describes the development of crop rotation schedules and the pesticide application scheme.

TABLE 3.1. Crop rotations for two monitored tile drained fields.

	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Year 7	Year 8	Year 9	Year 10
TileDF1	spring barley	maize	maize	maize	maize	spring barley	maize	maize	maize	maize
TileDF2	winter rape	winter wheat	winter wheat	winter wheat	spring barley	winter rape	winter wheat	winter wheat	winter wheat	spring barley

The Sequential Uncertainty Fitting Algorithm (SUFI2) implemented in the SWAT-CUP autocalibration software (Abbaspour, 2011), observed drain flow at the outlets of TileDF1 and TileDF2 and observed streamflow, sediment yield and pesticide concentration at the outlet of the catchment were used for calibration and validation. Calibration on drain flow, streamflow and sediment yield were performed on a daily time step from 1 Jan. 1999 to 31 Dec. 2004, with a previous 10-year warm-up period and the Nash-Sutcliffe Efficiency coefficient (NSE; Nash and Sutcliffe 1970) as the objective function. Validation was performed on daily values during 1. Jan. 2005 to 31 Dec. 2010. Drain flow and streamflow were calibrated simultaneously first, then sediment, and finally pesticides. A set of sensitive parameters was selected based on expert judgement and assigned initial calibration value ranges based on previous SWAT applications in Denmark. Because TileL1 and TileL2 were located upstream from the outlet of the catchment and the drain flow from TileL1 and TileL2 thus have an influence on the streamflow of the outlet, the weight for deriving the objective function for TileL1 and TileL2, were set to 2, and the weight for streamflow at the catchment outlet was set to 1. For the calibration on tile drain flow and streamflow, 28 parameters were calibrated in the original SWAT model and 3 additional parameters were calibrated in the DrainPST model (Table 3.2). Six stepwise iterations of each 1000 simulations were run for calibration of the hydrology part. For the calibration of sediment yield at the outlet, 10 parameters were calibrated in the original SWAT and two additional parameters were calibrated in the DrainPST model (Table 3.3).

For pesticide simulation, we could only obtain a few numbers of observed pesticide data for Bentazone, Propiconazole, and Pirimicarb during 1999-2001 which were not enough for calibrating the pesticide parameters (see section 4.2.3 for selection of test pesticides). Instead, we only ran one iteration of 1000 simulations with reasonable ranges of selected parameters according to relevant literature (Table 3.4) and presented how many observed pesticide data were included in the model simulation results with uncertainty bands. Eight parameters were selected in the original SWAT and one additional parameter was selected in the DrainPST model. Model performance was evaluated through visual inspection and statistical metrics (NSE).

TABLE 3.2. Initial ranges and calibrated values of the selected parameters for simulating daily streamflow using DrainPST and SWAT. Definition of parameter identifiers used in the calibration: 'v__' means that the existing parameter value is replaced by the given value; 'r__' means the existing parameter value is multiplied by (1 + a given value) (Abbaspour, 2011).

File	Parameters	Description	Ranges	Calibrated values	
				DrainPST	SWAT
.bsn	v__SFTMP	Snowfall temperature (°C)	-1-1	0.28	0.31
	v__SMFMN	Melt factor for snow on December 21 (mm H_2O °C^{-1} d^{-1})	-1-2	-0.39	-0.07
	v__SMFMX	Melt factor for snow on June 21 (mm H_2O °C^{-1} d^{-1})	1.6-3.5	2.42	2.08

	v__SMTMP	Snow melt base temperature (°C)	-2.3-1	-1.14	-0.44
	v__SURLAG	Surface runoff lag coefficient	1-10	6.76	3.19
.sol	r__SOL_AWC()	Available water capacity of the soil layer (mm H_2O mm $soil^{-1}$)	-0.8-0.8	0.65	0.74
	r__SOL_BD()	Moist bulk density (g cm^{-3})	-0.4-0.4	-0.38	-0.12
	r__SOL_K()	Saturated hydraulic conductivity (mm h^{-1})	-0.8-2	-0.72	0.43
.hru	v__EPCO	Plant uptake compensation factor	0-1	0.74	0.83
	v__ESCO	Soil evaporation compensation factor	0-1	0.28	0.11
	v__DEP_IMP	Depth to impervious layer in soil profile (mm)	1500-4000	3893	3172
	r__OV_N	Manning´s "n" value for overland flow	-0.2-0.2	0.20	0.11
.mgt	r__CN2	Initial SCS runoff curve number for moisture condition II	-0.4-0.4	-0.20	-0.23
	v__GDRAIN	Drain tile lag time (h)	1-3	2.11	2.00
	v__DDRAIN	Depth to subsurface drain (mm)	800-1200	844	959
	v__TDRAIN	Time to drain soil to field capacity (h)	16-48	40.6	47.5
.sdr	v__SDRAIN_BSN	Distance between two drain tubes or tiles (mm)	15000-25000	23671	19821
	v__DRAIN_CO_BSN	Daily drainage coefficient (mm day^{-1})	10-50	19.39	45.42
	v__LAT-KSATF_BSN	Multiplication factor to determine lateral saturated hydraulic conductivity (K_{sat}) from SWAT K_{sat} input value for HRU	1-4	2.09	2.47
.gw	v__GWQMN	Threshold depth of water in the shallow aquifer required for return flow to occur (mm)	0-2000	423	1495
	v__GW_DELAY	Groundwater delay time (d)	0-200	180.63	106.18
	v__GW_REVAP	Groundwater "revap" coefficient	0.02-0.1	0.06	0.02
	v__REVAPMN	Threshold depth of water in the shallow aquifer for "revap" or percolation to the deep aquifer to occur (mm)	1000-2000	1720	1557
	v__RCHRG_DP	Deep aquifer percolation fraction	0-0.4	0.20	0.21
	v__ALPHA_BF	Baseflow alpha factor (1/days)	0-1	0.71	0.53
	v__AL-PHA_BF_D	Baseflow alpha factor for deep aquifer (l d^{-1})	0-1	0.54	0.58
.rte	v__AL-PHA_BNK	Baseflow alpha factor for bank storage (l d^{-1})	0-1	0.10	0.33
	v__CH_K2	Effective hydraulic conductivity in main channel alluvium (mm h^{-1})	0-75	24.63	71.99
.bsn	v__WDPQ.bsn	Fraction of saturated soil water content , threshold for macropore onset (ranging from 0-1)	0-1	0.83	
	v__WGPQ.bsn	Depth of wet layers (range depend on input soil depth)	0-500	322	
	v__WDPS.bsn	Michaelis-Menten type half-saturation constant for the macropore flow fraction (default value 0.5, ranging 0-1)	0-1	0.86	

TABLE 3.3. Initial ranges and calibrated values of the selected parameters for simulating daily sediment yield using DrainPST and SWAT. Definition of parameter identifiers used in the calibration: 'v__' means that the existing parameter value is replaced by the given value; 'r__' means the existing parameter value is multiplied by (1 + a given value) (Abbaspour, 2011).

File	Description	Description	Ranges	Calibrated values	
				Drain-PST	SWAT
.bsn	v__SPEXP	Exponent parameter for calculating sediment reentrained in channel sediment routing	1-1.5	1.39	1.11
	v__SPCON	Linear parameter for calculating the maximum amount of sediment that can be reentrained during channel sediment routing	0.0001-0.002	0.0013	0.0002
	v__PRF()	Peak rate adjustment factor for sediment routing in the main channel	0-2	0.33	0.31
.rte	v__CH_ERODMO()	A value of 0.0 indicates a non-erosive channel, while a value of 1.0 indicates no resistance to erosion	0-1	0.00	0.61
	v__CH_COV1	Channel erodibility factor	-0.05-0.6	0.443	0.273
	v__CH_COV2	Channel cover factor	-0.001-0.2	0.069	0.020
.mgt	v__USLE_P	USLE equation support practice factor	0-0.1	0.030	0.025
plant.dat	v__USLE_C{115,122}	Minimum value of USLE C factor for water erosion applicable to the land cover/plant	0.1-0.3	0.200	0.191
.sol	r__USLE_K()	USLE equation soil erodibility (K) factor	-0.2-0.2	-0.093	-0.108
.hru	r__SLSUBBSN	Average slope length (m)	-0.2-0.2	0.135	0.146
.bsn	v__WGLPQ	Macropore sediment filtering when reaching tile drains (ranging 0-1)	0-1	0.159	
	v__WDLPQ	Macropore sediment replenishment rate coefficient (not calibrated)	1-10	8.641	

TABLE 3.4. Ranges for the selected parameters for simulating Bentazone, Propiconazole and Pirimicarb using DrainPST and SWAT. Information from The Pesticide Properties DataBase (University of Hertfordshire 2020) and Willis et al. 1980.

File	Parameter	Description	Ranges		
			Bentazone	Propiconazole	Pirimicarb
pest.dat	SKOC	Soil adsorption coefficient normalized for soil organic carbon content (ml/g).	34-51	382-1798	45-730
	WOF	Wash-off fraction	0.45-0.75	0.525-0.875	0.525-0.875
	HLIFE_F	Degradation half-life of the chemical on the foliage (days).	3.5-7	4.25-205.5	1.25-6.5
	HLIFE_S	Degradation half-life of the chemical in the soil (days).	4-21	17-411	5-13
	AP_EF	Application efficiency	0.5625-0.9375	0.5625-0.9375	0.5625-0.9375

	WSOL	Solubility of the chemical in water (mg/L or ppm)	375-625	75-125	2025-3375
.swq	CHPST_REA	Pesticide reaction coefficient in reach (day^{-1}).	0.006-0.011	0.016-0.026	0.087-0.144
.bsn	PERCOP	Pesticide percolation coefficient.	0-1	0-1	0-1
.bsn	WGPS	Pesticide percolation coefficient for the soluble pesticide concentration in macropore and tile drain flow.	0-1	0-1	0-1

3.3 Results

3.3.1 Model performance on simulation of hydrology, sediment yield and pesticides

Both the original SWAT model and the SWAT model extended with DrainPST represented well or satisfactory the hydrographs of streamflow and tile drain flow at the outlet of the catchment during the calibration period, while during the validation period the representations were worse (Figs. 3.2 and 3.3). Both models captured the seasonal variation of observed streamflow and tile drain flow – active in winter and inactive in summer. The values of NSE confirmed that the performance of simulated daily streamflow was “good” during calibration in both models (NSE > 0.70), remained “satisfactory” in DrainPST (NSE > 0.50) but became “unsatisfactory” in SWAT during validation (NSE < 0.50) (Fig. 3.2), relative to the criteria defined for streamflow by Moriasi et al. (2015), while the performance of tile drain flow was “satisfactory” during calibration (NSE > 0.50) and “unsatisfactory” during validation (NSE < 0.50) for both models.

Neither the SWAT nor DrainPST did represent well the temporal pattern of sediment yield at the outlet of the catchment during both calibration and validation periods, of which the performance was “unsatisfactory” relative to the criteria defined for sediment by Moriasi et al. (2015) (Fig. 3.4).

Fig. 3.5 shows time series plots of observed and simulated pesticide transport during the two years with pesticide measurements at the catchment outlet. The addition of the macropore module in DrainPST results in considerably higher pesticide transport values compared to SWAT. For Bentazone, DrainPST captures several of the observations and performs better than SWAT. The simulations of Propiconazole and Pirimicarb are unsatisfactory for both models. Additionally, Fig. 3.6 shows exceeding frequency curves for observed Bentazone concentrations and 95% prediction uncertainty (95PPU) and median 95PPU (M95PPU) of the simulated Bentazone concentrations by the SWAT model and DrainPST. The uncertainty band of DrainPST captures several of the observed Bentazone concentration values, especially the relatively high concentrations.

According to the values of NSE, the model performance on simulation of both hydrology and sediment yield in DrainPST was better than that in SWAT and similar for the simulation of Bentazone.

Regarding water balance, the two models simulated similar evapotranspiration (ET) values, but the simulated flow components differentiate. Comparing to SWAT, in the DrainPST model 81 mm (86.5%) more flow was transported through tile drains while less flow was transported through surface (14 mm, 66%), lateral subsurface (29 mm, 83.8%) and groundwater (27.7 mm, 20%), Table 3.5.

TABLE 3.5. Values for the main water inputs and outputs in the catchment and the contribution of streamflow components simulated by SWAT and DrainPST in the Lillebæk catchment for the entire simulation period.

	Original SWAT	DrainPST
Precipitation (mm)	843.7	843.7
Surface flow (mm)	21.2	7.1
Lateral subsurface flow (mm)	34.6	5.6
Tile drain flow (mm)	93.6	174.6
Groundwater flow (mm)	137.7	110
Actual evapotranspiration (mm)	540.5	536.6
Potential evapotranspiration (mm)	641.7	642.4

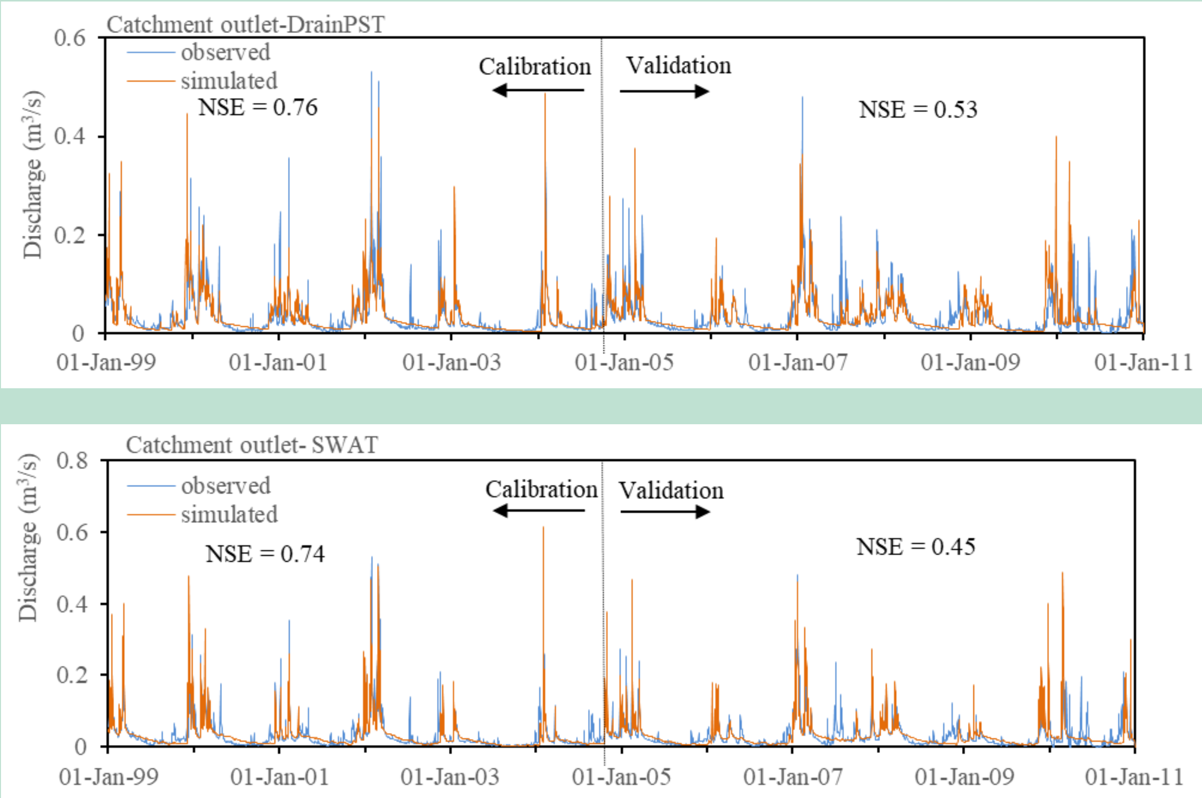

FIGURE 3.2. Observed, calibrated and validated daily stream flow at the outlet of the Lillebæk catchment. Upper panel: DrainPST. Lower panel: SWAT.

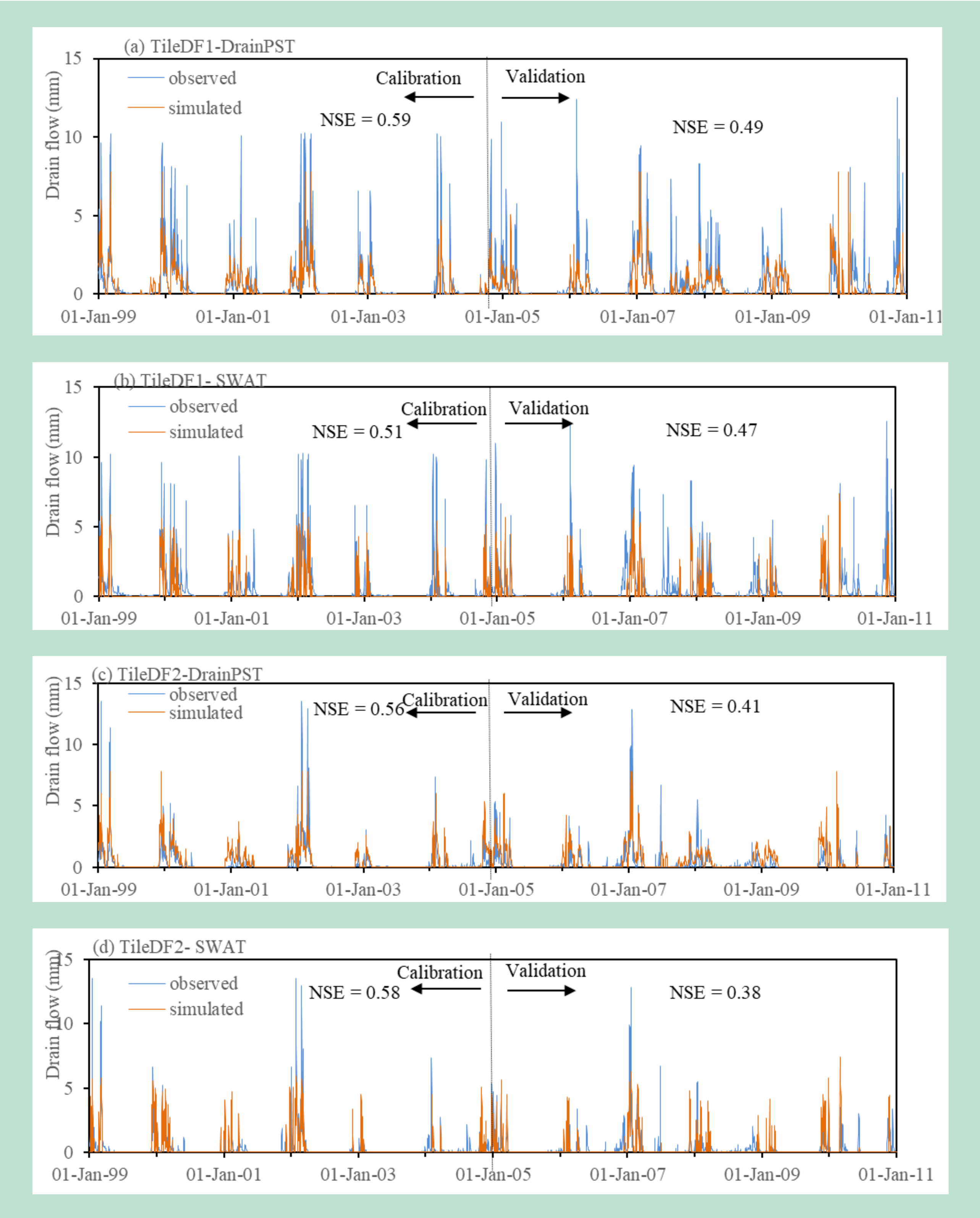

FIGURE 3.3. Observed, calibrated and validated daily drain flow at respectively TileDF1 and TileDF2 com-paring DrainPST and SWAT.

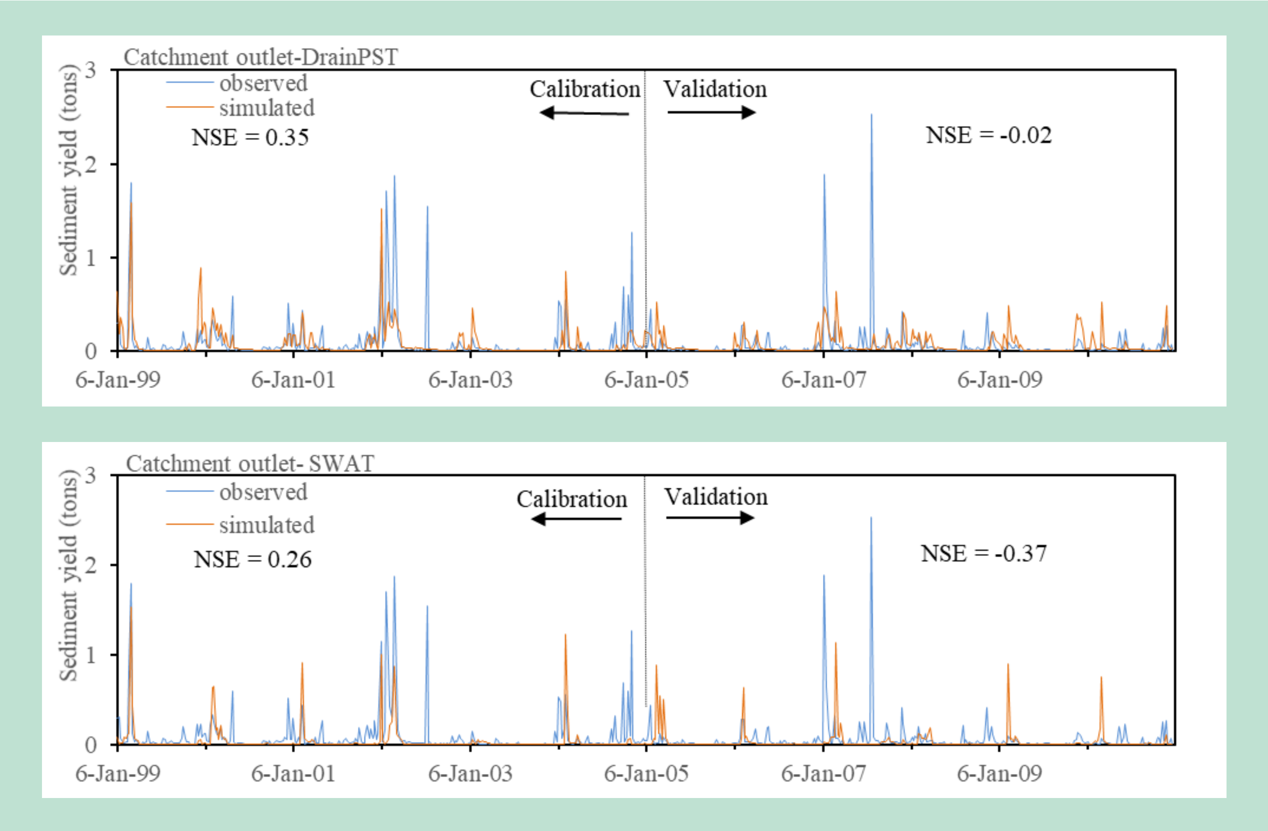

FIGURE 3.4. Observed, calibrated and validated daily sediment yield at the outlet of the Lillebæk catchment. Upper panel: DrainPST. Lower panel: SWAT.

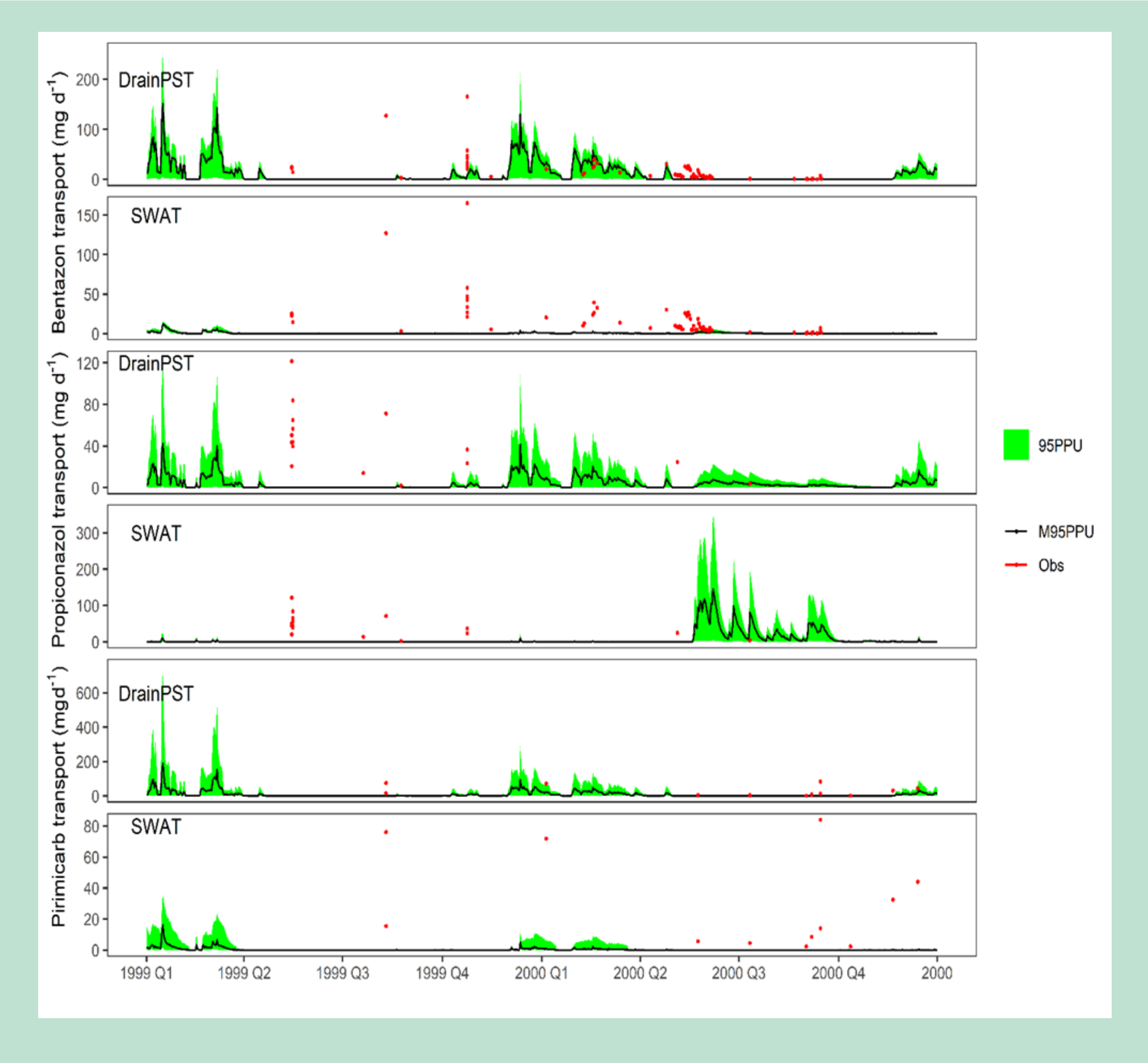

FIGURE 3.5. Time series plots comparing DrainPST and SWAT regarding simulation of stream water transport of Bentazone, Propiconazole and Pirimicarb.

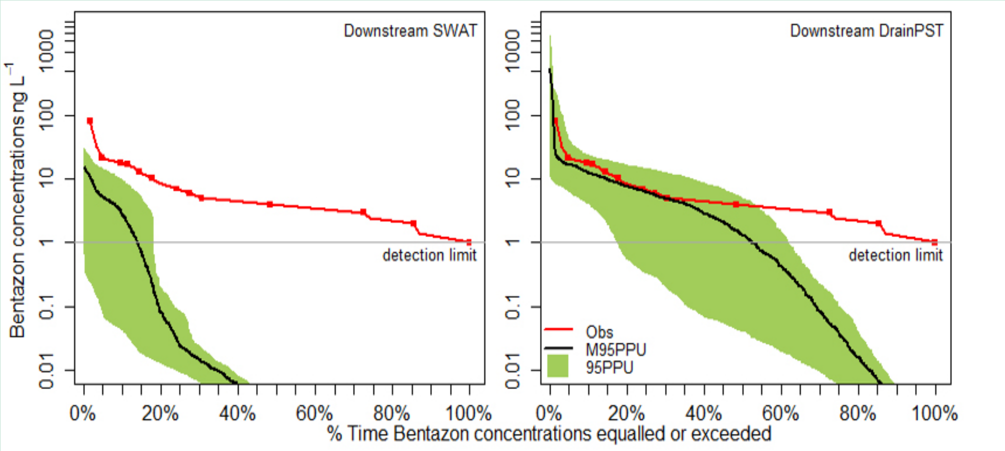

FIGURE 3.6. Exceeding frequency curves for observed Bentazone concentrations (Obs) and 95% prediction uncertainty (95PPU) and median 95PPU (M95PPU) of the simulated Bentazone concentra-tions by the SWAT model and DrainPST.

3.4 Discussion

The validation results reveal that both the original SWAT model and the SWAT model extended with DrainPST capture the hydrological behavior of the modelled system well not only a catchment scale but also at the small drained-field scale. This in spite of a more simplified description of water transport in soils than employed in e.g. the Daisy model (Hansen et al., 2012). The added macropore module in DrainPST results in a higher drain flow mainly on the expense of surface flow and lateral surface flow compared to SWAT.

Neither models deliver a satisfactorily simulation of sediment transport in the Lillebæk catchment based on NSE values. However, modelling sediment transport at catchment scale is challenging due to several sediment sources and transport pathways: soil erosion, surface runoff, transport via macropores and tile drains, and erosion of stream banks. Transport of sediment via these pathways is both spatially and temporally diverse, and some processes are even stochastic (failure of stream banks). However, the addition of DrainPST results in an improved simulation of sediment delivery and transport in the stream. Visual inspection of the simulated sediment transport by the SWAT model extended with DrainPST shows that the timing of the peaks is overall correct, albeit with a negative NSE value.

Pesticide transport is overall unsatisfactorily simulated when evaluated by NSE criteria. Neither models capture the timing in measured pesticide peaks in the stream. However, the addition of the macropore module in DrainPST results in considerably higher pesticide transport values compared to SWAT. For Bentazone, DrainPST captures several of the observations. The simulated timing of the measured peaks in Propiconazole and Pirimicarb transport is unsatisfactory for both models. Still, the measured amplitude in measured pesticide transport is captured by DrainPST for all three pesticides. The failure to correctly model the timing in pesticide transport peaks is very likely caused by the discrepancy in modelling quickly responding processes such as preferential transport with statistically representative data on land use and spraying practices rather than using actual and local data. In line with this objection is our use of daily precipitation data rather than hourly data. However, these choices were all based on our fundamental project idea to test if a more pragmatic model approach including using readily available input data rather than time consuming collecting and processing local data would provide robust and useful results.

3.5 Conclusions

Both the original SWAT and DrainPST are capable of simulating streamflow and tile drain flow with DrainPST performing slightly better. However, the added macropore module in DrainPST results in a higher drain flow mainly on the expense of surface flow and lateral surface flow compared to SWAT. This again results in an improved simulation of sediment delivery and transport in the stream. Although overall unacceptable based on the NSE criteria, DrainPST greatly improves the simulations of pesticide transport, most notably for Bentazone compared to SWAT. The SWAT model extended with DrainPST captures for all three pesticides the amplitude in measured transport, i.e. in spite of failing to correctly simulate the timing of pesticide transport peaks, the model can reproduce similar events.

4. Risk assessment of pesticide exposure of surface waters and groundwater at large catchment scale

4.1 Introduction

The aim of this part of the project is a demonstration and visualization of the abilities of the SWAT model to map critical source areas and to produce maps of potential pesticide exposure of groundwater and surface water bodies at the landscape level. Pesticide management, dynamics and transport has been described for the entire area of Fyn by a SWAT model extended with a module, DrainPST, for transport of water, sediment and pesticides in macropores to tile drains.

4.2 Materials and methods

4.2.1 Study area

The entire island of Fyn, Denmark is selected as test case for the large scale application. Fyn (latitude 55.21° N, longitude 10.21° E) is the third largest island in Denmark and has an area of 3025 km². Fyn encompasses the major catchment Odense Fjord including the largest river draining into the Odense Fjord, the Odense River.

Several water ecosystems on Fyn are damaged due to a high agricultural production, the industrialization of the agriculture areas with the use of fertilizers and pesticides together with urbanization, groundwater abstraction, summer droughts, and channelization of the streams and inclusion of wetlands for agriculture areas (Lewandowska 2020, Molina-Navarro et al. 2018, Fødevareministeriet 2016). Despite several initiatives taken to reduce the nutrient and pesticide load to fresh and coastal waters and to protect the water quality such as the EU Water Framework Directive (WFD), (European Parliament 2000) and the Danish water action plans (Lewandowska 2020), Odense Fjord and the other coastal waters around Fyn do not meet the WFD criteria of good ecological status and the same applies for the majority of the lakes and streams (Miljøministeriet 2021b).

The geology of Fyn consists of clayey moraines from the last glaciation (the Weichsel) and sandy loam soils dominates (Smed 1982). The altitude varies from 0 to 127 m.a.s.l. (Fig. 4.1). The mean annual precipitation was 812 mm during 2000-2010 with an annual mean temperature of 8.7 °C (Molina-Navarro et al. 2018). The land use on Fyn is composed of agriculture (69%), urban areas (16%), and forests (11%) (Levin 2017). The agricultural land cover consists mainly of the following crops: winter wheat (42%), spring barley (21%) and oil seed rape (14%) (Thodsen et al. 2015). Three crop types, which are very exposed to pesticide spraying, Christmas trees, fruit and berries, and vegetables cover respectively 1%, 0.7% and 1.9% of the agricultural land (Levin 2017) (Fig. 4.2).

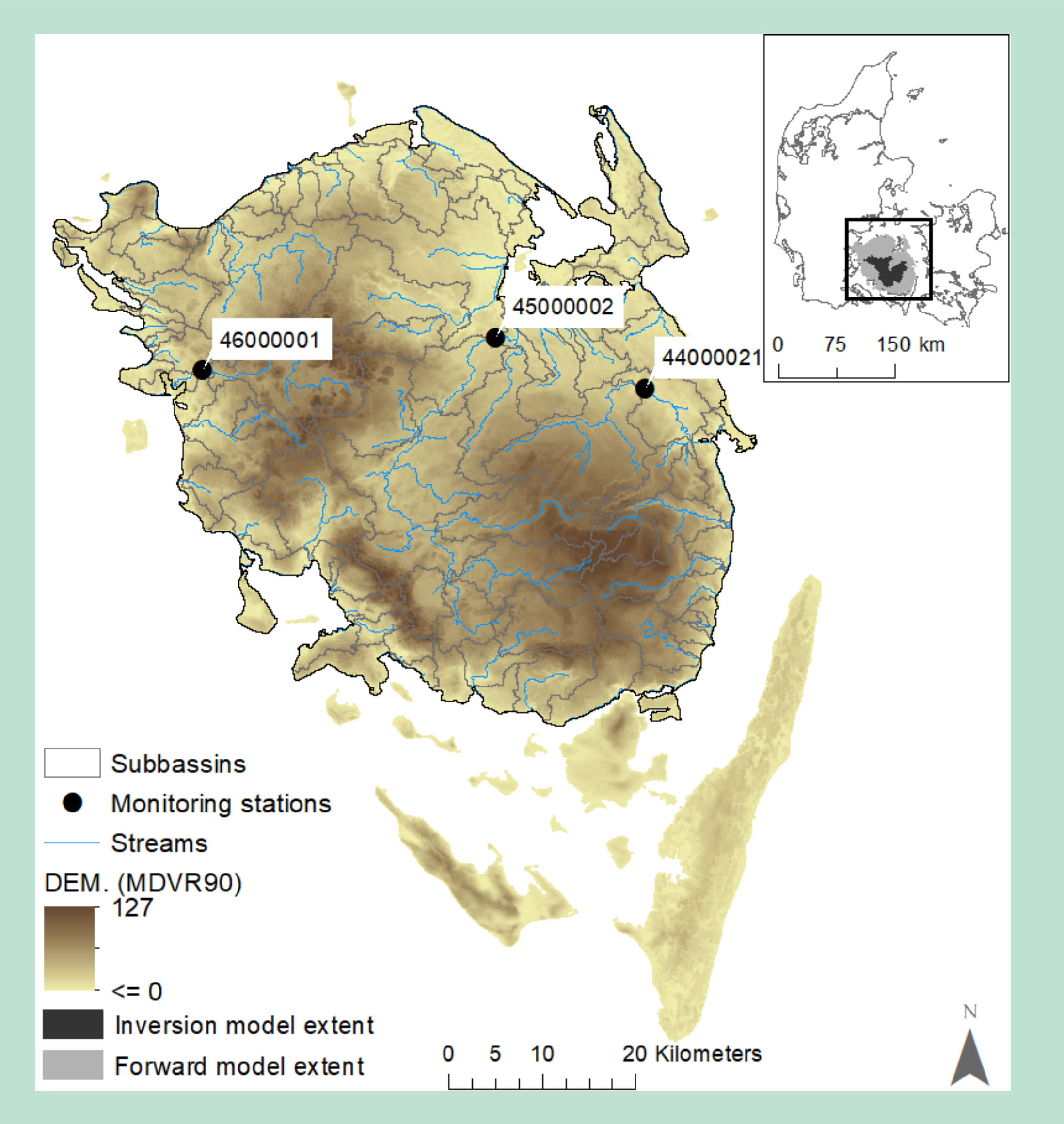

FIGURE 4.1. Digital elevation model of the study area, Fyn, Denmark and the extent of the two SWAT mod-els, the inversion model (smallest area) and the forward model (entire Fyn) (see section 4.2.3 for explanation of the two models). Also shown are the locations of stream water monitoring stations used for calibration and validation: 46000001: Brende Å, st. 5.3; 45000002: Odense Å, Ejby Sluse; 44000021: Vindinge Å, ns. Ullerslev rensningsanlæg

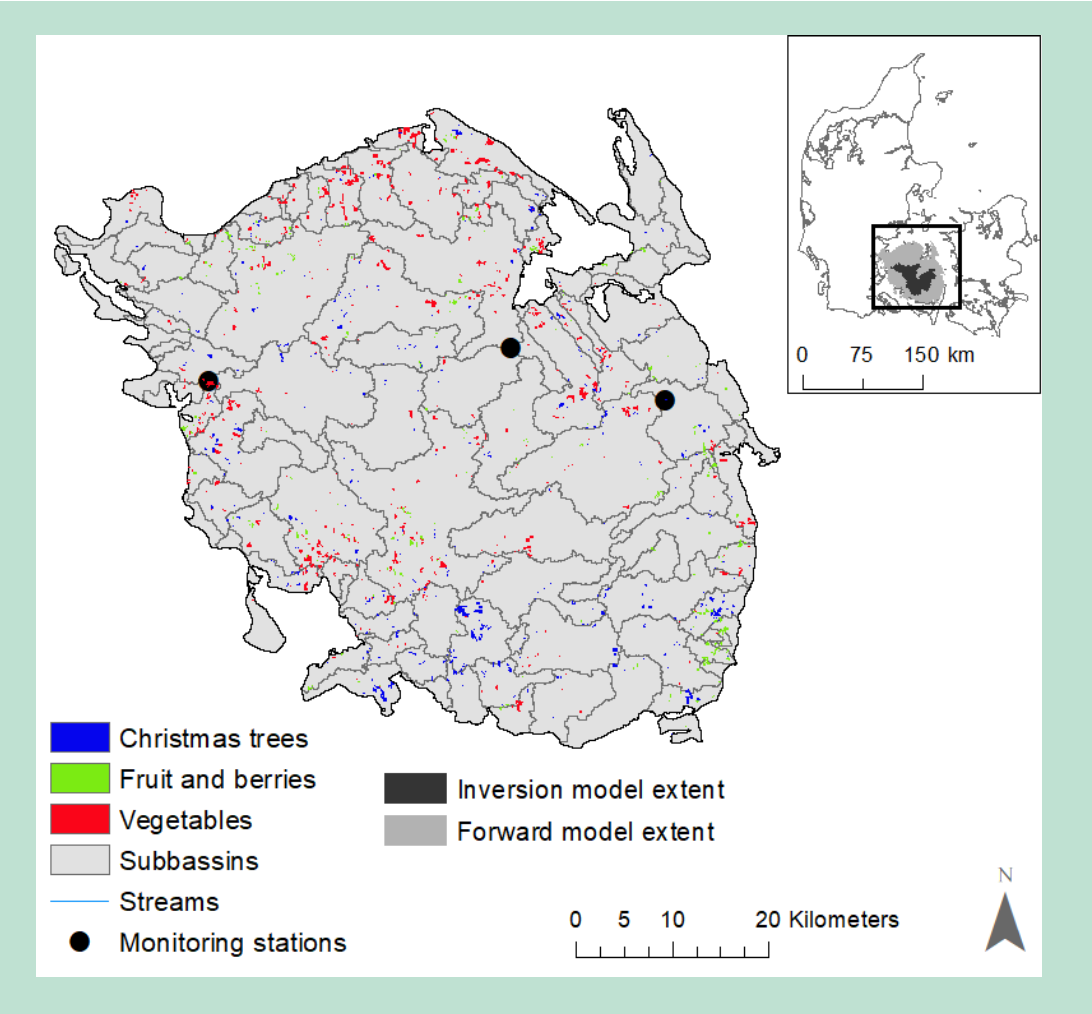

FIGURE 4.2. Localization of Christmas trees, fruit and berries, and vegetables in Fyn, Denmark.

4.2.2 Data input

The SWAT model for Fyn is driven by daily climate data for the period 1993 – 2017 provided by the Danish Meteorological Institute (Scharling, 2001): precipitation from a 10-km grid, wind speed and global radiation from a 20 km grid, and air temperature and relative humidity from climate stations. Information on topography, landuse and soil types was extracted for Fyn from the following maps: a 32 m digital elevation model covering Fyn (Rosenkranz and Frederiksen, 2011); Basemap 2016 (landuse, Levin et al., 2017); and the three layer national soil map at 250-m grid resolution (Greve et al., 2007).

Daily stream flow data at the outlets of three larger catchments in Fyn was used for calibration and validation of the SWAT model. The stream data was measured at stream station 45000002 (Odense Å, ns Ejby sluse), 46000001(Brende Å, st. 5.3) and 44000021 (Vindinge Å, ns Ullerslev rensningsanlæg), figure 4.1. Data covering the period 2006 - 2015 was downloaded from the Danish National Surface Water Database, ODA (Miljøministeriet 2021a). This period fits the pesticide management data available for the model set up.

Pesticide concentrations of Bentazone, Pirimicarb and Propiconazole measured at the same stations were downloaded from ODA (Miljøministeriet 2021a), however very little data is available for the period 2006 -2015. For stream station 45000002 only Bentazone concentrations measured on a monthly basis in 2006 is available. For stream station 46000001 only Bentazone concentrations measured on a monthly basis in 2012 is available and for stream station 44000021 no data for any of the three pesticides is available.

4.2.3 Model set-up

A Soil and Water Assessment Tool (SWAT) model covering Fyn was set up using the SWAT2012 version 664 extended with DrainPST allowing simulation of water, sediment and pesticide transport through macropores to tile drains and further to surface waters (chapter 2). The QSWAT version 1.7, which is a QGIS interface for SWAT (Dile et al. 2016), was used to build the model and to delineate the catchments and stream network. The same delineation procedure was used as in (Thodsen et al. 2015).

Three stream water discharge monitoring stations, all located on major streams, were chosen to be as representative of the island's hydrology as possible. The three stations were, besides stream size, chosen because of, for Fyn, normal runoff (320 mm yr-1) amounts. This is of importance because groundwater often seeps in or out of Danish topographic catchments (Ovesen et al. 2000). SWAT cannot conceptually simulate this process. The usual way to obtain a good and representative model water balance is to modify the evapotranspiration during the calibration process. If substantial amounts of groundwater exits or enters the catchment this will lead to large differences in simulated evapotranspiration, which are not justified in reality, but originates from a calibration compensation for a physical process that SWAT does not handle. The two largest lakes in Fyn were included in the model, the Arreskov Lake and the Brændegård Lake. Tile drainage was installed in the model for all agricultural areas with slope less than 8% and soil clay content above 8%.

Because the final SWAT model, in the following named the forward model, is very computer demanding due to the large area of Fyn and large management files including the pesticide operations, it was chosen to set up a separate calibration model, named the inversion model, only including the sub-basins upstream the monitoring stations and to calibrate with a simplified description of agricultural management, i.e. without including the 17 splits of the agricultural area, see section Management. The calibrated parameters of the inversion model were subsequently transferred to the forward model. Both the inversion model and the forward model are run with SWAT extended with DrainPST. The forward model is run with full agricultural management input including pesticide applications. The extents of the two models and the delineation into sub-basins are found in Fig. 4.3. The inversion model has 11 sub-basins and 1280 HRUs and was running 52 times faster than the forward model. The forward model has 102 sub-basins and 16632 HRUs and the running time was 55 minutes including the 17 splits of the agricultural area. The management files for the HRU's was created with help from python programming to avoid computer crash when trying to split the agricultural area in the normal SWAT interface.

The calibration-validation procedure was carried out using the periods shown in table 4.1. It was decided to include every second year in respectively the calibration and the validation period due to known issues with the homogeneity of the Danish precipitation data before and after 2011 primarily due to changes in the procedure of correcting the precipitation for gauge under-catch (Allerup and Madsen 1980); Thodsen et al., 2020). In this way, both periods include years before and after 2011. It was checked that dry and wet years are represented in both the calibration and validation period (Rubek 2018).

TABLE 4.1 Model simulation periods for the inversion and forward models

	Total run period (inversion model)	Model warm up period (inversion and forward model)	Calibration period/period 1 (inversion model)	Validation period/period 2 (inversion model)	Simulation period for the forward model	Total run period (forward model)
Periods	1993-2017	1993-2002	2003, 2005, 2007, 2009, 2011, 2013, 2015, 2017	2004, 2006, 2008, 2010, 2012, 2014, 2016	2006-2015	1993-2015
Number of years	25	10	8	7	10	23

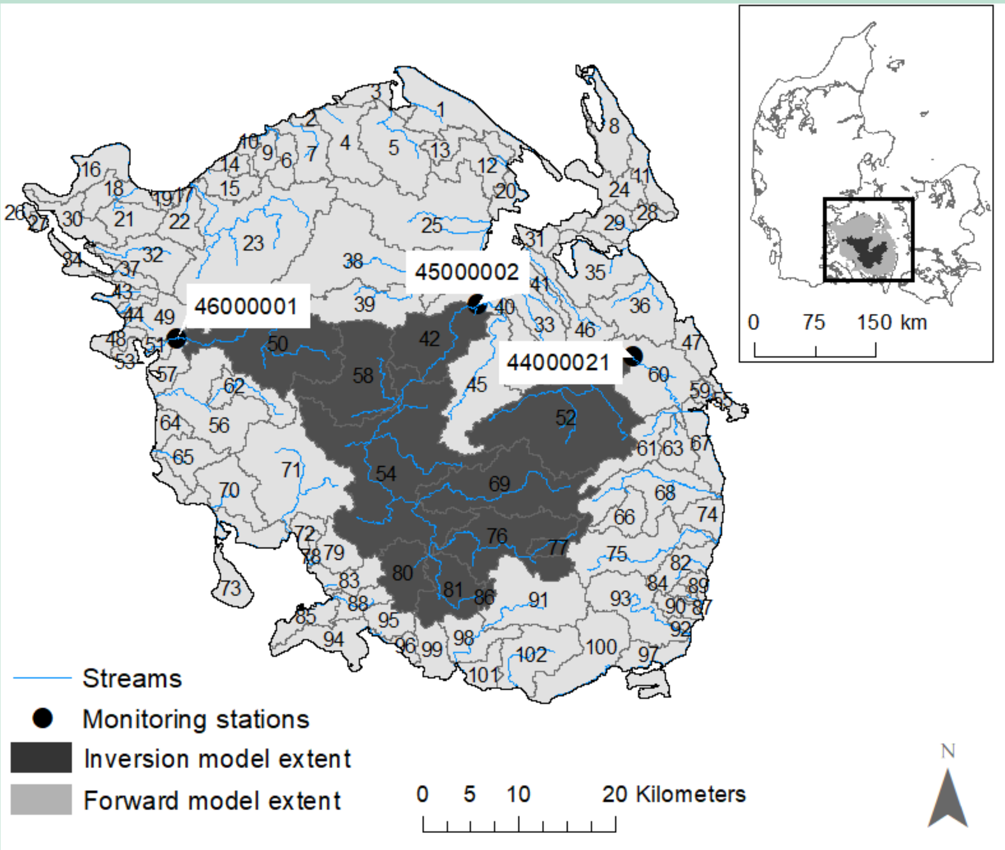

FIGURE 4.3. The extent of the two SWAT models and delineated sub-basins: the inversion model (smallest area) and the forward model (entire Fyn). Also shown are the locations of stream water moni-toring stations used for calibration and validation: 46000001: Brende Å, st. 5.3; 45000002: Odense Å, Ejby Sluse; 44000021: Vindinge Å, ns. Ullerslev rensningsanlæg.

The calibration was performed uniformly across the three monitoring stations using daily streamflow data and without calibrating the sub-basins upstream each station separately. The calibrated parameter values were transferred to those sub-basins in the forward model which are not part of the inversion model. Subsequently, the groundwater parameters in the inversion model were calibrated separately, as it is often done in studies with multi-station SWAT setups (Molina-Navarro et al. 2017, Thodsen et al. 2017, Trolle et al. 2015). We chose the uniform approach in order to assure as uniform conditions across the model domain as possible and thereby avoiding a situation where the final geospatial pesticide exposure analysis was

spatially biased as a result of different calibrations in different parts of the model domain. This approach is also used in for example (Thodsen et al. 2015).
The calibration was carried out using the SUFI2 procedure in the SWAT-cup calibration program (Abbaspour, Vejdani and Haghighat 2007). Parameter ranges were for each iteration narrowed manually. The Nash-Sutcliffe coefficient (NSE), the correlation coefficient (R2), and the mass balance error (PBIAS) objective functions were used (Nash and Sutcliffe 1970, Abbaspour et al. 2007, Moriasi et al. 2015). As the NSE theoretically ranges from $-\infty$ to 1, but a good model only experiences narrow ranges between for example 0.60 and 0.90 it should be used with care in multi-monitoring station setups, as a station with below zero values may have a much larger range and thereby dominate the overall NSE value. Therefore, it was tested that the three stations in this study had approximately the same NSE values (which was the case) before the NSE was chosen.

The parameterization of the two parameters WDLPQ.bsn and WGLPQ.bsn concerning macropore sediment replenishment and filtering was transferred from the Lillebæk model (chapter 3) due to lack of calibration data for the inversion model.

Agricultural management

Agricultural management data in the forward model is extended with pesticide information by a transfer function linking pesticide application amount, type and timing to individual crops. The transfer function is developed based on data from the national agricultural monitoring program LOOP (part of NOVANA) in which information on pesticide application amount, type and timing to individual crops has been collected by annual farmer interviews since 1998 from more than 1200 fields representing the variation in crop types and farm types found in Denmark (Blicher-Mathiesen et al. 2015). This data set is supplemented with farmers spraying records held by the Ministry of Environment. The database of spraying records holds information since 2011 at field level on pesticide application amount and type for all farms larger than 10 ha using pesticides.

Land use information is expanded with information on the location of major orchards and Christmas tree plantations and coupled to management data for these land uses including spaying practices.

Data on crop cover at the field scale and agricultural management at the farm scale (total fertilizer usage, amount and type of livestock) are collected from all farms annually by Danish authorities for administrative purposes. These data are also made available for research. Based on these data we divided the agricultural area for Fyn into a series of farm types, including arable farms, pig farms and dairy farms. These farm types were further subdivided into two or three groups according to the reported usage of nitrogen from organic manure. Each farm type-livestock group combination was represented by two 5-year crop rotation schedules giving a total of 14 unique schedules, table 4.2. The last 3 rotations (1-17 in table 4.2) are set up for the land use classes vegetables, fruit and Christmas trees. For all 17 rotations, a pesticide management scheme has been developed based on the LOOP monitoring and the national pesticide monitoring at national level for the specific years 2006-2015, which is included in the model (rotation 17 is, however, not included as it turned out from pesticide data that the amount of the three test pesticides sprayed on Christmas trees on Fyn was minimal): The reported dose levels (g/ha) from the LOOP catchments were used to distribute the pesticides between crop types. The dose levels were not used directly but adjusted to be consistent with the country sales statistics of Denmark (Miljøstyrelsen, 2017a) using the total crop type area of Denmark as reported by the General Agricultural Register. The timing of spraying was estimated based on the LOOP data where an active ingredient could be assigned to one to three different dates of spraying for each crop type. This was done for each combination of an active ingredient and crop type in the following way: If all the spaying events were done within a short period (about one week) then a single date is selected as the date of spraying and placed in the middle of the period between first and last spraying in the data set. If the spraying events were distributed over a longer period or even in different periods, then two or three spraying dates were selected to represent the spraying for this case. Consequently, in the model, a specific crop type is assumed to be sprayed simultaneously at one, two or three dates for a specific active ingredient. The spraying dates were allowed to change from year to year in order to take into account different temporal need of pest control from year to year (see appendix 1 for details).

TABLE 4.2. The crop rotations used in the model to describe agricultural management in Fyn.

	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Year 7	Year 8	Year 9	Year 10
Rotation scheme	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
1	winter wheat	winter wheat	spring barley	winter wheat	winter wheat	winter wheat	winter wheat	spring barley	winter wheat	winter wheat
2	seed grass	spring barley	grass	grass	winter wheat	seed grass	spring barley	grass	grass	winter wheat
3	winter wheat	winter wheat	winter wheat	spring barley	winter rape	winter wheat	winter wheat	winter wheat	spring barley	winter rape
4	winter wheat	spring barley	seed grass	sugar beet	spring barley	winter wheat	spring barley	seed grass	sugar beet	spring barley
5	winter wheat	seed grass	sugar beet	spring barley	winter wheat	winter wheat	seed grass	sugar beet	spring barley	winter wheat
6	spring barley	winter wheat	winter wheat	spring barley	grass	spring barley	winter wheat	winter wheat	spring barley	grass
7	sugar beet	spring barley	spring barley	seed grass	winter wheat	sugar beet	spring barley	spring barley	seed grass	winter wheat
8	grass	spring barley	winter wheat	winter wheat	spring barley	grass	spring barley	winter wheat	winter wheat	spring barley
9	winter rape	winter wheat	winter wheat	winter wheat	spring barley	winter rape	winter wheat	winter wheat	winter wheat	spring barley
10	spring barley	seed grass	spring barley	winter wheat	winter wheat	spring barley	seed grass	spring barley	winter wheat	winter wheat
11	maize	Maize	maize	spring barley	spring barley	maize	maize	maize	spring barley	spring barley
12	winter wheat	winter wheat	grass	sugar beet	spring barley	winter wheat	winter wheat	grass	sugar beet	spring barley
13	spring barley	maize	maize	maize	maize	spring barley	maize	maize	maize	maize
14	spring barley	maize	spring barley	grass	spring barley	spring barley	maize	spring barley	grass	spring barley
15	vegetables	vegetables	vegetables	vegetables	vegetables	vegetables	vegetables	vegetables	vegetables	vegetables
16	fruit / berries	fruit / berries	fruit / berries	fruit / berries	fruit / berries	fruit / berries	fruit / berries	fruit / berries	fruit / berries	fruit / berries
17	Christmas trees	Christmas trees	Christmas trees	Christmas trees	Christmas trees	Christmas trees	Christmas trees	Christmas trees	Christmas trees	Christmas trees

Pesticide characteristics

One herbicide, Bentazone, one insectide, Pirimicarb, and one fungicide, Propiconazole, are used as test pesticides in the project. These three pesticides are selected because they represent a large range in characteristics, table 4.3. The characteristics of the pesticides are found in the Pesticide Properties DataBase (PPDB) (University of Hertfordshire 2020) and if no data was available here the EU footprint 2009 was used (Dubus et al., 2009) together with information from (Willis et al, 1980). The HLIFE_F parameter is calculated based on the assumption that HLIFE_F must be smaller than Hlife_S by a factor of 0.5 (Willis et al, 1980). The characteristics for the three pesticides are imported to the model pesticide database.

TABLE 4.3. Characteristics of Bentazone, Propiconazole and Pirimicarb (information from The Pesticide Properties DataBase (University of Hertfordshire 2020) and (Willis et al. 1980).

File in SWAT	Parameter	Description	Bentazone	Propicon-azole	Pirimi-carb
pest.dat	SKOC	Soil adsorption coefficient normalized for soil organic carbon content (ml/g).	55.3	1086	388
	WOF	Wash-off fraction	0.6	0.7	0.7
	HLIFE_F	Degradation half-life of the chemical on the foliage (days).	2	13	27
	HLIFE_S	Degradation half-life of the chemical in the soil (days).	20	71.8	73.6
	AP_EF	Application efficiency	0.75	0.75	0.75
	WSOL	Solubility of the chemical in water (mg/L or ppm)	7112	150	3100

4.3 Results

4.3.1 Model calibration and validation: Inversion model

Figures 4.4 and 4.5 show the hydrographs at the three monitoring stations for the calibration and validation periods for the inversion model. Station 45000002 has a higher discharge compared to the two other stations due to a larger catchment area. The simulated discharge follows the observed discharge both at baseflow and peak flow situations relatively well. For some of the peaks the model does not fit the observed discharge perfectly, especially for station 45000002 the model has some difficulties to fit the highest peaks especially for the calibration years. It is seen that the falling and rising limp of the simulated discharge in general is following the observed discharge suggesting that the model represents the hydrological conditions at the study site.

Table 4.4 shows the corresponding performance statistics for the calibration and validation periods for the inversion model. All R^2 values are in the range from 0.66 to 0.82 and thus above 0.60 which is deemed acceptable according to (Moriasi et al. 2015) for watershed-scale models in daily time steps. Within groundwater modelling R^2 values for discharge are deemed acceptable above 0.50 (Sonnenborg and Henriksen 2005). The NSE values are for both the validation and calibration period in the range from 0.73 to 0.82 except for the validation period for station 44000021 where the NSE is 0.57. These values are however all still above 0.50 which is the criteria for acceptable models according to (Moriasi et al. 2015). The water balance error, PBIAS, ranges from -8.3% to 3.5% which is within the acceptable range of ≤ ±15% for watershed-scale models with daily time steps (Moriasi et al. 2015).

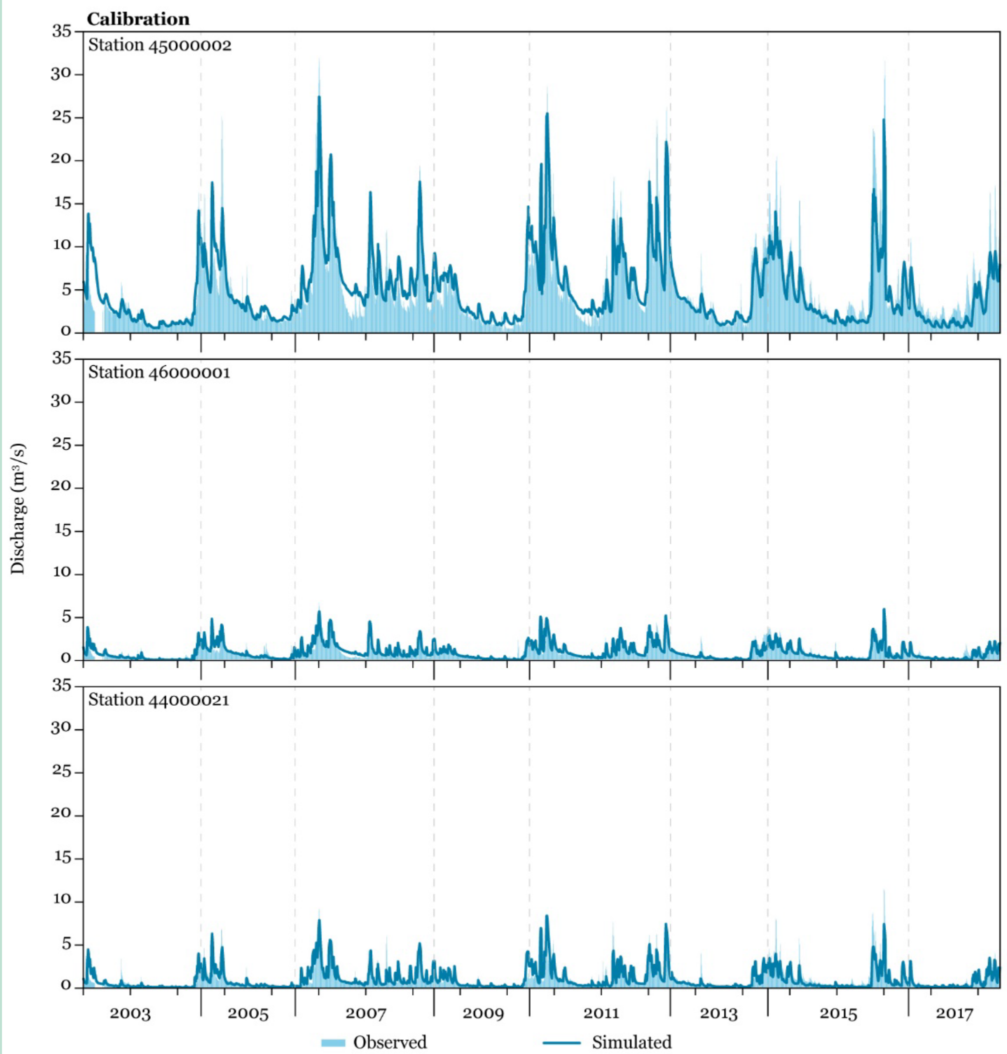

FIGURE 4.4 Simulated and observed daily discharge values for the calibration period for the three monitor-ing stations in the inversion model of Fyn, Denmark.

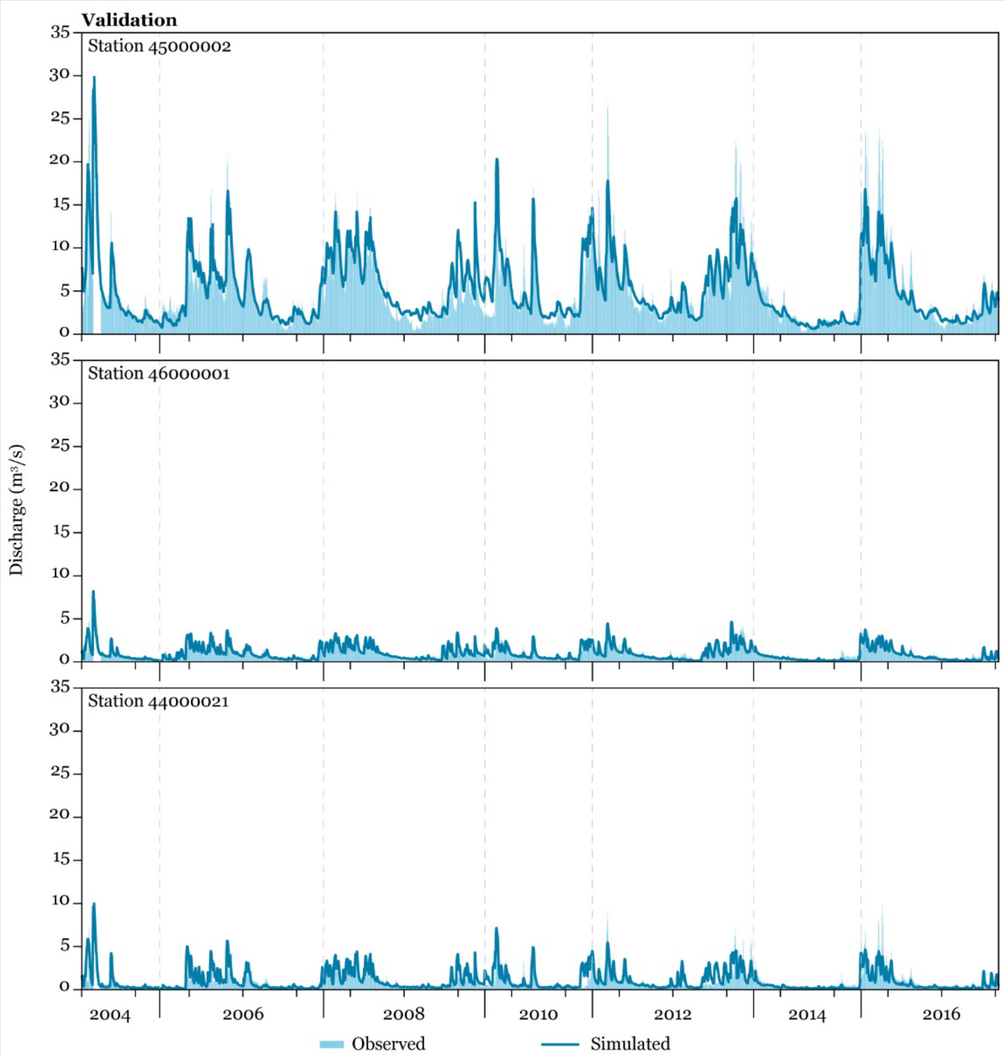

FIGURE 4.5. Simulated and observed daily discharge values for the validation period for the three monitor-ing stations in the inversion model of Fyn, Denmark.

TABLE 4.4. Discharge performance statistics calculated based on daily discharge values for the three monitoring stations in Fyn in the inversion model for the calibration and validation periods. Calibration: 2003, 2005, 2007, 2009, 2011, 2013, 2015, 2017, and validation: 2004, 2006, 2008, 2010, 2012, 2014, 2016.

Inversion model	Station 45000002		Station 46000001		Station 44000021	
	Cali.	Vali.	Cali.	Vali.	Cali.	Vali.
NSE	0.82	0.80	0.74	0.76	0.73	0.57
R^2	0.82	0.81	0.77	0.80	0.74	0.66
PBIAS	3.5	-2.3	2.8	0.9	1.0	-8.3

The calibrated parameter values are shown in table 4.5 together with the initial ranges.

TABLE 4.5. Initial ranges and calibrated values of the selected parameters for simulating daily streamflow using SWAT. 'Sub' refers to individual sub-basins, Fig. 4.3. Sub-basins 42, 54, 58, 69, 76, 80, 81, 86 drain to station 45000002; sub-basin 50 drains to station 4600001; sub-basin 52 drains to station 44000021.

Parameter	Level	Initial range		Calibrated values	Calibrated values		
		lower	upper		Sub 42,54,58, 69,76,80,81,86	Sub 50	Sub 52
v__SFTMP.bsn	Entire Fyn	-5	5	0.29			
V__SMTMP.bsn	Entire Fyn	-5	5	-1.40			
v__SMFMX.bsn	Entire Fyn	1	5	1.76			
v__SMFMN.bsn	Entire Fyn	1.5	2	1.59			
v__SURLAG.bsn	Entire Fyn	1	15	12.12			
r__CN2.mgt	Entire Fyn	-0.3	0.3	0.02			
v__ESCO.hru	Entire Fyn	0	1	0.31			
v__EPCO.hru	Entire Fyn	0.01	1	0.47			
r__HRU_SLP.hru	Entire Fyn	-0.2	0.2	0.06			
v__CH_N2.rte	Entire Fyn	0	0.3	0.14			
v__CH_K2.rte	Entire Fyn	0	75	59.63			
r__CH_W2.rte	Entire Fyn	-0.3	0.5	-0.12			
r__CH_D.rte	Entire Fyn	-0.3	0.5	0.32			
v__ALPHA_BNK.rte	Entire Fyn	0	1	0.33			
r__SOL_AWC().sol	Entire Fyn	-0.4	0.4	0.005			
r__SOL_K().sol	Entire Fyn	-0.5	1.8	-0.18			
r__SOL_BD().sol	Entire Fyn	-0.1	0.2	0.09			
v__SOL_Z3().sol	Entire Fyn	1500	1500	1500			
r__TDRAIN.mgt	Entire Fyn	-0.3	0.3	-0.02			
r__DDRAIN.mgt	Entire Fyn	-0.3	0.3	0.05			
r__GDRAIN.mgt	Entire Fyn	-0.3	0.3	0.15			
r__OV_N.hru	Entire Fyn	-0.2	0.2	0.05			
v__WDPQ.bsn	Entire Fyn	0	1	0.77			
r__WGPQ.bsn	Entire Fyn	0	1000	647.36			
v__WDLPQ.bsn	Entire Fyn	0	10	8.64			
v__WGLPQ.bsn	Entire Fyn	0	3	0.159			
v__WDPS.bsn	Entire Fyn	0	1	0.43			
v__WGPS.bsn	Entire Fyn	0	1	0.07			
v__ALPHA_BF.gw	Sub-basin	0	1	0.28	0.25	0.41	0.25
v__GW_DELAY.gw	Sub-basin	1	750	169.32	205.63	100.97	219.93
v__GWQMN.gw	Sub-basin	0	2000	983.66	1337.50	1310.50	1481.50
v__GW_REVAP.gw	Sub-basin	0.02	0.2	0.07	0.07	0.02	0.15
v__REVAPMN.gw	Sub-basin	0	500	444.96	435.50	494.10	379.90
v__ALPHA_BF_D.gw	Sub-basin	0	1	0.79	0.78	0.91	0.84
v__RCHRG_DP.gw	Sub-basin	0	1	0.16	0.35	0.30	0.38

4.3.2 Model validation: Forward model

The simulation period for the forward model is 2006 - 2015 to fit the agricultural management and pesticide application data. Fig. 4.6 shows the observed and simulated hydrographs at the three monitoring stations for this period for the forward model. It is seen that the simulated discharge at the three monitoring stations follows the observed discharge both in baseflow and peak flow situations relatively well. The forward model even seems to simulate the peaks in the discharge for station 45000002 better than the inversion model, however the simulated peaks also follows the observed peaks for the two other stations well (Fig. 4.6). Also, for the forward model the falling and rising limp of the simulated discharge in general follows the observed discharge suggesting a good representation of the hydrological conditions in the study site, i.e. the entire Fyn.

Table 4.6 shows the performance statistics for the forward model. All values are in the acceptable range according to (Moriasi et al. 2015) except NSE for monitoring station 44000021 which is 0.48. R2 values range from 0.71 to 0.81, NSE from 0.48 to 0.72 and PBIAS from 0.4% to -12.6% (table 4.6). The differences in performance statistics between the inversion and the forward models are due to (i) the forward model is run with the agricultural area divided into 17 splits, and, most importantly, (ii) the different time periods used (inversion model: validation every second year 2004 - 2016; forward model: validation 2006 – 2015).

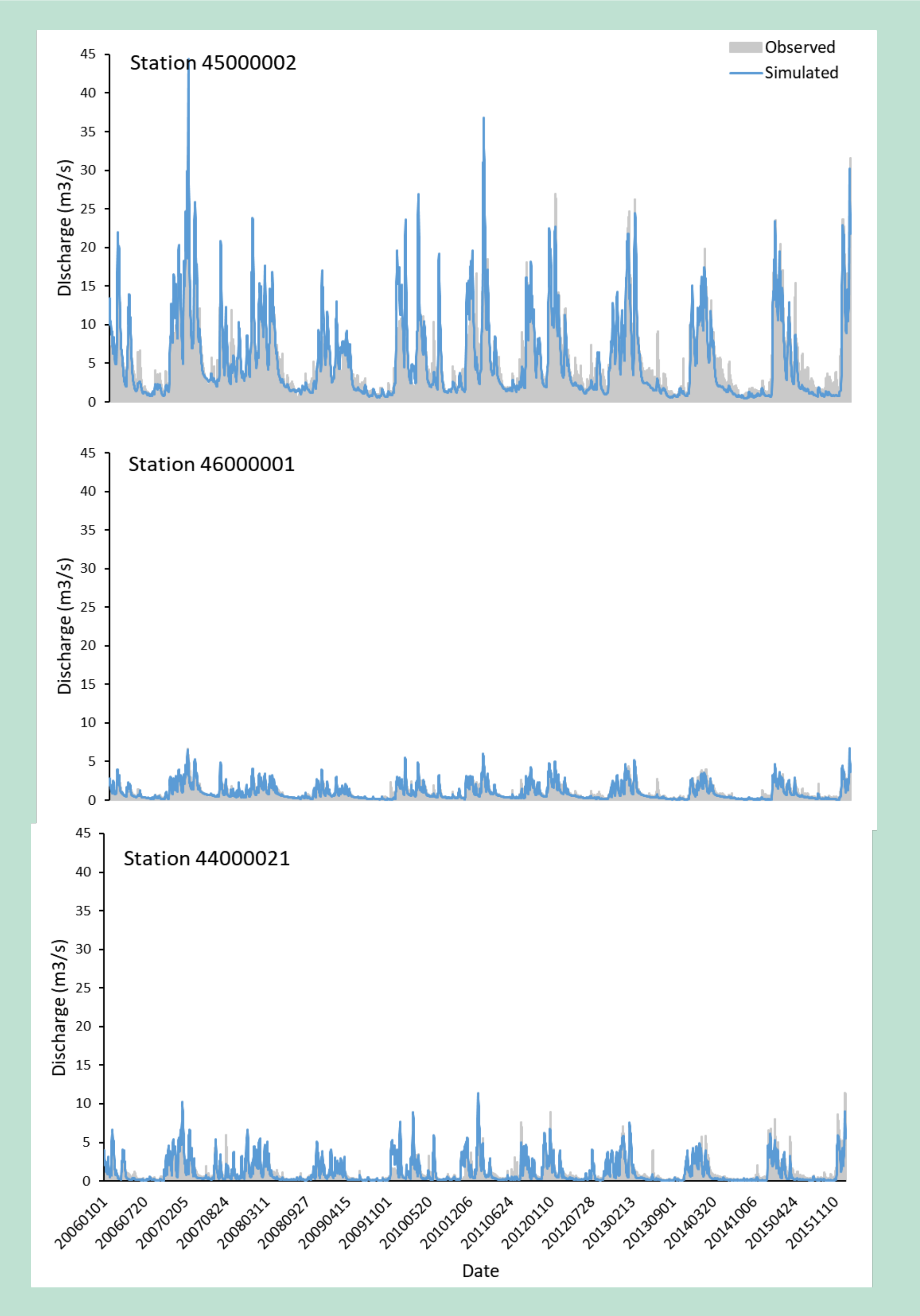

FIGURE 4.6. Simulated and observed daily discharge values for the simulation period for the three monitoring stations in the forward model of Fyn, Denmark.

TABLE 4.6. Discharge performance statistics for the forward model based on daily discharge observations for the simulation period 2006-2015.

Forward model	Station 45000002	Station 46000001	Station 44000021
NSE	0,72	0,69	0,48
R^2	0,81	0,79	0,70
PBIAS	-3.2	0.4	-12.6

4.3.3 Spatial variation

Figures 4.7 and 4.8 illustrate the spatial variability within Fyn divided into sub-basins. The average precipitation ranges from 706 to 897 mm/year with highest precipitation in the north-western part of Fyn. The average runoff calculated with the forward model is in the range 186 to 363 mm/year with lowest values in the north-eastern part of Fyn.

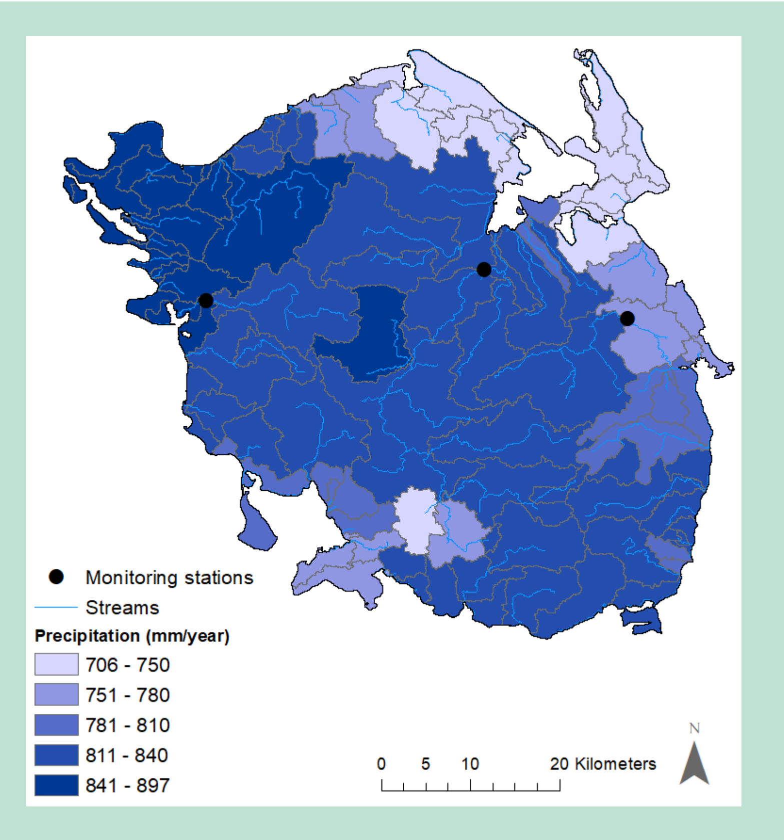

FIGURE 4.7. Average precipitation 2006-2015.

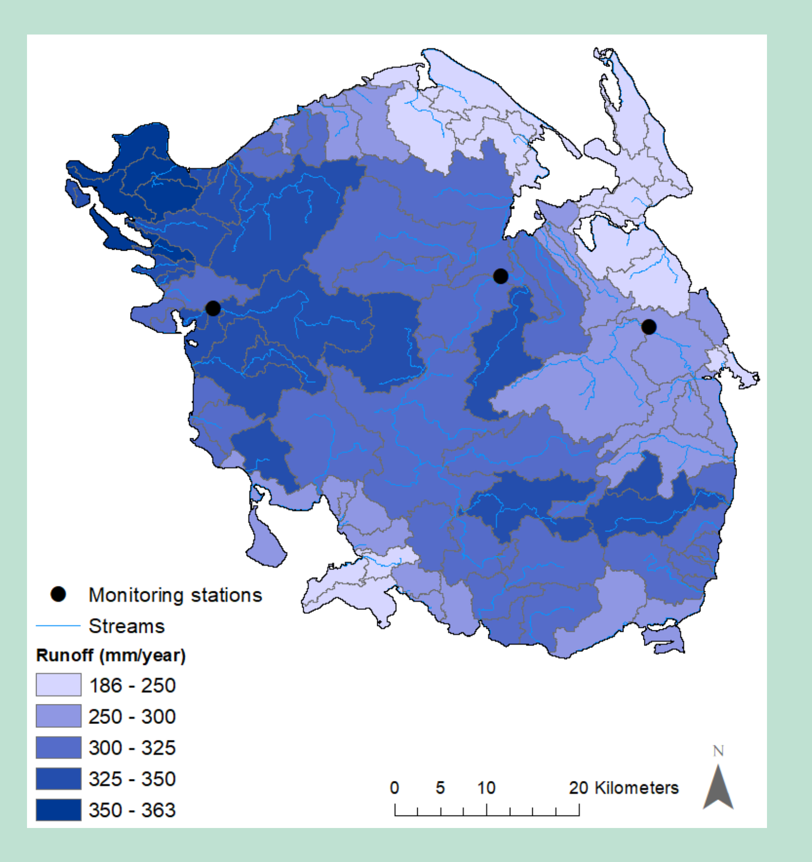

FIGURE 4.8. Average runoff (mm/year) 2006-2015 per sub-basin calculated with the forward model.

4.3.4 Pesticide measurements in streams on Fyn

The data available for Bentazone, Pirimicarb and Propizonazole measured at the three selected monitoring stations at Fyn are very limited. During 2006 - 2015, Bentazone was only measured monthly at station 45000002 in 2006 and at station 46000001 in 2012. Pirimicarb and Propizonzole were not measured at all during 2006-2015. Figures 4.9 and 4.10 illustrate that the observed pesticide measurements are generally higher than the simulated concentrations from the forward model. The simulated concentrations during the summer are more comparable to the observed concentrations. Table 4.7 reveals that the performance statistics is unsatisfactory for the forward model for the periods with measured data.

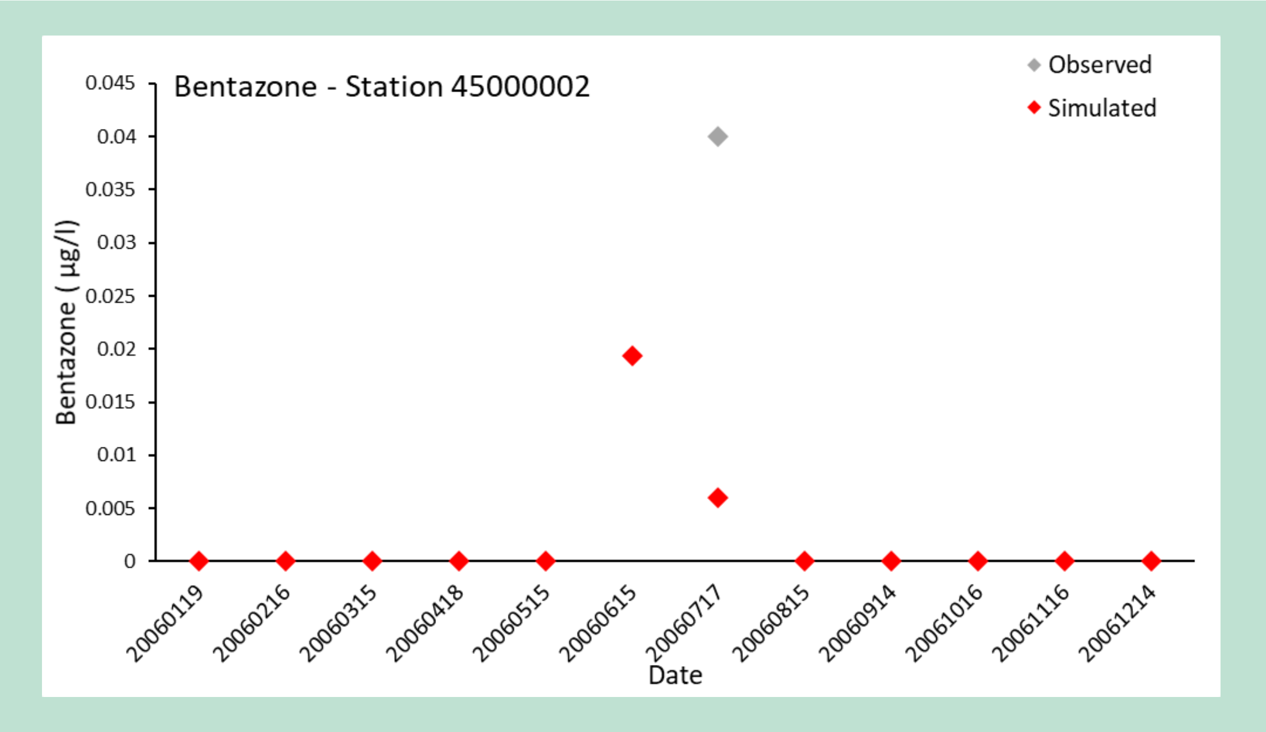

FIGURE 4.9. Observed versus simulated Bentazone concentrations at monitoring station 45000002 at sam-pling dates. Note that there are only measurements from 2006. The detec-tion limit is 0.01 µg/l. Measurements below the detection limit are not shown.

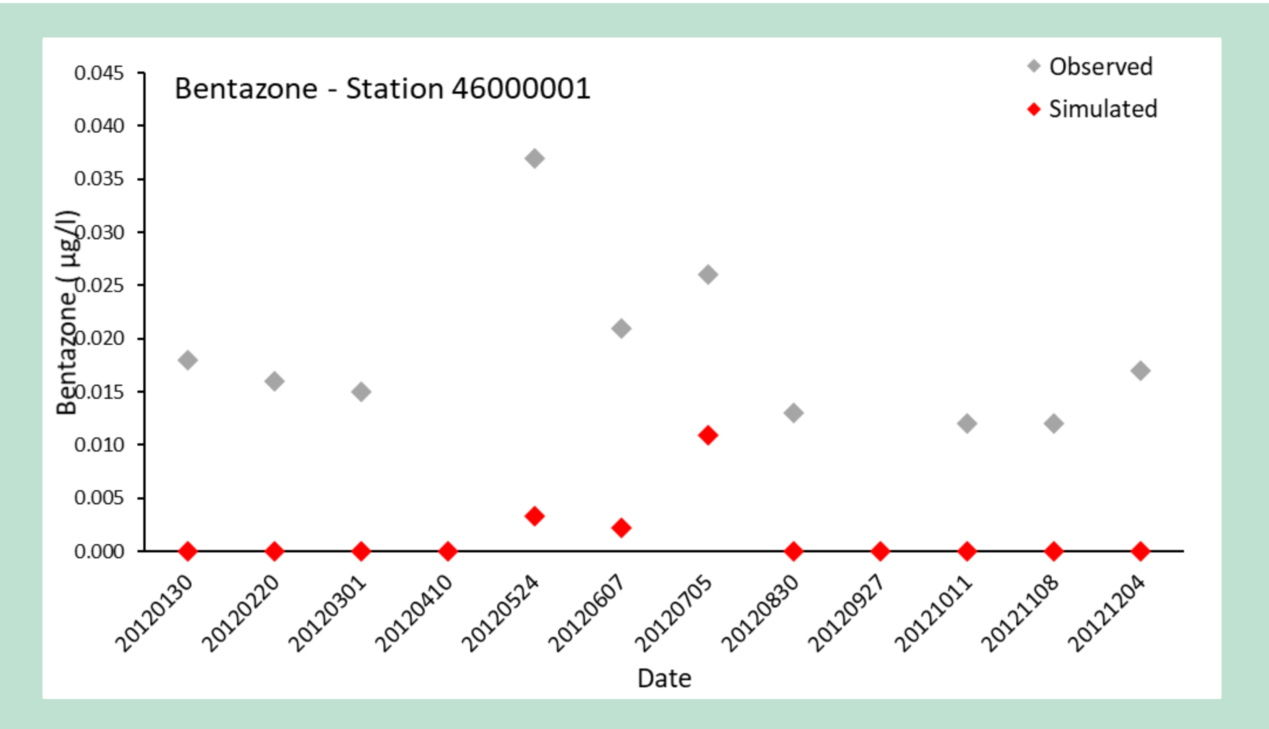

FIGURE 4.10. Observed versus simulated Bentazone concentrations at monitoring station 46000001 at sam-pling dates. Note that there are only measurements from 2012.The detec-tion limit is 0.01 µg/l. Measurements below the detection limit are not shown.

Table 4.7: Bentazone performance statistics for the forward model based on available Bentazone measurements for monitoring station46000001 in 2012

Forward model	Station 46000001 Bentazone
NSE	-5.04
R^2	0.36

4.3.5 Pesticide exposure risk maps, streams

The average concentrations per sub-basin of respectively Bentazone, Pirimicarb and Propiconazole are calculated for the period 2006 – 2015 based on daily values simulated by the forward model, figures 4.11, 4.12 and 4.13. The simulated concentration values are generally low, however concentrations are relatively higher for all pesticides in the northeastern part of Fyn. Additionally, for Bentazone, also sub-basins in the western and eastern part have relatively high simulated average concentrations. For Pirimicarb, several sub-basins along the northern and eastern shoreline have relatively high simulated concentrations. The simulated average concentrations for Propiconazole are generally lower than for Bentazone and Pirimicarb.

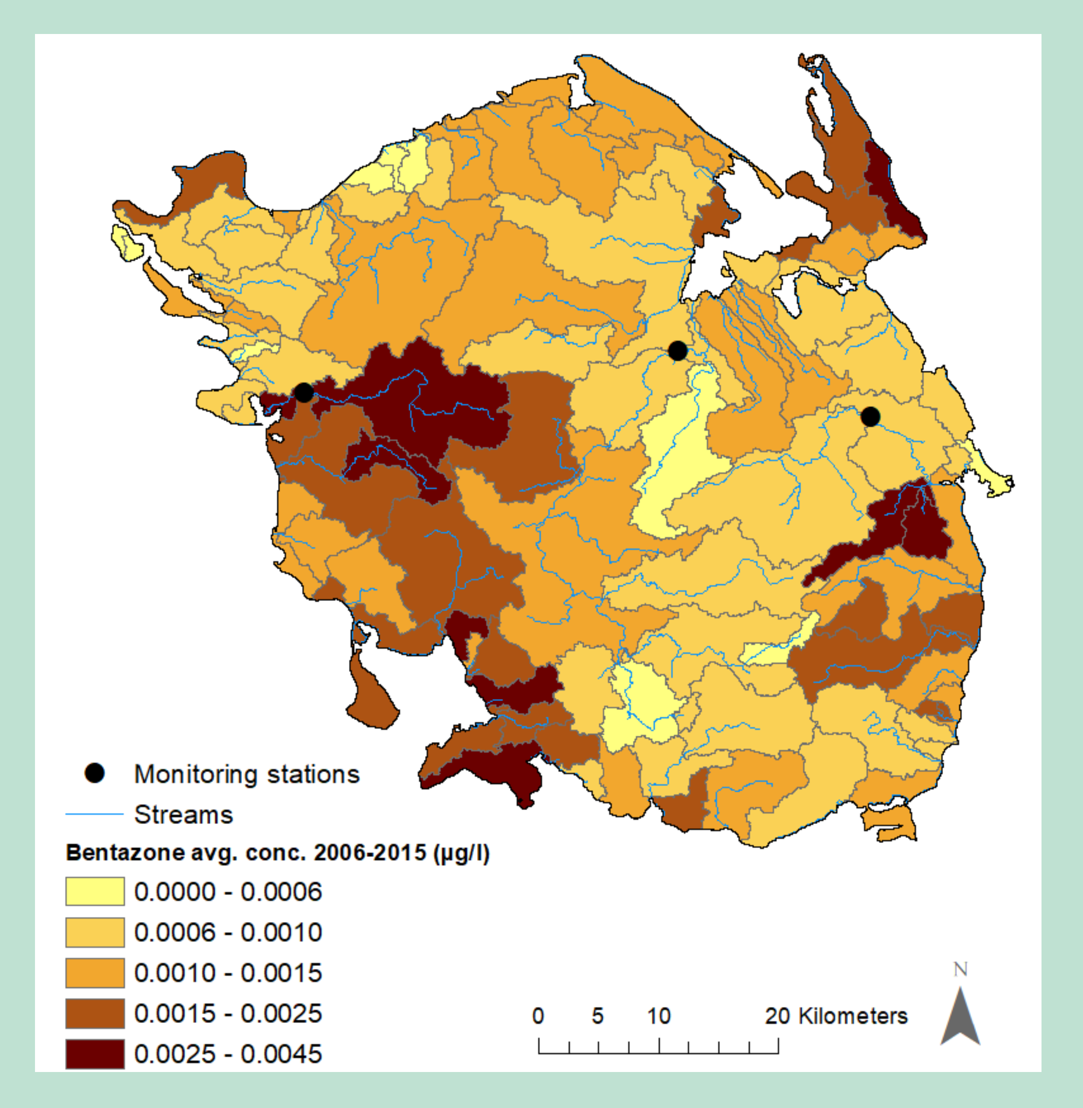

FIGURE 4.11. The average Bentazone concentration (μg/L) per sub-basin for the period 2006-2015.

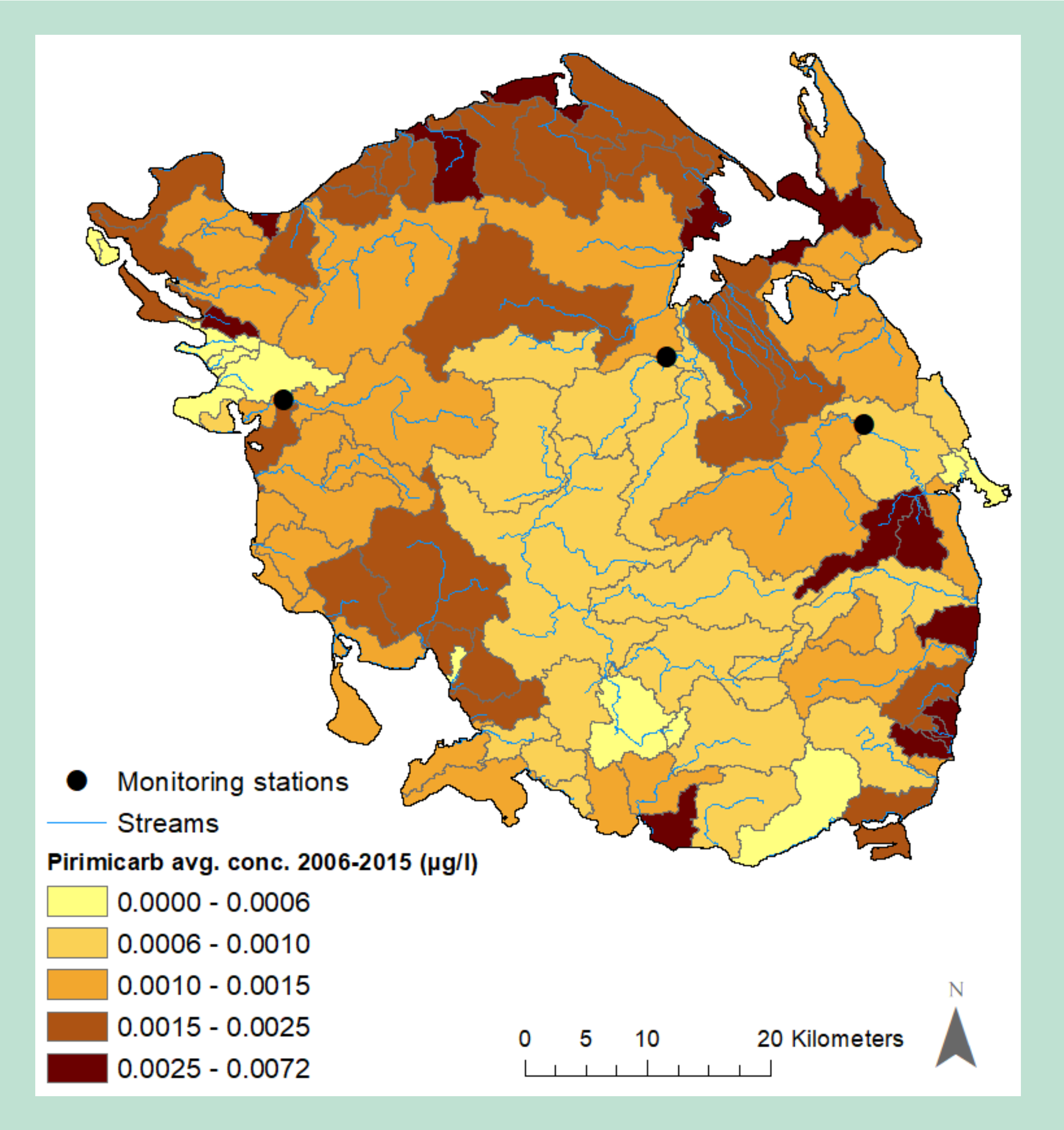

FIGURE 4.12. The average Pirimicarb concentration (µg/L) per sub-basin for the period 2006-2015.

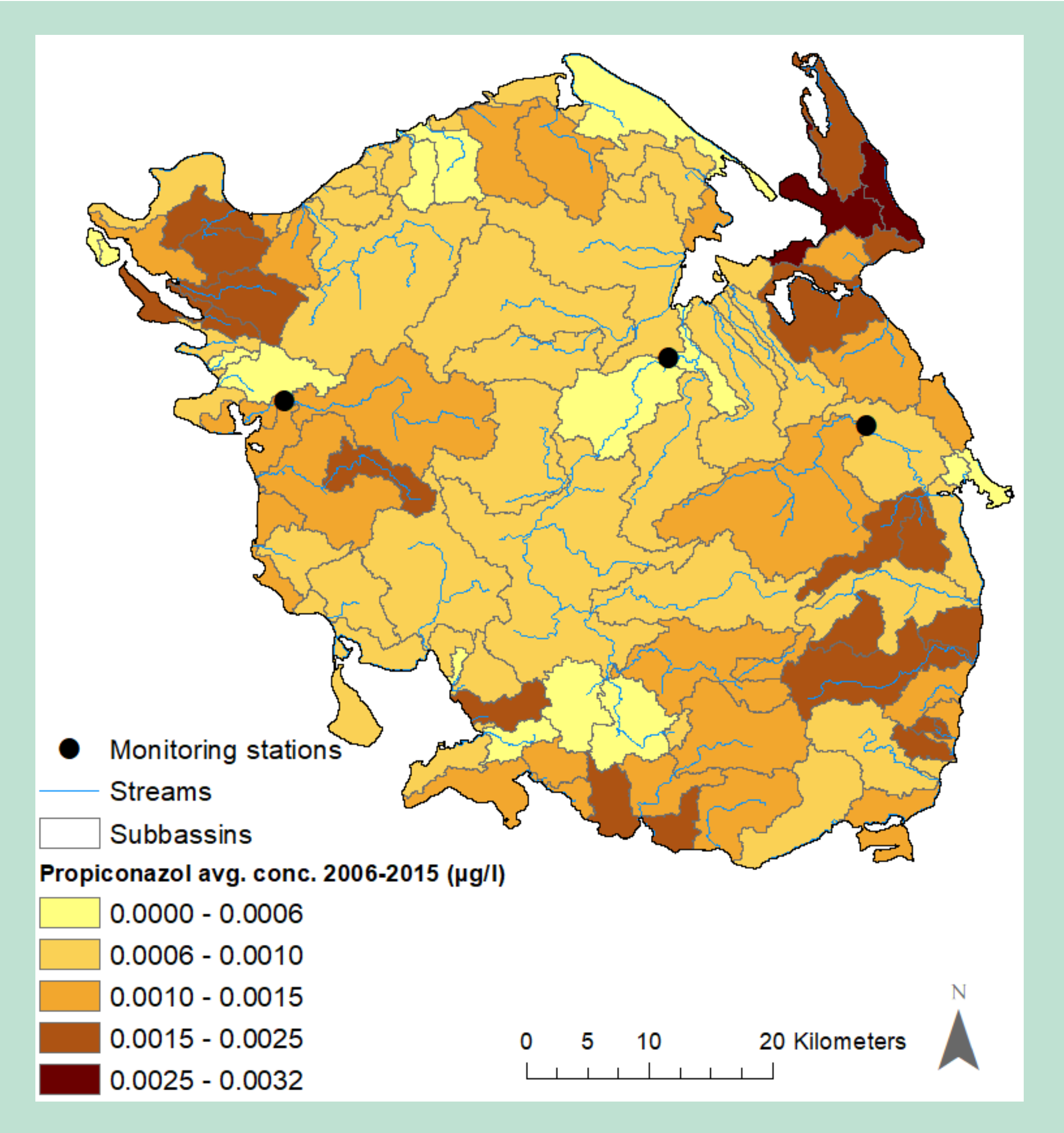

FIGURE 4.13. The average Propiconazole concentration (µg/L) per sub-basin for the period 2006-2015.

Additionally, for all three pesticides, maps are produced showing per sub-basin the maximum daily simulated concentration for the entire period 2006 – 2015, Figures 4.14, 4.15, and 4.16. For Bentazone, the maximum concentration occurs on May 30, 2007 in sub-basin 75. For both Pirimicarb and Propiconazole, the maximum concentrations occur on June 11, 2010 in sub-basin 40 for both pesticides.

The highest Bentazone concentration is found in the southeastern part of the model where subbassin 66, 68, 74, 75, 82, 84, 87, 89 and 90 all have simulated concentrations above 0.5 µg/l and up to 3.4 µg/l (Fig. 4.14).

There are no simulated Pirimicarb concentrations above 0.5 µg/l and in general most of the simulated concentrations are between 0.1 and 0.5 µg/l (Fig. 4.15).
For Propiconazol it is only the streams in subbassin 25 and 62 which experience concentrations above 0.1 µg/l and no subbassins have concentrations above 0.5 µg/l (Fig. 4.16).

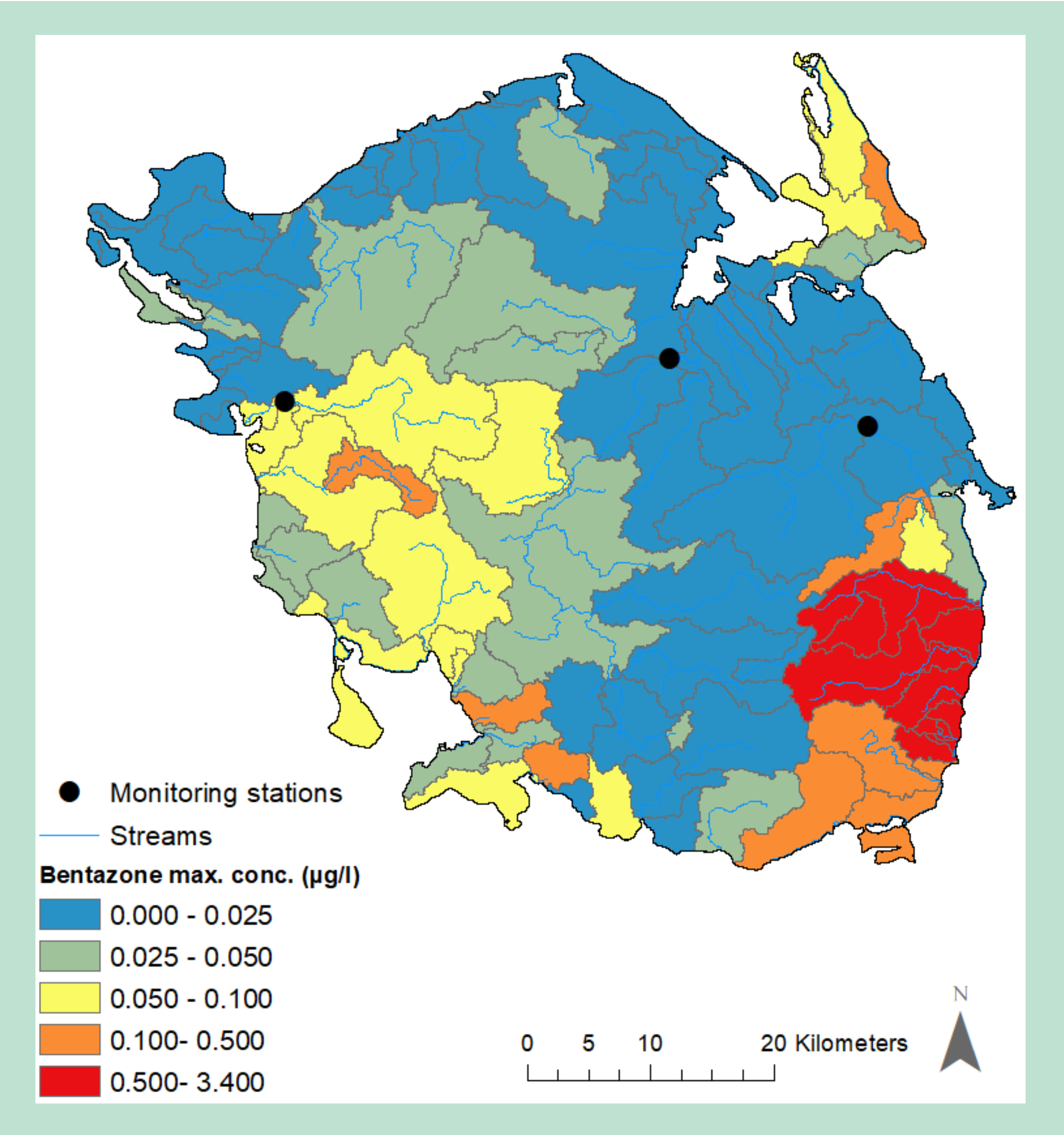

FIGURE 4.14. The Bentazone concentrations (µg/L) per sub-basin at the day with the highest simulated concentration, May 30, 2007.

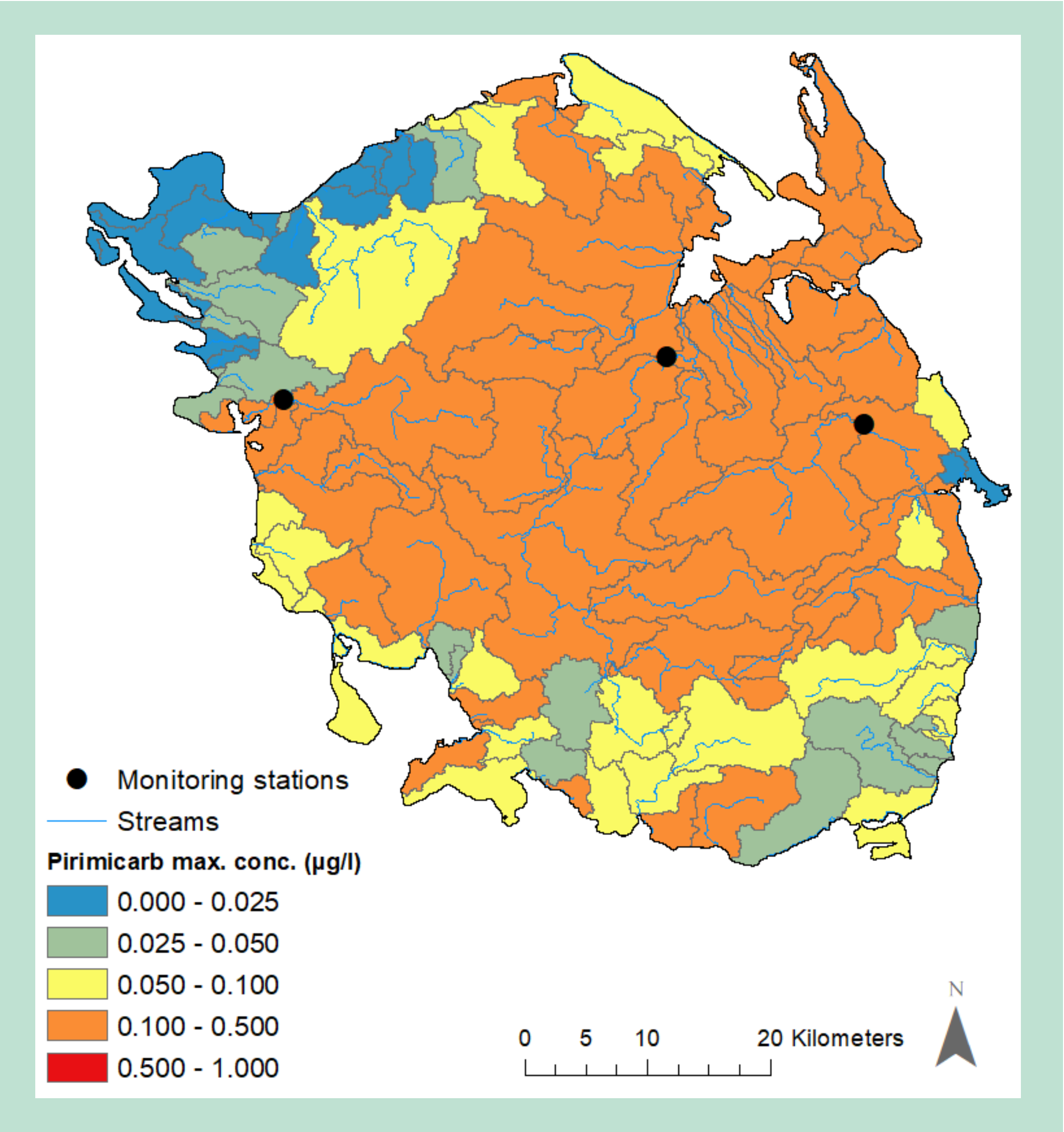

FIGURE 4.15 The Pirimicarb concentrations (µg/L) per sub-basin at the day with the highest simulated con-centration, June 11, 2010.

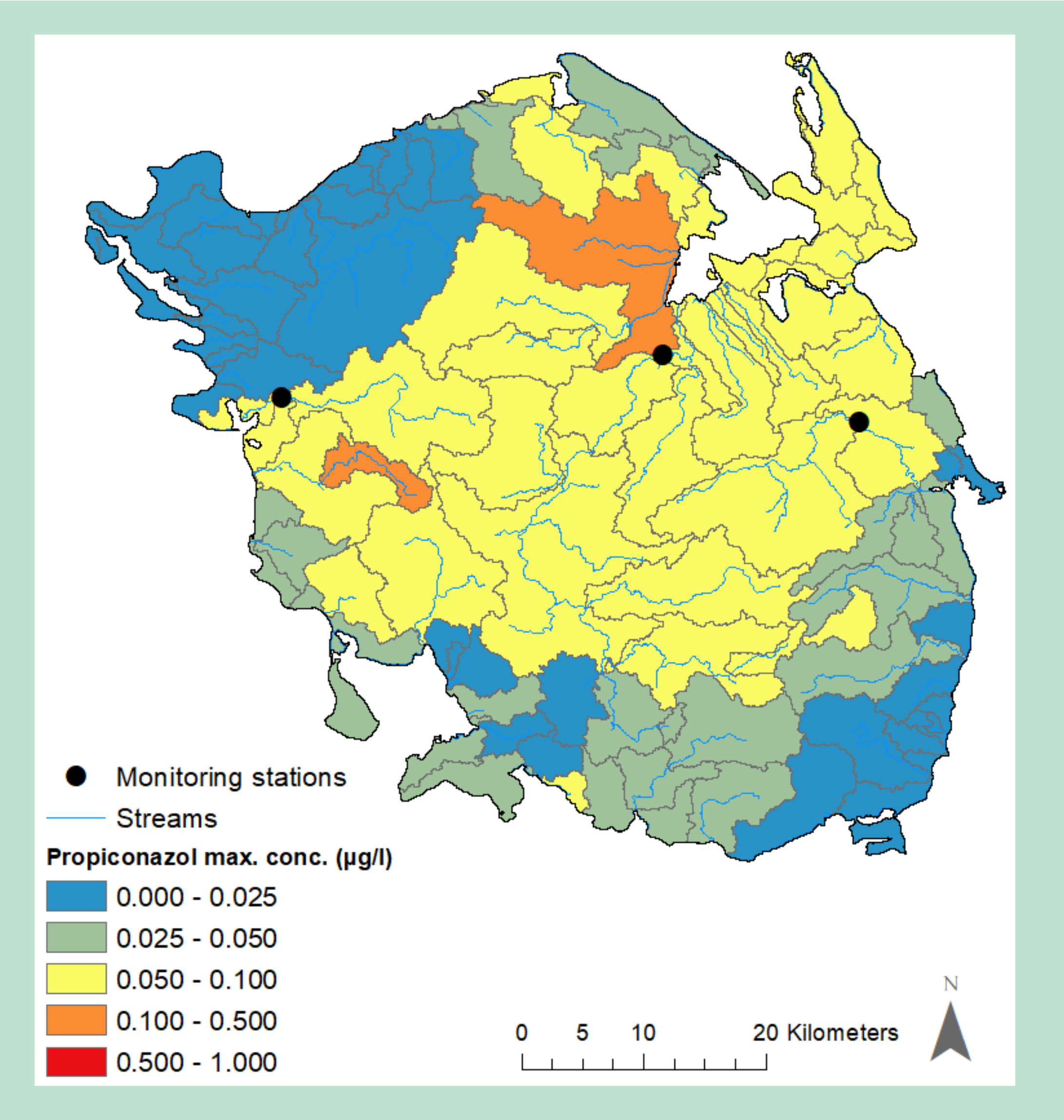

FIGURE 4.16. The Propiconazol concentrations (µg/L) per sub-basin at the day with the highest simulated concentration, June 11, 2010.

4.3.6 Pesticide exposure risk maps, groundwater

SWAT does not track pesticides in groundwater. Therefore, the risk of pesticide leaching to groundwater aquifers is evaluated by post-processing SWAT output at HRU level for the entire catchment. Pesticide concentrations in the bottom most soil layer (soil layer #3) and the daily percolation of water out of this layer is used to estimate the potential pesticide leaching to aquifers at daily intervals for each HRU (g/ha/yr). Additionally, risk maps are produced showing the maximum daily percolation of each pesticide at HRU level, figures 4.17 – 4.19.

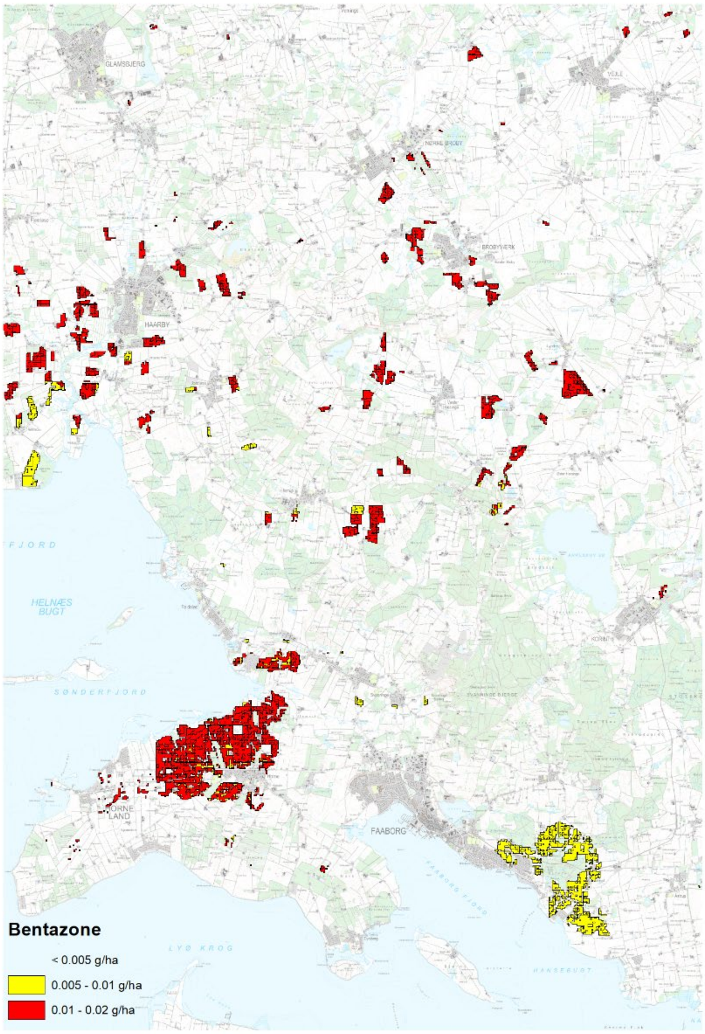

FIGURE 4.17. Maximum daily percolation of Bentazone, g/ha.

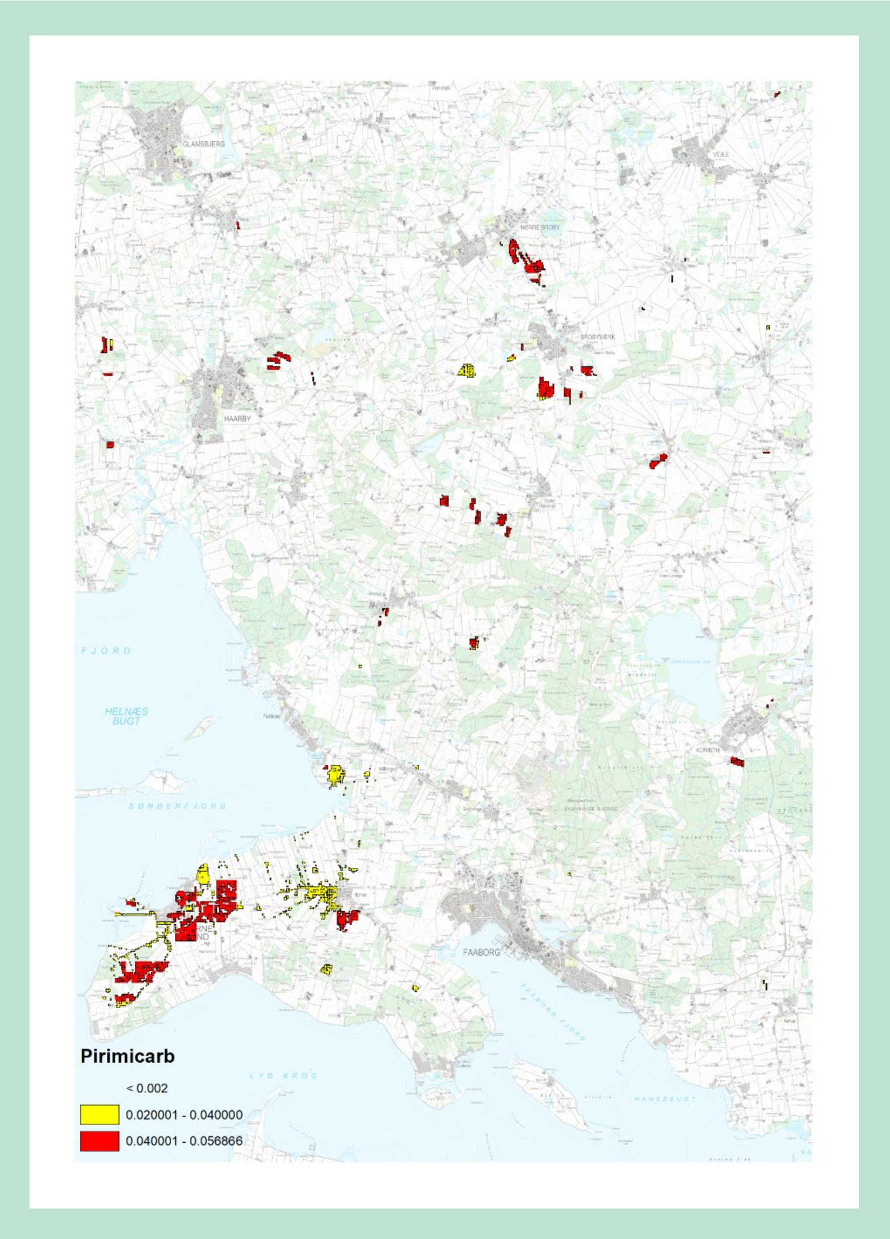

FIGURE 4.18 Maximum daily percolation of Pirimicarb, g/ha.

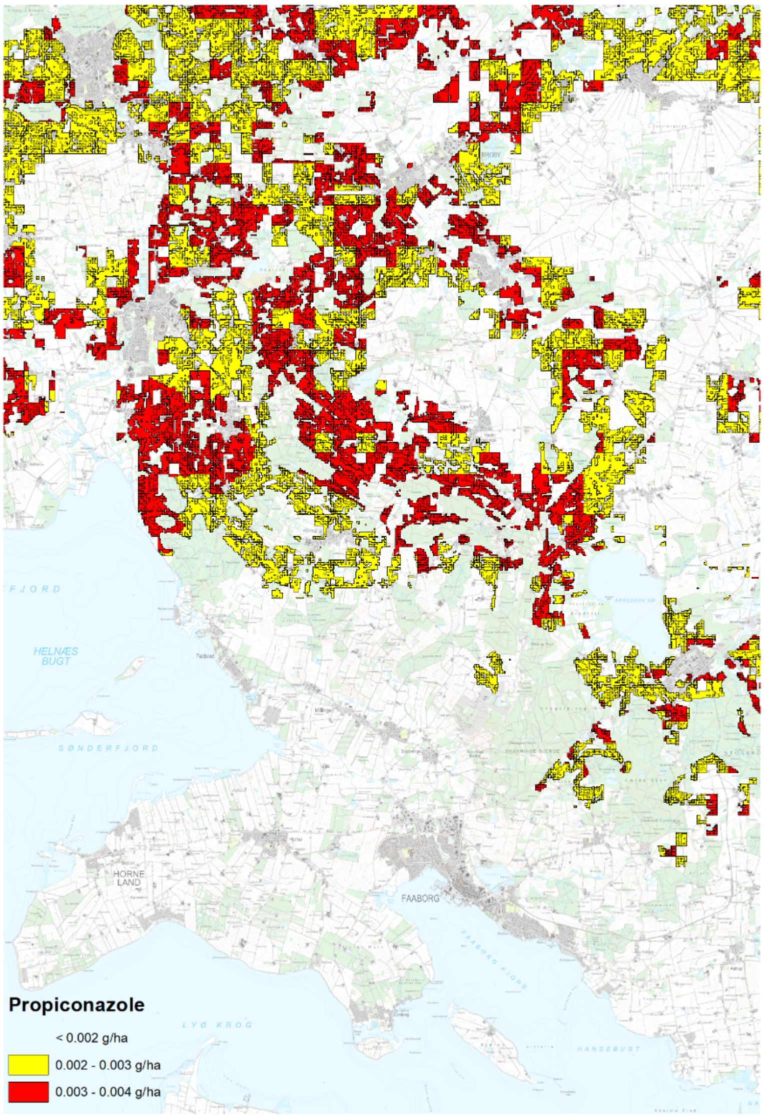

FIGURE 4.19. Maximum daily percolation of Propiconazol, g/ha.

4.4 Discussion

4.4.1 Inversion and forward model – calibration and validation method

The performance statistics for simulated water discharge for the forward model were for all three stations in the acceptable range according to (Moriasi et al. 2015), except the NSE for monitoring station 44000021 which was 0.48, which is however still close to the acceptable NSE value at 0.50. This indicates that the calibrated parameterization of the parameters in the inversion model with a high possibility represents the hydrological conditions of Fyn. More monitoring stations with observed hydrographs could have been introduced in the validation of the forward model to further evaluate model performance in all of Fyn, however this was not possible within the framework of this project. The inversion model with 11 sub-basins, 1280 HRU's and less detailed agricultural management information was running 52 times faster than the forward model with 102 sub-basins, 16632 HRU's and detailed agricultural information including pesticide management.

The calibration-validation procedure with only every second year included in respectively the validation and calibration periods was chosen in order to minimize the influence of known issues with the homogeneity of Danish precipitation data before and after 2011. However, even with this method we cannot completely avoid influence from this. Still, it was ensured that years after 2011 are included in both calibration and validation as it was also ensured that both dry and wet years are represented in both the calibration and validation periods (Rubek 2018).

4.4.2 Pesticide exposure risk maps, streams. Potential impact on aquatic organisms

The simulated Bentazone concentrations by the forward model (figs 4.9 and 4.10) are in the same order of magnitude as the few observations at two stations on Fyn, albeit generally lower. For Propiconazole and Pirimicarb there are no observations from streams on Fyn. The scarcity of measured data from streams on Fyn hampers a proper validation of the modelling results. To put the SWAT simulated values into perspective, we collected all observations of the three pesticides in Danish streams from the Danish freshwater database ODA (https://odaforalle.au.dk/). For Bentazone, data are from 2006 – 2015 similar to the SWAT simulation period, whereas for Propiconazole and Pirimicarb, all available observations were collected, i.e. data during 1993 to 2003.

For Bentazone, the SWAT simulated average concentration values are very low (fig. 4.11). However, the simulated daily maximum concentrations are above 0.025 µg/L in several streams on Fyn and in a few streams maximum values range from 0.1 to above 3 µg/L (fig. 4.14). This compares well to observations from Danish streams during 2006 – 2015 (fig. 4.20): there are several streams where all observations are below the detection limit. The maximum observed value is 0.23 µg/L. It should be noted that sampling frequency is monthly meaning that higher but undetected values very likely occur in Danish streams.

For Pirimicarb, again the SWAT simulated average concentrations are very low (fig. 4.12). Simulated daily maximum values ranges in several streams on Fyn from 0.1 to 0.5 µg/L (fig. 4.15). In comparison, the observed data (fig. 4.21) show several Danish streams where all Pirimicarb measurements are below the detection limit and generally values are below 0.05 µg/L. One stream has a maximum observed value of 3 µg/L.

The simulated average Propiconazole concentration values are, as for the other two pesticides, very low (fig. 4.13). Several streams on Fyn have simulated daily maximum values above 0.05 µg/L and a few streams have maximum daily values in the range 0.1 – 0.5 µg/L (4.21). In the observed data, several streams have either no measurements above the detection limit or no measurements above 0.05 µg/L. Five streams have maximum values larger than 0.5 µg/L and one stream have a single observation of 1.5 µg/L (fig. 4.22).

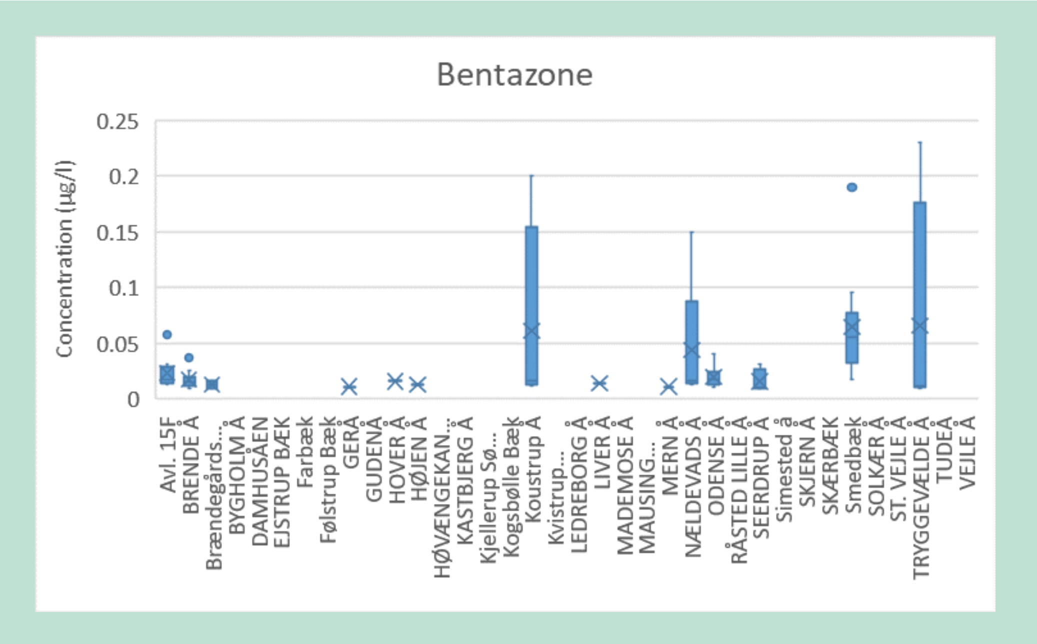

FIGURE 4.20. Measured Bentazone concentration in Danish streams during 2006 – 2015. Monthly sampling. Values below the detection limit (0.01 µg/L) not shown. Total number of analyses: 453. Data source: the Danish freshwater database ODA (https://odaforalle.au.dk/).

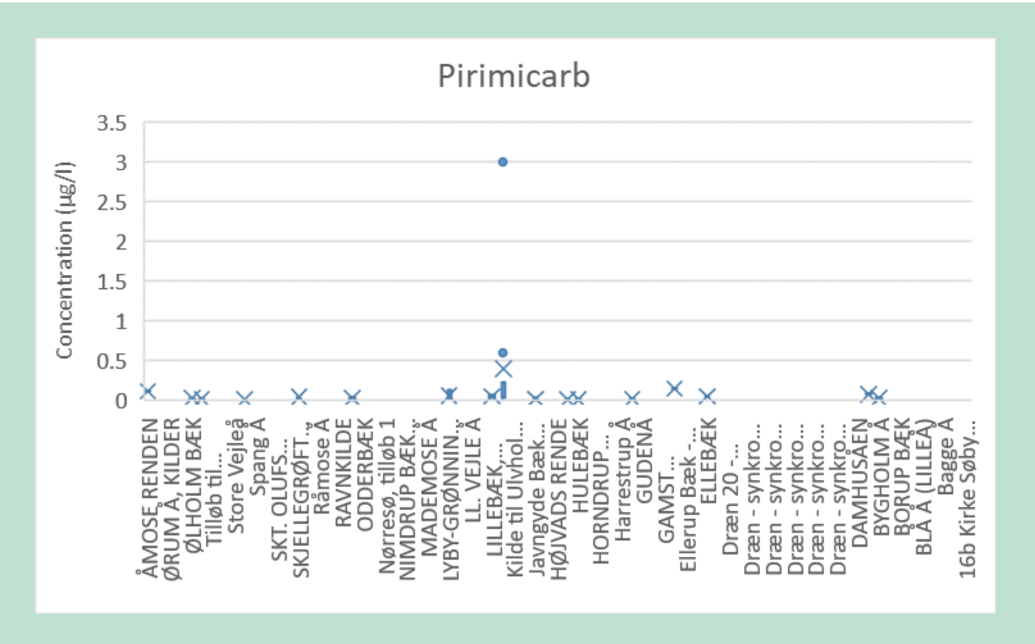

FIGURE 4.21. Measured Pirimicarb concentration in Danish streams 1994 - 2003. Monthly sampling. Values below the detection limit (0.01 µg/L) not shown. Total number of analyses: 1315. Data source: the Danish freshwater database ODA (https://odaforalle.au.dk/).

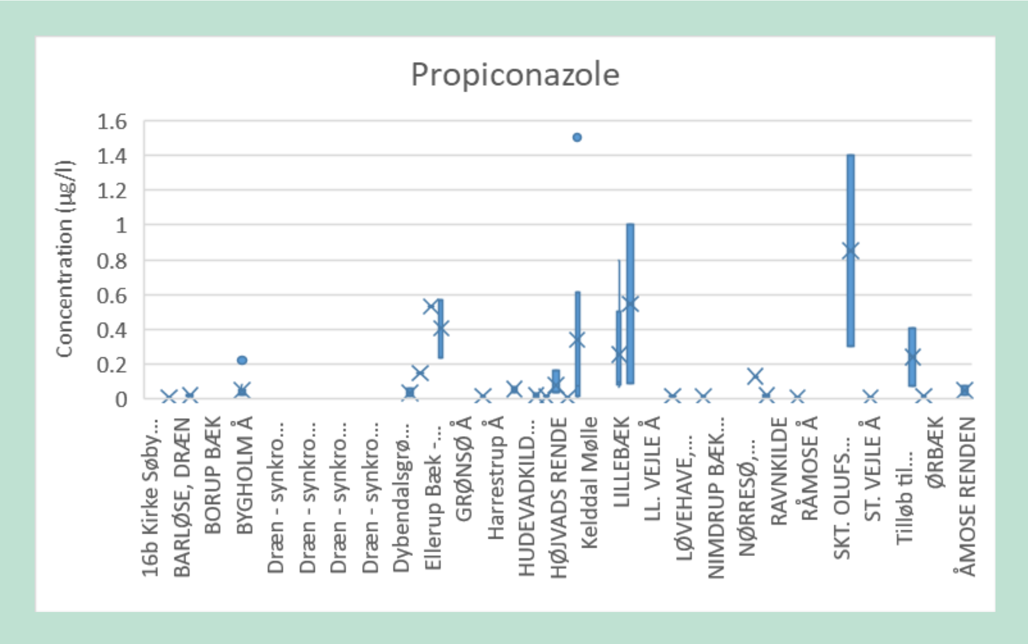

FIGURE 4.22. Measured Propiconazole concentration in Danish streams 1993 - 2003. Monthly sampling. Values below the detection limit (0.01 µg/L) not shown. Total number of analyses: 1314. Data source: the Danish freshwater database ODA (https://odaforalle.au.dk/).

Ecotoxicological evaluation

The potential impact of the three pesticides on aquatic organisms was evaluated by commonly used principles for risk assessment (OECD 1992, EU Commission 1996), i.e. the relation PEC/PNEC, where PEC is the Predicted Environmental Concentration, and PNEC is the Predicted No-Effect Concentration. In the present study, both the maximum modelled concentrations and the highest modelled mean values were used as proxies for PEC. Test results found in PPDB (Pesticide Properties DataBase, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm, visited the 10th of May 2021). As suggested in EU Commission (1996) and OECD (1992), an application factor of 1000 was used for PEC/PNEC based on acute LC50 or EC 50 values, and an application factor of 10 was used for PEC/PNEC based on chronic NOEC values, to account for the uncertainty regarding species differences.

A PEC/PNEC value larger than 1 would indicate the possibility of harmful effects. The PEC/PNEC values of Table 4.8 indicate that the maximum levels of pesticides modelled for the MOMAPEST sub-basins, especially Pirimicarb and Propiconazole, may have detrimental effects on aquatic organisms, whereas the mean levels are all very low and not expected to have negative effects.

TABLE 4.8. Test values for relevant species for the herbicide Bentazone, the insecticide Pirimicarb and the fungicide Propiconazole. The values (from PPDB, Pesticide Properties DataBase, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm, visited the 10th of May 2021) were found in standard tests used for risk assessment of pesticides, and the lowest values are presented in bold. The PEC/PNEC ratio is established from the test values, using the principles and application factors described in OECD (1992) and EU Commission (1996). PEC: Predicted Environmental Concentration, PNEC: Predicted No-Effect Concentration (lowest value in bold).

Test species	Fish, *Oncorhynchus mykiss*	Invertebrate, *Daphnia magna*	Crustacean, *Americamysis bahia*	Sediment-dwelleing organism, *Chironomus riparius*	Algae, species varies	Plant, *Lemna gibba*	Fish, *Oncorhynchus mykiss*	Invertebrate, *Daphnia magna*	Algae, not specified	Modelled values of MOMAPEST sub-basins (PEC's)		Risk assessment, max predicted value (mean predicted value) PEC/PNEC
Test Active ingredient	Acute 96 h LC_{50} mg/l	Acute 48 h EC_{50} immobilisation mg/l	Acute 96 h LC_{50} mg/l	Chronic 28 d NOEC immobilisation mg/l	Acute 72 h EC_{50} growth mg/l	Acute 7d EC_{50} biomass mg/l	Chronic 21 d NOEC development, growth, survival and behaviour mg/l	Chronic 21 d NOEC reproduction mg/l	Chronic 96 h NOEC growth mg/l	Mean values mg/l	Max values mg/l	
Bentazone (h)	>100	>100	132.5	-	10.1*	5.4	48	>101	25.7	0-0.0000045	0-0.0034	0.63 (0.0008)
PNEC	0.1	0.1	0.13	-	0.01	**0.0054**	4.8	10	2.57			
Pirimicarb (i)	>100)	0.017	-	>10	140**	-	<18	0.0009	50	0-0.0000072	0-0.001	11 (0.08)
PNEC	0.1	0.00017	-	1	0.14	-	1.8	**0.00009**	5			
Propiconazole (f)	2.6	10.2	0.37	8.0	0.093 ***	4.9	0.068	0.31	0.32	0-0.0000032	0-0.001	11 (0.03)
PNEC	0.0026	0.01	0.00037	0.8	**0.000093**	0.0049	0.0068	0.031	0.032			

* *Anabaena flos-aquae*, 120 t, ** *Pseudokirchneriella subcapitata*. *** *Navicula seminulum* ,11 d

The strength of the SWAT model is that it considers pesticide dynamics (degradation, evaporation, transport) as a function of topography, soils, geology, management and weather in the calculation of pesticide fate from application to possible arrival in the stream. This is not possible without a model. The model pointed to subcatchments with predicted maximum pesticide concentrations with potentially detrimental effects on aquatic organisms. These subcatchments could be further investigated with a targeted monitoring campaign. Thus, despite limitations in process descriptions and the uncertainty surrounding model predictions, the extended SWAT model may be a useful tool for assessing the risk of pesticide exposure of surface waters at landscape level.

4.4.3 Relevance of the modelling results for groundwater

In the following the relevance of the modelled potential leaching of three pesticides (Bentazone, Propiconazole, and Pirimicarb) to groundwater will be evaluated.

The approach consists of presenting the available groundwater data in relation to the produced maps of pesticide leaching. The hypothesis is that wells with detected pesticides are more likely to be in areas with relatively higher potential leaching, while areas with lower potential leaching should not have wells with detected pesticides. However, it must be noted that even though we discuss the relative leaching, i.e. areas with lower vs. higher leaching, overall the simulated absolute leaching values are extremely low and would not be detectable in groundwater with the present laboratory methods. See quick and dirty conversion of the modelled potential leaching from flux to concentration (Box 1).

Box 1. Converting flux (g/ha/y) to average concentration (µg/l)
If we assume that the net precipitation was 350 mm/yr (Bolbro and Eksercermarken catchment areas), then 100 µg/ha/y would be equal to 0.00003 µg/l. The most frequent detection limit in groundwater is 0.01 µg/l, thus this concentration is way below the currently detectable levels of pesticides.

Conversion factors:
1 g/ha/y = 1,000,000 µg/ha/y, thus 0,0001 g/ha/y is equal to 100 µg/ha/y
1 ha = 10,000 m^2
350 mm = 0.35 m
0.35 m * 10,000 m^2 = 3,500 m^3 = 3,500,000 l
100 µg/ha/y = 100/3,500,000 = 0.00003 µg/l

Nevertheless, we have decided to present the available data on the detected pesticides Bentazone, Propiconazole, and Pirimicarb (and their degradation products), together with the modelled potential leaching. The discussion on the methods' limitations could inform future work on the modelling of pesticide leaching to the groundwater.

4.4.3.1 Methods and data, groundwater

The comparison is done based on 1) visual inspection of maps showing the modelled potential leaching overlaid with the wells where groundwater was analyzed for pesticides, and more formally, 2) a comparison between the maximum potential leaching within 1km buffer around the wells and the well-status (detected/not detected pesticide).
The simplification with the 1km-buffer is necessary because there is no information on the catchment areas (or the recharge areas) of all individual wells. We have assumed that the

pesticides' source would most probably be within this 1km buffer. This buffer-approach is better than using the modelled leaching at the location of the well, however it is possible that the recharge area is further away (or larger). We use the maximum, modelled leaching within the buffer, as this represents the worst-case scenario. The modelled leaching data was converted from g/ha/yr to µg/ha/yr to facilitate the comparison with the concentrations in the groundwater. The buffer-analysis was done in QGIS 3.10 or 3.22 (QGIS.org, 2021). The results from this comparison were visualized using boxplots, produced in R v. 4.0.2 (R Core Team, 2019) with R package ggplot2 v.3.3.3 (Wickham, 2016).

The groundwater pesticides data used in this comparison comes from the dataset prepared annually for the NOVANA program, including the wells from the national groundwater monitoring network (GRUMO and LOOP) and the waterworks' wells used for drinking water purposes (BK). The data used here was extracted from Jupiter database (https://www.geus.dk/produkter-ydelser-og-faciliteter/data-og-kort/national-boringsdatabase-jupiter) on 22 June 2021 (Thorling et al 2021). The LOOP data was used only for the small scale (LOOP 4, Lillebæk catchment) comparison, while BK and GRUMO wells were used for the comparison at the larger scale (Fyn area). The LOOP data was supplemented with new analyses of samples taken on 4 March 2021 at well with DGU no. 165.285 (well-screen 1).

The potential leaching was modelled for Bentazone, Propiconazole, and Pirimicarb. However, when selecting the groundwater pesticides data, we also included the degradation products of these three pesticides in the initial data selection (Table 4.9). This was done because the metabolites are more often detected in Danish groundwater, in comparison to the parent compounds. Table 4.9 provides information necessary to identify the compounds and indicates if the substance is a parent or metabolite.

TABLE 4.9. Identified pesticides and selected degradation products.

Compounds	Parent/degradation product	CAS no
Bentazone	Parent	25057-89-0
N-methyl Bentazone	Degradation product of Bentazone	61592-45-8
Propiconazole	Parent	60207-90-1
1,2,4-Triazole	Degradation product of Propiconazole & other Triazole-pesticides	288-88-0
Pirimicarb	Parent	23103-98-2
Pirimicarb-desmethyl	Degradation product of Pirimicarb	30614-22-3
Desmethyl-formamido-Pirimicarb	Degradation product of Pirimicarb	27218-04-8

4.4.3.2 Results, groundwater

Of all seven compounds (Table 4.9), only two were detected in groundwater at Fyn (and LOOP 4): Bentazone and 1,2,4-Triazole. The comparison between the modelled potential leaching and the groundwater concentrations, therefore, was carried out in detail for only these two compounds. Table 4.10 shows an overview of the compounds included in the groundwater datasets for the different types of wells (GRUMO, BK, LOOP) and an indication of the number of detections.

TABLE 4.10. Data availability for each of the used sub-sets; the table shows number (n) of analyzed samples below limit of detection (< LOD) and the number of analyzed samples with detected substance (Det.)

Compounds	GRUMO (n)		BK (n)		LOOP (n)		LOOP* (n)	
	< LOD	Det.	< LOD	Det.	< LOD	Det.	< LOD	Det.
Bentazone	1544	91	3017	80	234	9	1	-
N-methyl Bentazone	-	-	-	-	-	-	1	-
Propiconazole	509	-	255	-	149	-	1	-
1,2,4-Triazole	175	4	560	1	-	-	1	-
Pirimicarb	508	-	249	-	148	-	1	-
Pirimicarb-desmethyl	19	-	-	-	-	-	1	-
Desmethyl-formamido-Pirimicarb	19	-	-	-	-	-	-	-

* additional data from the sampling on 4 Mar 2021

While Table 4.10 shows the number of analyzed samples, the maps, figures, and statistical overviews shown in the next sections were prepared based on the maximum concentration measured at each sampling point. If there were multiple measurements equal to the maximum concentration, the latest date was used. This resulted in datasets, where each sampling point was represented by a single value equal to the maximum concentration for each of the compounds. We decided to use the maximum concentration, as this is the worst-case scenario. However, we discuss briefly also the time-series, as the maximum concentration does not represent the latest measurement. The time-series were also plotted and can be found in appendix 5.

First, we present the spatial distribution and the time-series of the compounds in groundwater, both for the smaller scale (LOOP 4 area) and for the larger scale (Fyn). After that, the results from the formal comparison for Fyn are presented.

Spatial distribution and time-series of pesticides in groundwater

LOOP 4, Lillebæk catchment

Pesticides were analyzed at 26 wells from the LOOP network with 27 sampling points in total (one well had two sampling points). Bentazone was detected at five (18.5%) of these sampling points (Figure 4.23). The detections were from the beginning of the period with available data, before 2000. There was a single Bentazone sample with detection at two of the sampling points (165.297, 1 and 165.384, 1), while the rest had two (165.303, 1 and 165.306, 1) or three samples with detected Bentazone (165.305, 1). The other two pesticides (Propiconazole and Pirimicarb) were never detected in the LOOP wells. See Appendix 5, Figures 1, 2 and 3 for the time-series with measurements of the three pesticides.

Figure 4.23 shows that the five wells with detected Bentazone were in areas with relatively low potential leaching (≤ 50 µg/ha/y). Bentazone was not detected at the LOOP wells near the areas with higher leaching (50-100 µg/ha/y).

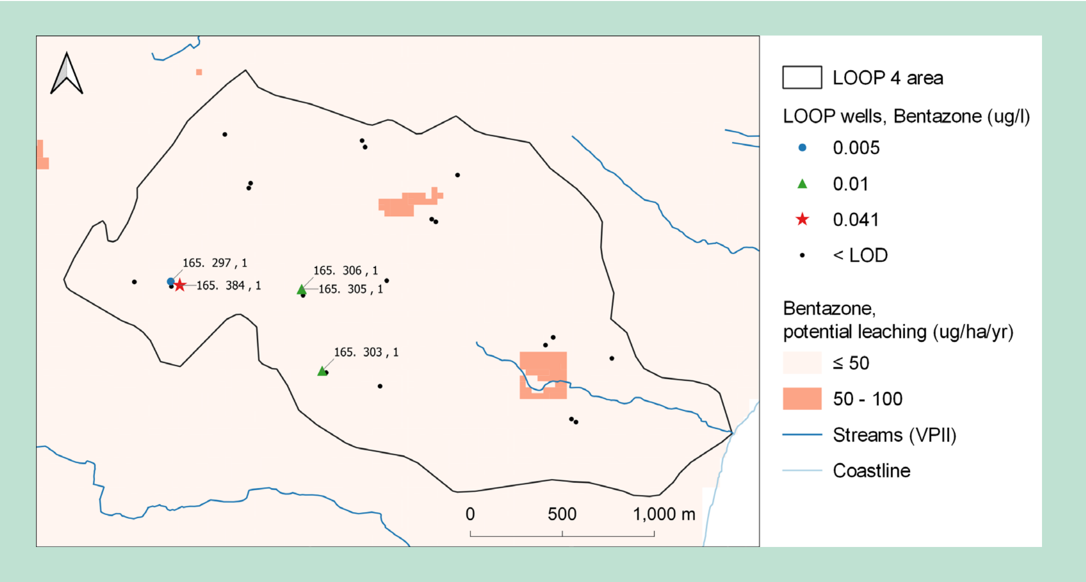

FIGURE 4.23. Location of LOOP wells with groundwater analyses (µg/l) and modelled potential leaching (µg/ha/yr) for Bentazone; only the wells with detections are labelled (label format: DGU num-ber, intake number).

Fyn area

Bentazone was detected at 12 (7.3%) of the GRUMO (n=165) and at 31 (5.8%) of the BK (n=539) well intakes. The detected Bentazone at the GRUMO wells was within the range 0.01 – 1.25 µg/l with a mean ±SD equal to 0.21 ±0.40 µg/l, based on the maximum concentration at each sampling point. The sampling depths (top of well-screen) where Bentazone was detected ranged from 2.8 m to 40 m below ground surface (m b.g.s.) with mean ±SD depth equal to 17.2 ±11.9 m b.g.s. At the BK wells, the concentrations were lower, in the range 0.01 – 0.08 µg/l, with a mean ±SD equal to 0.20 ±0.2 µg/l, based on the maximum concentration at each sampling point. The depth to top of the well-screen where the Bentazone was detected was in the range 10.7 – 63 m b.g.s. with mean ±SD equal to 27.5 ±12.6 m b.g.s. Figure 4.24 shows the locations of these wells, while the time-series of Bentazone measurements at wells where there was at least one detection of Bentazone (or 1,2,4-triazole) in the GRUMO and BK wells can be seen in Appendix 5, Figures 4 and 5.

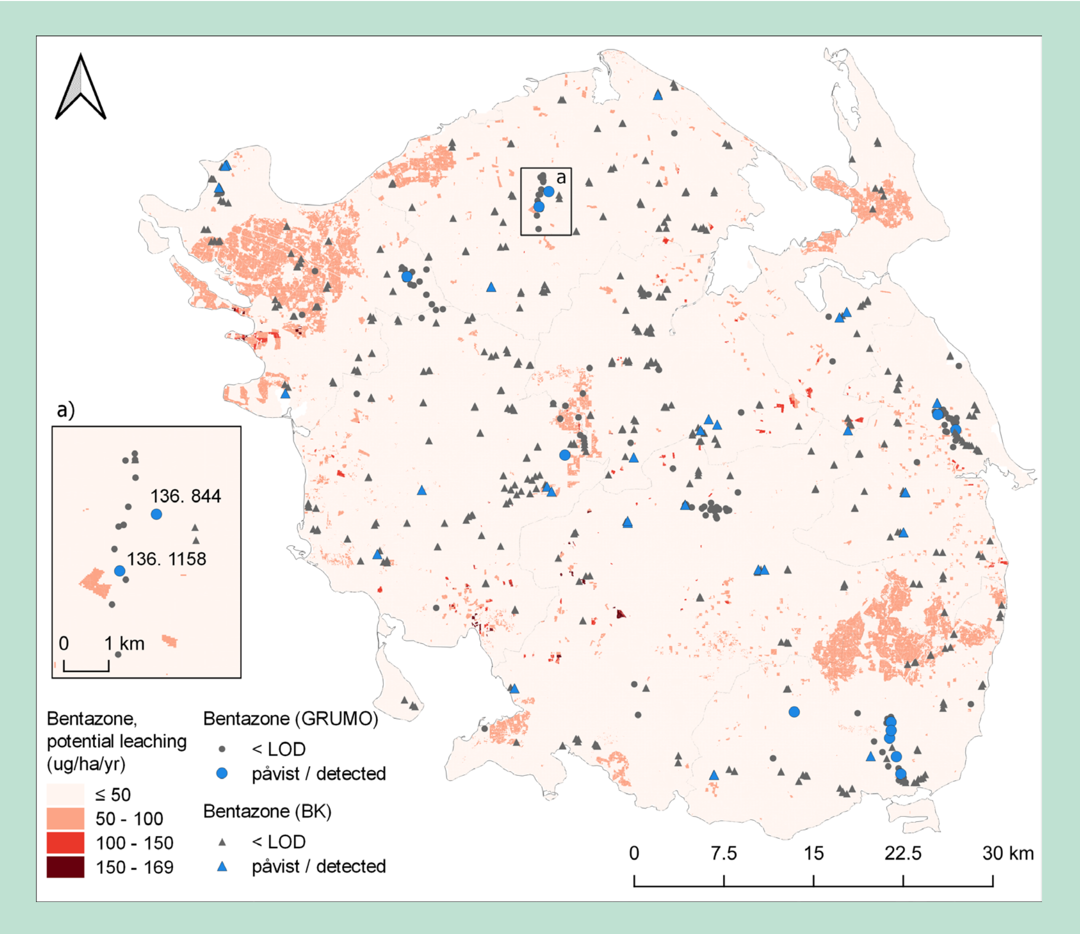

FIGURE 4.24. Bentazone detections (blue) in BK and GRUMO wells overlaying the modelled potential leach-ing (µg/ha/yr); the wells where all measurements were below the limit of detec-tion (LOD) are also shown (grey symbols); a) the two GRUMO wells with highest concentra-tions of Benta-zone.

Four of the 12 GRUMO wells were with single detections in the period, while the rest had more. Four sampling points had more than 10 detections (29 at 136.844, 1; 15 at 136.1158, 1; 13 at 164.1492, 1; and 12 at 164.935, 3).

The two GRUMO wells with DGU no. 136.844 and 136.1158 (Figure 4.24, inset a) have also the highest detected concentrations of Bentazone (Appendix 5, Figure 4) and the most anal-yses with detections in the period. Within 1km of well 136.1158 there is an area with relatively high potential leaching (50-100 µg/ha/y).

Propiconazole was not detected at any of the GRUMO (n= 99) and BK (n=108) well-screens. However, 1,2,4-triazole, which is a degradation product from Propiconazole and other triazole fungicides, was found at both GRUMO and BK wells. The degradation product was detected at four (4.8%) of the GRUMO wells (n=83) – DGU no. 128.155, 146.2551, 164.1483, 164.1484. Only one of the 384 BK well-screens had a detection (DGU no. 145.719, well-screen nr 1).

The concentrations of the detected 1,2,4-triazole at the GRUMO wells were in the range 0.1 – 0.021 µg/l with a mean ±SD equal to 0.017 ±0.005 µg/l, based on the maximum concentration at each sampling point. The sampling depths where it was detected were in the range 2.8 – 16 m b.g.s. with mean ±SD equal to 7.75 ±5.97 m b.g.s. The concentration at the BK well was 0.03 µg/l (sampling date 14 Apr 2021) at depth 36.2 m b.g.s. (top, bottom – 47.3 m b.g.s). The time-series for 1,2,4-triazole measurements are shown in Appendix 5, Figures 5 and 7. It can

be noted that for 1,2,4-triazole there are no multiple detections in time (as opposed to Bentazone).
Figure 4.25 shows the locations of the wells with detected 1,2,4-triazole, while a map with the wells sampled for Propiconazole is provided in the Appendix 5, (Figure 8). The GRUMO wells with detections are within 1 km of areas with medium potential leaching (50-100 µg/ha/y), however the BK well with detected 1,2,4-triazole is in an area without leaching of Propiconazole (0 µg/ha/y). However, it must be noted also that the wells in areas with highest leaching of Propiconazole have no detections of either Propiconazole or the metabolite 1,2,4-triazole. This could be explained by the very low absolute leaching which would most probably result in concentrations that cannot be detected in groundwater currently.

However, a direct comparison between leaching of Propiconazole and the 1,2,4-triazole detected in groundwater is not possible, because:

1. The leaching of 1,2,4-triazole (not Propiconazole) should be compared to the detections in groundwater. The conversion of Propiconazole to 1,2,4-triazole takes place already in the plough layer[1], as Propiconazole is only slightly mobile[2].
2. 1,2,4-triazole is a degradation product of Propiconazole, Tebuconazole, Expoxiconaxole, Metconazole, Difenoconazole and Prothioconazole, so the total input of the parent compounds and their different molecular masses should be considered, not just that of Propiconazole.
3. Despite the expected rapid degradation and retention in the topsoil[3], 1,2,4-triazole still leaches to the groundwater, showing that most models based on sorption and degradation cannot predict the fate of 1,2,4-triazole in the sub-surface.

[1] The results from the Danish Pesticide Leaching Assessment program show that 1,2,4-triazole leaches to drains and the shallow groundwater, whereas there are very few detections of Propiconazole (Rosenbom et al, 2021).

[2] Propiconazole is slightly mobile based on its organic-carbon normalized Freundlich distribution coefficient (K_{foc}) range 387-1817 ml/g (source: http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/551.htm accessed: 22 Feb 2022).

[3] 1,2,4-triazole is non-persistent with a half-life (DT50) of 5.5-9.9 days, and moderately mobile based on its organic-carbon normalized Freundlich distribution coefficient (Kfoc) of 43-202 ml/g (source: http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/708.htm accessed: 22 Feb 2022).

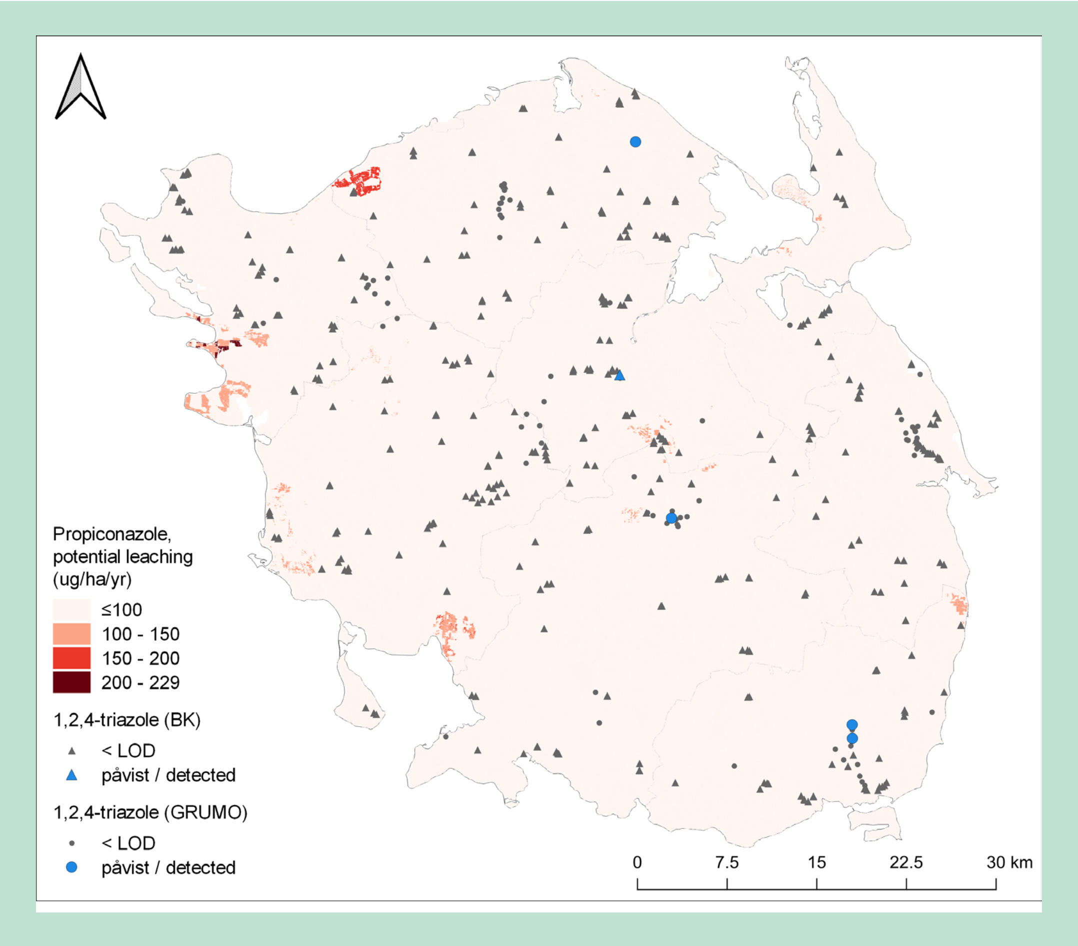

FIGURE 4.25. 1,2,4-triazole detections (blue) in BK and GRUMO wells overlaying the modelled potential leaching of Propiconazole (1,2,4-triazole is a metabolite of Propiconazole and other triazole fungicides); the wells where all measurements were below the limit of detection (LOD) are also shown (grey symbols)

Pirimicarb was not detected at any of the GRUMO (n= 99) and BK (n=106) well-screens (Appendix 5, Figure 9). The degradation products Pirimicarb-desmethyl and desmethyl-formamido-Pirimicarb were analyzed only at some of the GRUMO wells (n=19), and they were also not detected (not shown on a map).

Formal comparison with the modelled potential leaching of Bentazone (Fyn)

Figure 4.26 shows that the leaching distribution for the wells with detected vs wells without detected Bentazone are not significantly different. As discussed in the previous sections in this chapter, these leaching levels would most probably result in concentrations that are below the current laboratory detection limits. There seems to be no pattern in the detected Bentazone with respect to the relative leaching (lower-higher) on Fyn.

It must be noted also that the actual recharge zones of the wells are most probably further away or larger than the selected 1km buffer. Without performing more detailed hydrogeological assessment it is not possible to determine the actual recharge areas for all wells included in this comparison.

The waterworks catchment areas (dk: “indvindingsoplande”) have been simulated as part of the Danish groundwater mapping programme and are available for download from Miljøgis (https://miljoegis.mim.dk/cbkort?&profile=grundvand, accessed 25 Nov 2021). However, these cannot always be linked to single wells, as only the waterworks name is available, not the well number. There is also little information about the simulated period, which matters since the abstraction volumes of the waterworks may have changed, thus their catchment areas would have changed. However, Figure 4.27 shows clearly that some of the wells may potentially have their recharging area further away.

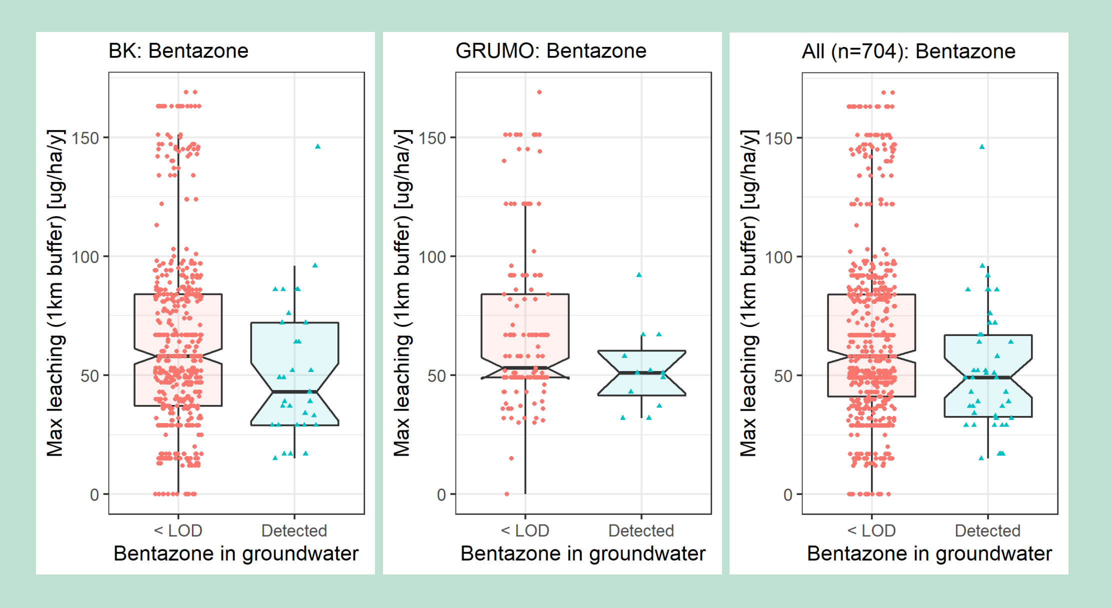

FIGURE 4.26. Sampling points where Bentazone was analyzed (GRUMO, BK, and all together) and the modelled max potential leaching of Bentazone within 1km-buffer of the well (points); standard boxplots are used: Q1 & Q3 – box, median horizontal thick black line, whiskers extend to min/max value or to 1.5*IQR, the notches extend to 1.58 * IQR / sqrt(n), which is ~95% confi-dence interval; If the notches overlap, the medians are not significantly different.

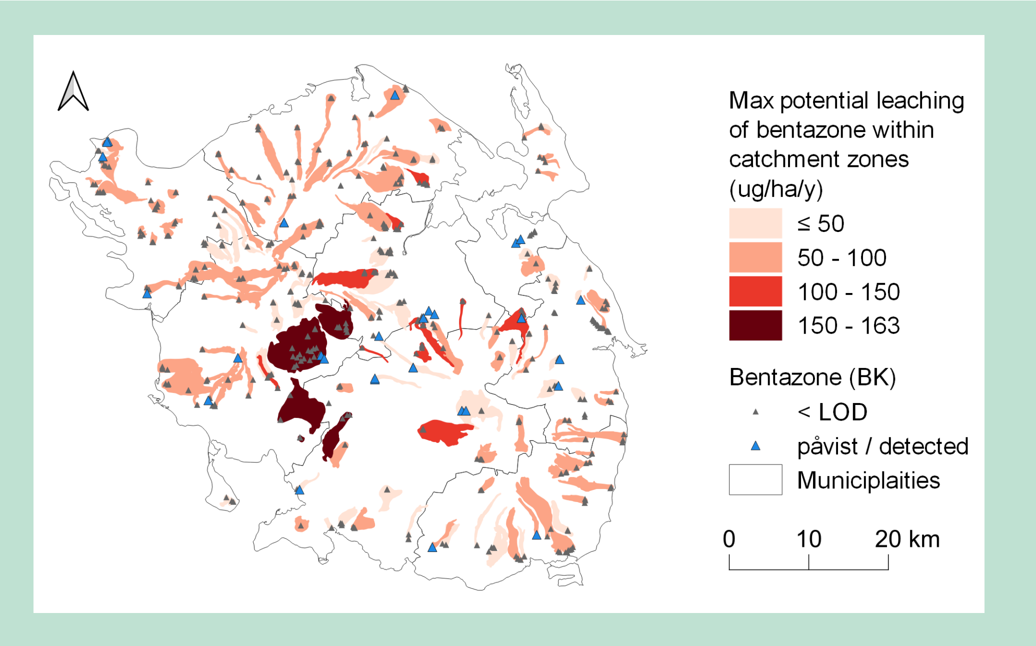

FIGURE 4.27. Maximum leaching within the catchment zones for Bentazone overlaid with the BK wells; note that some wells are in areas with multiple simulated catchment zones or no catchment zone.

It must also be noted that the waterwork catchment areas in Figure 4.27 show the flow paths projected to terrain and it is not necessary that the entire area is a recharge area, from where the pesticides leach to the specific well.

Summary

To summarize, we found that:

1. From the selected pesticides and metabolites, only Bentazone and 1,2,4-Triazole were detected in the groundwater at Fyn. Both Bentazone and 1,2,4-triazole were also found to be leaching to the shallow groundwater under the experimental fields of the Danish Pesticide Leaching Assessment programme (Rosenbom et al, 2021)
2. There is no statistically significant spatial association between the maximum pesticide leaching within 1km of the well and the detected pesticides (or degradation product) in groundwater at the larger scale (Fyn) (based on Figure 4.26).
3. The modelled potential leaching throughout the entire Fyn is most probably going to result in concentrations in groundwater that are below the current detection limits for pesticides.
4. In general, detailed studies at field-scale or catchment scale are necessary to validate produced risk maps with respect to groundwater; there is a need to include process-based understanding for the transport and degradation in the sub-surface.

Factors that were not considered here, but are important when comparing modelled leaching and groundwater contamination:

- The actual recharge zone of the wells – as discussed previously, the 1km buffer was used as the recharge zone of the wells, however it is very possible that for some of them this is an insufficient representation, as the recharge zone could be further way.
- The lag-time – the recharge age of the groundwater and the delay of pesticide transport in the sub-surface are unknown currently, so in such comparison there could be a discrepancy between the represented time-periods (leaching period vs. groundwater age).
- The difference in the units/scales – there is discrepancy between the units, as the leaching is represented in mass per area per year (g/ha/y or the converted µg/ha/y), while the groundwater concentrations are in mass per volume of water (µg/l). The µg is more intuitive, as the values in g were extremely small. We decided against converting the units from g/ha/y to µg/l, as this would introduce additional uncertainties, however a quick-and-dirty conversion is presented in Box 1.
- The uncertainty – the uncertainty in the modelled leaching and the uncertainty in the groundwater measurements were not considered in the comparison, as these were unknown. However, in a more detailed study, those should also be accounted for.

Considering these limitations in the data, methodology, and the current knowledge, it can be concluded that at this time, it is not possible to confirm that the risk-modelling of pesticides exposure to groundwater is useful for decision-making and to inform policy.

More detailed studies at field or catchment scale are required to address the listed limitations. Given the complexity of pesticides fate in the subsurface, it may be more realistic to focus on small-scale risk assessments, where the hydrogeological and hydrogeochemical conditions can be better described.

5. Overall conclusion and perspectives

The original SWAT model (revision 622) was extended with a new module, DrainPST, enabling simulation of the processes of preferential transport of water, sediment and pesticide through soil macropores to tile drains and further to surface waters. The SWAT model extended with DrainPST and the original SWAT were both applied to a small tile drained catchment, Lillebæk, in Denmark. The simulation performance of tile drain flow, streamflow, sediment yield and occurrence of three types of pesticides (Bentazone, Propiconazole, Pirimicarb) by the two models were evaluated and compared.

Both the original SWAT and DrainPST are capable of simulating streamflow and tile drain flow with DrainPST performing slightly better. However, the added macropore module in DrainPST results in a higher drain flow mainly on the expense of surface flow and lateral surface flow compared to SWAT. This again results in an improved simulation of sediment delivery and transport in the stream. Although overall unacceptable based on Nash Sutcliffe Efficiency criteria, DrainPST greatly improves the simulations of pesticide transport, most notably for Bentazone compared to SWAT. The SWAT model extended with DrainPST captures for all three pesticides the amplitude in measured transport, i.e. in spite of failing to correctly simulate the timing of pesticide transport peaks, the model can reproduce similar events.

Pesticide management rotations for the crops in Fyn were developed from 2006-2015 based on the Danish national environmental LOOP monitoring program NOVANA. These pesticide management rotations were adapted to a large SWAT catchment scale model covering the entire Fyn, Denmark. A smaller inversion model was developed only including three main catchments in Fyn in order to reduce computation time. The inversion model was calibrated and validated using daily discharge data for every second year for respectively calibration and validation with acceptable performance. The calibrated parameters were transferred to the forward model covering the entire Fyn. The forward model was validated against daily discharge measurements for the entire study period with acceptable performance.

SWAT calculates combinations on a daily basis of actual weather, soil conditions, topography, and land management including timing of pesticide application. The forward model was used to produce maps of pesticide exposure for the entire Fyn for the pesticides Bentazone, Primicarb and Propiconazol. The simulated average concentrations were low, however the model pointed to specific sub-basins with relatively elevated values. The simulated daily maximum values are two to three orders of magnitude higher than the average values. For Bentazone, several sub-basins had concentrations above 0.5 µg/l and up to 3.4 µg/l. For Pirimicarb, no simulated maximum concentrations were above 0.5 µg/l and in general most of the simulated maximum concentrations were between 0.1 and 0.5 µg/l. For Propiconazol, only two sub-basins experience had concentrations above 0.1 µg/l and no subbassins had concentrations above 0.5 µg/l.

An ecotoxicological evaluation of the simulated streams water concentrations indicate that the maximum levels of pesticides modelled for the MOMAPEST sub-basins, especially Pirimicarb and Propiconazole, may have detrimental effects on aquatic organisms, whereas the mean levels are all very low and not expected to have negative effects.

Scarcity of pesticide measurements in streams on Fyn hampered a proper validation of the modelling results. However, a comparison to all available pesticide measurements in Danish streams indicated that modelling results are in the right order of magnitude for all three test pesticides. Thus, despite the uncertainty surrounding model predictions, the extended SWAT model may be a useful tool for assessing the risk of pesticide exposure of surface waters at landscape level and used e.g. as a guide for setting up strategic monitoring campaigns.

Maps of potential leaching to groundwater were produced by post processing SWAT output at HRU level for the entire catchment as SWAT does not track pesticides in groundwater. The performance of SWAT was evaluated by comparing simulated pesticide leaching to groundwater to pesticide measurements in the dataset prepared annually for the NOVANA program, including the wells from the national groundwater monitoring network (GRUMO and LOOP) and the waterworks' wells used for drinking water purposes.

From the selected pesticides and metabolites, only Bentazone and 1,2,4-triazole were detected in the groundwater at Fyn. There is no statistically significant spatial association between the simulated maximum pesticide leaching within 1km of the well and the detected pesticides (or degradation product) in groundwater at the larger scale (Fyn). Thus, it can be concluded that regarding groundwater, SWAT is currently not useful for decision-making or to inform policy on the risk of pesticides exposure.

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Appendix 1.

Appendix 1.1 Pesticide emission scheme

Crop rotation #	Pesticide	Crop	Year	Month	Day	Dose(g/ha)
1	Propiconazol	vinterkorn	2006	5	11	2.50
1	Propiconazol	vinterkorn	2006	6	5	2.50
1	Pirimicarp	vinterkorn	2006	6	10	0.25
1	Propiconazol	vinterkorn	2006	6	29	2.50
1	Propiconazol	vinterkorn	2007	5	1	2.02
1	Propiconazol	vinterkorn	2007	5	20	2.02
1	Propiconazol	vinterkorn	2007	6	6	2.02
1	Bentazon	vårkorn	2008	5	14	0.00
1	Propiconazol	vårkorn	2008	5	23	4.30
1	Pirimicarp	vårkorn	2008	6	10	3.87
1	Propiconazol	vårkorn	2008	6	10	4.30
1	Propiconazol	vårkorn	2008	6	17	4.30
1	Propiconazol	vinterkorn	2009	4	25	2.60
1	Propiconazol	vinterkorn	2009	5	6	2.60
1	Propiconazol	vinterkorn	2009	6	6	2.60
1	Pirimicarp	vinterkorn	2009	6	10	0.53
1	Pirimicarp	vinterkorn	2009	7	2	0.53
1	Propiconazol	vinterkorn	2010	5	18	1.78
1	Propiconazol	vinterkorn	2010	5	20	1.78
1	Propiconazol	vinterkorn	2010	6	18	1.78
1	Pirimicarp	vinterkorn	2010	7	10	3.50
1	Propiconazol	vinterkorn	2011	4	25	2.31
1	Propiconazol	vinterkorn	2011	5	1	2.31
1	Propiconazol	vinterkorn	2011	5	20	2.31
1	Propiconazol	vinterkorn	2012	4	21	4.68
1	Propiconazol	vinterkorn	2012	5	18	4.68
1	Propiconazol	vinterkorn	2012	6	12	4.68
1	Pirimicarp	vinterkorn	2012	6	28	1.63
1	Bentazon	vårkorn	2013	5	4	4.90
1	Propiconazol	vårkorn	2013	6	5	1.71
1	Pirimicarp	vårkorn	2013	6	11	7.03
1	Propiconazol	vårkorn	2013	6	18	1.71
1	Propiconazol	vinterkorn	2014	4	25	3.22
1	Propiconazol	vinterkorn	2014	5	9	3.22
1	Propiconazol	vinterkorn	2014	5	25	3.22
1	Pirimicarp	vinterkorn	2014	6	17	0.37
1	Propiconazol	vinterkorn	2015	4	10	2.10
1	Propiconazol	vinterkorn	2015	5	2	2.10
1	Propiconazol	vinterkorn	2015	5	25	2.10
1	Pirimicarp	vinterkorn	2015	6	20	0.18

1	Pirimicarp	vinterkorn	2015	7	3	0.18
2	Propiconazol	vårkorn	2007	2	10	1.78
2	Bentazon	vårkorn	2007	5	20	0.00
2	Propiconazol	vårkorn	2007	6	2	1.78
2	Pirimicarp	vårkorn	2007	6	7	0.61
2	Propiconazol	vårkorn	2007	6	20	1.78
2	Bentazon	græs	2008	5	17	1.58
2	Propiconazol	vinterkorn	2010	5	18	1.78
2	Propiconazol	vinterkorn	2010	5	20	1.78
2	Propiconazol	vinterkorn	2010	6	18	1.78
2	Pirimicarp	vinterkorn	2010	7	10	3.50
2	Bentazon	vårkorn	2012	5	3	6.79
2	Bentazon	vårkorn	2012	5	16	6.79
2	Propiconazol	vårkorn	2012	5	20	0.97
2	Pirimicarp	vårkorn	2012	6	10	2.79
2	Propiconazol	vårkorn	2012	6	11	0.97
2	Propiconazol	vårkorn	2012	6	15	0.97
2	Pirimicarp	vårkorn	2012	6	20	2.79
2	Pirimicarp	vårkorn	2012	7	2	2.79
2	Bentazon	græs	2013	5	25	22.52
2	Bentazon	græs	2014	5	20	17.98
2	Propiconazol	vinterkorn	2015	4	10	2.10
2	Propiconazol	vinterkorn	2015	5	2	2.10
2	Propiconazol	vinterkorn	2015	5	25	2.10
2	Pirimicarp	vinterkorn	2015	6	20	0.18
2	Pirimicarp	vinterkorn	2015	7	3	0.18
3	Propiconazol	vinterkorn	2006	5	11	2.50
3	Propiconazol	vinterkorn	2006	6	5	2.50
3	Pirimicarp	vinterkorn	2006	6	10	0.25
3	Propiconazol	vinterkorn	2006	6	29	2.50
3	Propiconazol	vinterkorn	2007	5	1	2.02
3	Propiconazol	vinterkorn	2007	5	20	2.02
3	Propiconazol	vinterkorn	2007	6	6	2.02
3	Propiconazol	vinterkorn	2008	5	8	4.40
3	Propiconazol	vinterkorn	2008	5	27	4.40
3	Propiconazol	vinterkorn	2008	6	8	4.40
3	Propiconazol	vårkorn	2009	5	9	1.39
3	Bentazon	vårkorn	2009	5	12	46.76
3	Propiconazol	vårkorn	2009	5	18	1.39
3	Propiconazol	vårkorn	2009	6	14	1.39
3	Pirimicarp	vårkorn	2009	6	16	4.48
3	Pirimicarp	vårkorn	2009	7	2	4.48
3	Propiconazol	vinterkorn	2011	4	25	2.31
3	Propiconazol	vinterkorn	2011	5	1	2.31
3	Propiconazol	vinterkorn	2011	5	20	2.31
3	Propiconazol	vinterkorn	2012	4	21	4.68

3	Propiconazol	vinterkorn	2012	5	18	4.68
3	Propiconazol	vinterkorn	2012	6	12	4.68
3	Pirimicarp	vinterkorn	2012	6	28	1.63
3	Propiconazol	vinterkorn	2013	5	5	5.32
3	Propiconazol	vinterkorn	2013	5	20	5.32
3	Propiconazol	vinterkorn	2013	6	2	5.32
3	Pirimicarp	vinterkorn	2013	7	7	0.97
3	Bentazon	vårkorn	2014	5	1	2.77
3	Bentazon	vårkorn	2014	5	5	2.77
3	Bentazon	vårkorn	2014	5	25	2.77
3	Propiconazol	vårkorn	2014	5	26	0.25
3	Pirimicarp	vårkorn	2014	6	7	2.77
3	Propiconazol	vårkorn	2014	6	10	0.25
3	Pirimicarp	vårkorn	2014	6	16	2.77
3	Propiconazol	vårkorn	2014	6	16	0.25
4	Propiconazol	vinterkorn	2006	5	11	2.50
4	Propiconazol	vinterkorn	2006	6	5	2.50
4	Pirimicarp	vinterkorn	2006	6	10	0.25
4	Propiconazol	vinterkorn	2006	6	29	2.50
4	Propiconazol	vårkorn	2007	2	10	1.78
4	Bentazon	vårkorn	2007	5	20	0.00
4	Propiconazol	vårkorn	2007	6	2	1.78
4	Pirimicarp	vårkorn	2007	6	7	0.61
4	Propiconazol	vårkorn	2007	6	20	1.78
4	Propiconazol	vårkorn	2010	5	15	1.97
4	Bentazon	vårkorn	2010	5	23	66.32
4	Propiconazol	vårkorn	2010	5	29	1.97
4	Propiconazol	vårkorn	2010	6	15	1.97
4	Pirimicarp	vårkorn	2010	6	22	0.69
4	Propiconazol	vinterkorn	2011	4	25	2.31
4	Propiconazol	vinterkorn	2011	5	1	2.31
4	Propiconazol	vinterkorn	2011	5	20	2.31
4	Bentazon	vårkorn	2012	5	3	6.79
4	Bentazon	vårkorn	2012	5	16	6.79
4	Propiconazol	vårkorn	2012	5	20	0.97
4	Pirimicarp	vårkorn	2012	6	10	2.79
4	Propiconazol	vårkorn	2012	6	11	0.97
4	Propiconazol	vårkorn	2012	6	15	0.97
4	Pirimicarp	vårkorn	2012	6	20	2.79
4	Pirimicarp	vårkorn	2012	7	2	2.79
4	Bentazon	vårkorn	2015	5	15	1.71
4	Propiconazol	vårkorn	2015	5	27	0.41
4	Bentazon	vårkorn	2015	6	5	1.71
4	Pirimicarp	vårkorn	2015	6	16	2.88
4	Propiconazol	vårkorn	2015	6	17	0.41
4	Propiconazol	vårkorn	2015	6	27	0.41

5	Propiconazol	vinterkorn	2006	5	11	2.50
5	Propiconazol	vinterkorn	2006	6	5	2.50
5	Pirimicarp	vinterkorn	2006	6	10	0.25
5	Propiconazol	vinterkorn	2006	6	29	2.50
5	Pirimicarp	roer	2008	5	22	25.57
5	Bentazon	roer	2008	5	22	0.00
5	Pirimicarp	roer	2008	6	25	25.57
5	Bentazon	roer	2008	6	25	0.00
5	Propiconazol	vårkorn	2009	5	9	1.39
5	Bentazon	vårkorn	2009	5	12	46.76
5	Propiconazol	vårkorn	2009	5	18	1.39
5	Propiconazol	vårkorn	2009	6	14	1.39
5	Pirimicarp	vårkorn	2009	6	16	4.48
5	Pirimicarp	vårkorn	2009	7	2	4.48
5	Propiconazol	vinterkorn	2010	5	18	1.78
5	Propiconazol	vinterkorn	2010	5	20	1.78
5	Propiconazol	vinterkorn	2010	6	18	1.78
5	Pirimicarp	vinterkorn	2010	7	10	3.50
5	Propiconazol	vinterkorn	2011	4	25	2.31
5	Propiconazol	vinterkorn	2011	5	1	2.31
5	Propiconazol	vinterkorn	2011	5	20	2.31
5	Bentazon	vårkorn	2014	5	1	2.77
5	Bentazon	vårkorn	2014	5	5	2.77
5	Bentazon	vårkorn	2014	5	25	2.77
5	Propiconazol	vårkorn	2014	5	26	0.25
5	Pirimicarp	vårkorn	2014	6	7	2.77
5	Propiconazol	vårkorn	2014	6	10	0.25
5	Pirimicarp	vårkorn	2014	6	16	2.77
5	Propiconazol	vårkorn	2014	6	16	0.25
5	Propiconazol	vinterkorn	2015	4	10	2.10
5	Propiconazol	vinterkorn	2015	5	2	2.10
5	Propiconazol	vinterkorn	2015	5	25	2.10
5	Pirimicarp	vinterkorn	2015	6	20	0.18
5	Pirimicarp	vinterkorn	2015	7	3	0.18
6	Bentazon	vårkorn	2006	5	15	5.03
6	Bentazon	vårkorn	2006	6	5	5.03
6	Propiconazol	vårkorn	2006	6	6	4.48
6	Propiconazol	vårkorn	2006	6	15	4.48
6	Pirimicarp	vårkorn	2006	6	22	0.22
6	Propiconazol	vårkorn	2006	6	26	4.48
6	Propiconazol	vinterkorn	2007	5	1	2.02
6	Propiconazol	vinterkorn	2007	5	20	2.02
6	Propiconazol	vinterkorn	2007	6	6	2.02
6	Propiconazol	vinterkorn	2008	5	8	4.40
6	Propiconazol	vinterkorn	2008	5	27	4.40
6	Propiconazol	vinterkorn	2008	6	8	4.40

6	Propiconazol	vårkorn	2009	5	9	1.39
6	Bentazon	vårkorn	2009	5	12	46.76
6	Propiconazol	vårkorn	2009	5	18	1.39
6	Propiconazol	vårkorn	2009	6	14	1.39
6	Pirimicarp	vårkorn	2009	6	16	4.48
6	Pirimicarp	vårkorn	2009	7	2	4.48
6	Propiconazol	vårkorn	2011	5	10	1.98
6	Bentazon	vårkorn	2011	5	28	0.85
6	Propiconazol	vårkorn	2011	6	1	1.98
6	Propiconazol	vårkorn	2011	6	8	1.98
6	Pirimicarp	vårkorn	2011	6	16	3.29
6	Propiconazol	vinterkorn	2012	4	21	4.68
6	Propiconazol	vinterkorn	2012	5	18	4.68
6	Propiconazol	vinterkorn	2012	6	12	4.68
6	Pirimicarp	vinterkorn	2012	6	28	1.63
6	Propiconazol	vinterkorn	2013	5	5	5.32
6	Propiconazol	vinterkorn	2013	5	20	5.32
6	Propiconazol	vinterkorn	2013	6	2	5.32
6	Pirimicarp	vinterkorn	2013	7	7	0.97
6	Bentazon	vårkorn	2014	5	1	2.77
6	Bentazon	vårkorn	2014	5	5	2.77
6	Bentazon	vårkorn	2014	5	25	2.77
6	Propiconazol	vårkorn	2014	5	26	0.25
6	Pirimicarp	vårkorn	2014	6	7	2.77
6	Propiconazol	vårkorn	2014	6	10	0.25
6	Pirimicarp	vårkorn	2014	6	16	2.77
6	Propiconazol	vårkorn	2014	6	16	0.25
6	Bentazon	græs	2015	5	1	24.28
7	Propiconazol	vårkorn	2007	2	10	1.78
7	Bentazon	vårkorn	2007	5	20	0.00
7	Propiconazol	vårkorn	2007	6	2	1.78
7	Pirimicarp	vårkorn	2007	6	7	0.61
7	Propiconazol	vårkorn	2007	6	20	1.78
7	Bentazon	vårkorn	2008	5	14	0.00
7	Propiconazol	vårkorn	2008	5	23	4.30
7	Pirimicarp	vårkorn	2008	6	10	3.87
7	Propiconazol	vårkorn	2008	6	10	4.30
7	Propiconazol	vårkorn	2008	6	17	4.30
7	Propiconazol	vinterkorn	2010	5	18	1.78
7	Propiconazol	vinterkorn	2010	5	20	1.78
7	Propiconazol	vinterkorn	2010	6	18	1.78
7	Pirimicarp	vinterkorn	2010	7	10	3.50
7	Bentazon	vårkorn	2012	5	3	6.79
7	Bentazon	vårkorn	2012	5	16	6.79
7	Propiconazol	vårkorn	2012	5	20	0.97
7	Pirimicarp	vårkorn	2012	6	10	2.79

7	Propiconazol	vårkorn	2012	6	11	0.97
7	Propiconazol	vårkorn	2012	6	15	0.97
7	Pirimicarp	vårkorn	2012	6	20	2.79
7	Pirimicarp	vårkorn	2012	7	2	2.79
7	Bentazon	vårkorn	2013	5	4	4.90
7	Propiconazol	vårkorn	2013	6	5	1.71
7	Pirimicarp	vårkorn	2013	6	11	7.03
7	Propiconazol	vårkorn	2013	6	18	1.71
7	Propiconazol	vinterkorn	2015	4	10	2.10
7	Propiconazol	vinterkorn	2015	5	2	2.10
7	Propiconazol	vinterkorn	2015	5	25	2.10
7	Pirimicarp	vinterkorn	2015	6	20	0.18
7	Pirimicarp	vinterkorn	2015	7	3	0.18
8	Bentazon	græs	2006	5	5	17.98
8	Bentazon	græs	2006	6	8	17.98
8	Propiconazol	vårkorn	2007	2	10	1.78
8	Bentazon	vårkorn	2007	5	20	0.00
8	Propiconazol	vårkorn	2007	6	2	1.78
8	Pirimicarp	vårkorn	2007	6	7	0.61
8	Propiconazol	vårkorn	2007	6	20	1.78
8	Propiconazol	vinterkorn	2008	5	8	4.40
8	Propiconazol	vinterkorn	2008	5	27	4.40
8	Propiconazol	vinterkorn	2008	6	8	4.40
8	Propiconazol	vinterkorn	2009	4	25	2.60
8	Propiconazol	vinterkorn	2009	5	6	2.60
8	Propiconazol	vinterkorn	2009	6	6	2.60
8	Pirimicarp	vinterkorn	2009	6	10	0.53
8	Pirimicarp	vinterkorn	2009	7	2	0.53
8	Propiconazol	vårkorn	2010	5	15	1.97
8	Bentazon	vårkorn	2010	5	23	66.32
8	Propiconazol	vårkorn	2010	5	29	1.97
8	Propiconazol	vårkorn	2010	6	15	1.97
8	Pirimicarp	vårkorn	2010	6	22	0.69
8	Bentazon	græs	2011	5	10	13.28
8	Bentazon	vårkorn	2012	5	3	6.79
8	Bentazon	vårkorn	2012	5	16	6.79
8	Propiconazol	vårkorn	2012	5	20	0.97
8	Pirimicarp	vårkorn	2012	6	10	2.79
8	Propiconazol	vårkorn	2012	6	11	0.97
8	Propiconazol	vårkorn	2012	6	15	0.97
8	Pirimicarp	vårkorn	2012	6	20	2.79
8	Pirimicarp	vårkorn	2012	7	2	2.79
8	Propiconazol	vinterkorn	2013	5	5	5.32
8	Propiconazol	vinterkorn	2013	5	20	5.32
8	Propiconazol	vinterkorn	2013	6	2	5.32
8	Pirimicarp	vinterkorn	2013	7	7	0.97

8	Propiconazol	vinterkorn	2014	4	25	3.22
8	Propiconazol	vinterkorn	2014	5	9	3.22
8	Propiconazol	vinterkorn	2014	5	25	3.22
8	Pirimicarp	vinterkorn	2014	6	17	0.37
8	Bentazon	vårkorn	2015	5	15	1.71
8	Propiconazol	vårkorn	2015	5	27	0.41
8	Bentazon	vårkorn	2015	6	5	1.71
8	Pirimicarp	vårkorn	2015	6	16	2.88
8	Propiconazol	vårkorn	2015	6	17	0.41
8	Propiconazol	vårkorn	2015	6	27	0.41
9	Propiconazol	vinterkorn	2007	5	1	2.02
9	Propiconazol	vinterkorn	2007	5	20	2.02
9	Propiconazol	vinterkorn	2007	6	6	2.02
9	Propiconazol	vinterkorn	2008	5	8	4.40
9	Propiconazol	vinterkorn	2008	5	27	4.40
9	Propiconazol	vinterkorn	2008	6	8	4.40
9	Propiconazol	vinterkorn	2009	4	25	2.60
9	Propiconazol	vinterkorn	2009	5	6	2.60
9	Propiconazol	vinterkorn	2009	6	6	2.60
9	Pirimicarp	vinterkorn	2009	6	10	0.53
9	Pirimicarp	vinterkorn	2009	7	2	0.53
9	Propiconazol	vårkorn	2010	5	15	1.97
9	Bentazon	vårkorn	2010	5	23	66.32
9	Propiconazol	vårkorn	2010	5	29	1.97
9	Propiconazol	vårkorn	2010	6	15	1.97
9	Pirimicarp	vårkorn	2010	6	22	0.69
9	Propiconazol	vinterkorn	2012	4	21	4.68
9	Propiconazol	vinterkorn	2012	5	18	4.68
9	Propiconazol	vinterkorn	2012	6	12	4.68
9	Pirimicarp	vinterkorn	2012	6	28	1.63
9	Propiconazol	vinterkorn	2013	5	5	5.32
9	Propiconazol	vinterkorn	2013	5	20	5.32
9	Propiconazol	vinterkorn	2013	6	2	5.32
9	Pirimicarp	vinterkorn	2013	7	7	0.97
9	Propiconazol	vinterkorn	2014	4	25	3.22
9	Propiconazol	vinterkorn	2014	5	9	3.22
9	Propiconazol	vinterkorn	2014	5	25	3.22
9	Pirimicarp	vinterkorn	2014	6	17	0.37
9	Bentazon	vårkorn	2015	5	15	1.71
9	Propiconazol	vårkorn	2015	5	27	0.41
9	Bentazon	vårkorn	2015	6	5	1.71
9	Pirimicarp	vårkorn	2015	6	16	2.88
9	Propiconazol	vårkorn	2015	6	17	0.41
9	Propiconazol	vårkorn	2015	6	27	0.41
10	Bentazon	vårkorn	2006	5	15	5.03
10	Bentazon	vårkorn	2006	6	5	5.03

10	Propiconazol	vårkorn	2006	6	6	4.48
10	Propiconazol	vårkorn	2006	6	15	4.48
10	Pirimicarp	vårkorn	2006	6	22	0.22
10	Propiconazol	vårkorn	2006	6	26	4.48
10	Bentazon	vårkorn	2008	5	14	0.00
10	Propiconazol	vårkorn	2008	5	23	4.30
10	Pirimicarp	vårkorn	2008	6	10	3.87
10	Propiconazol	vårkorn	2008	6	10	4.30
10	Propiconazol	vårkorn	2008	6	17	4.30
10	Propiconazol	vinterkorn	2009	4	25	2.60
10	Propiconazol	vinterkorn	2009	5	6	2.60
10	Propiconazol	vinterkorn	2009	6	6	2.60
10	Pirimicarp	vinterkorn	2009	6	10	0.53
10	Pirimicarp	vinterkorn	2009	7	2	0.53
10	Propiconazol	vinterkorn	2010	5	18	1.78
10	Propiconazol	vinterkorn	2010	5	20	1.78
10	Propiconazol	vinterkorn	2010	6	18	1.78
10	Pirimicarp	vinterkorn	2010	7	10	3.50
10	Propiconazol	vårkorn	2011	5	10	1.98
10	Bentazon	vårkorn	2011	5	28	0.85
10	Propiconazol	vårkorn	2011	6	1	1.98
10	Propiconazol	vårkorn	2011	6	8	1.98
10	Pirimicarp	vårkorn	2011	6	16	3.29
10	Bentazon	vårkorn	2013	5	4	4.90
10	Propiconazol	vårkorn	2013	6	5	1.71
10	Pirimicarp	vårkorn	2013	6	11	7.03
10	Propiconazol	vårkorn	2013	6	18	1.71
10	Propiconazol	vinterkorn	2014	4	25	3.22
10	Propiconazol	vinterkorn	2014	5	9	3.22
10	Propiconazol	vinterkorn	2014	5	25	3.22
10	Pirimicarp	vinterkorn	2014	6	17	0.37
10	Propiconazol	vinterkorn	2015	4	10	2.10
10	Propiconazol	vinterkorn	2015	5	2	2.10
10	Propiconazol	vinterkorn	2015	5	25	2.10
10	Pirimicarp	vinterkorn	2015	6	20	0.18
10	Pirimicarp	vinterkorn	2015	7	3	0.18
11	Bentazon	majs	2006	5	1	23.32
11	Bentazon	majs	2006	5	17	23.32
11	Bentazon	majs	2006	6	1	23.32
11	Bentazon	majs	2007	5	4	72.24
11	Bentazon	majs	2007	5	15	72.24
11	Bentazon	majs	2007	6	4	72.24
11	Bentazon	majs	2008	5	13	44.81
11	Bentazon	majs	2008	5	15	44.81
11	Bentazon	majs	2008	5	26	44.81
11	Propiconazol	vårkorn	2009	5	9	1.39

11	Bentazon	vårkorn	2009	5	12	46.76
11	Propiconazol	vårkorn	2009	5	18	1.39
11	Propiconazol	vårkorn	2009	6	14	1.39
11	Pirimicarp	vårkorn	2009	6	16	4.48
11	Pirimicarp	vårkorn	2009	7	2	4.48
11	Propiconazol	vårkorn	2010	5	15	1.97
11	Bentazon	vårkorn	2010	5	23	66.32
11	Propiconazol	vårkorn	2010	5	29	1.97
11	Propiconazol	vårkorn	2010	6	15	1.97
11	Pirimicarp	vårkorn	2010	6	22	0.69
11	Bentazon	majs	2011	4	28	0.99
11	Bentazon	majs	2011	5	8	0.99
11	Bentazon	majs	2011	6	2	0.99
11	Bentazon	majs	2012	5	17	12.04
11	Bentazon	majs	2012	5	24	12.04
11	Bentazon	majs	2013	5	20	6.65
11	Bentazon	vårkorn	2014	5	1	2.77
11	Bentazon	vårkorn	2014	5	5	2.77
11	Bentazon	vårkorn	2014	5	25	2.77
11	Propiconazol	vårkorn	2014	5	26	0.25
11	Pirimicarp	vårkorn	2014	6	7	2.77
11	Propiconazol	vårkorn	2014	6	10	0.25
11	Pirimicarp	vårkorn	2014	6	16	2.77
11	Propiconazol	vårkorn	2014	6	16	0.25
11	Bentazon	vårkorn	2015	5	15	1.71
11	Propiconazol	vårkorn	2015	5	27	0.41
11	Bentazon	vårkorn	2015	6	5	1.71
11	Pirimicarp	vårkorn	2015	6	16	2.88
11	Propiconazol	vårkorn	2015	6	17	0.41
11	Propiconazol	vårkorn	2015	6	27	0.41
12	Propiconazol	vinterkorn	2006	5	11	2.50
12	Propiconazol	vinterkorn	2006	6	5	2.50
12	Pirimicarp	vinterkorn	2006	6	10	0.25
12	Propiconazol	vinterkorn	2006	6	29	2.50
12	Propiconazol	vinterkorn	2007	5	1	2.02
12	Propiconazol	vinterkorn	2007	5	20	2.02
12	Propiconazol	vinterkorn	2007	6	6	2.02
12	Bentazon	græs	2008	5	17	1.58
12	Propiconazol	vårkorn	2010	5	15	1.97
12	Bentazon	vårkorn	2010	5	23	66.32
12	Propiconazol	vårkorn	2010	5	29	1.97
12	Propiconazol	vårkorn	2010	6	15	1.97
12	Pirimicarp	vårkorn	2010	6	22	0.69
12	Propiconazol	vinterkorn	2011	4	25	2.31
12	Propiconazol	vinterkorn	2011	5	1	2.31
12	Propiconazol	vinterkorn	2011	5	20	2.31

12	Propiconazol	vinterkorn	2012	4	21	4.68
12	Propiconazol	vinterkorn	2012	5	18	4.68
12	Propiconazol	vinterkorn	2012	6	12	4.68
12	Pirimicarp	vinterkorn	2012	6	28	1.63
12	Bentazon	græs	2013	5	25	22.52
12	Bentazon	vårkorn	2015	5	15	1.71
12	Propiconazol	vårkorn	2015	5	27	0.41
12	Bentazon	vårkorn	2015	6	5	1.71
12	Pirimicarp	vårkorn	2015	6	16	2.88
12	Propiconazol	vårkorn	2015	6	17	0.41
12	Propiconazol	vårkorn	2015	6	27	0.41
13	Bentazon	vårkorn	2006	5	15	5.03
13	Bentazon	vårkorn	2006	6	5	5.03
13	Propiconazol	vårkorn	2006	6	6	4.48
13	Propiconazol	vårkorn	2006	6	15	4.48
13	Pirimicarp	vårkorn	2006	6	22	0.22
13	Propiconazol	vårkorn	2006	6	26	4.48
13	Bentazon	majs	2007	5	4	72.24
13	Bentazon	majs	2007	5	15	72.24
13	Bentazon	majs	2007	6	4	72.24
13	Bentazon	majs	2008	5	13	44.81
13	Bentazon	majs	2008	5	15	44.81
13	Bentazon	majs	2008	5	26	44.81
13	Bentazon	majs	2009	5	13	65.76
13	Bentazon	majs	2010	5	23	3.26
13	Bentazon	majs	2010	6	1	3.26
13	Propiconazol	vårkorn	2011	5	10	1.98
13	Bentazon	vårkorn	2011	5	28	0.85
13	Propiconazol	vårkorn	2011	6	1	1.98
13	Propiconazol	vårkorn	2011	6	8	1.98
13	Pirimicarp	vårkorn	2011	6	16	3.29
13	Bentazon	majs	2012	5	17	12.04
13	Bentazon	majs	2012	5	24	12.04
13	Bentazon	majs	2013	5	20	6.65
13	Bentazon	majs	2014	5	20	6.83
13	Bentazon	majs	2014	6	5	6.83
13	Bentazon	majs	2015	5	20	7.18
13	Bentazon	majs	2015	5	21	7.18
14	Bentazon	vårkorn	2006	5	15	5.03
14	Bentazon	vårkorn	2006	6	5	5.03
14	Propiconazol	vårkorn	2006	6	6	4.48
14	Propiconazol	vårkorn	2006	6	15	4.48
14	Pirimicarp	vårkorn	2006	6	22	0.22
14	Propiconazol	vårkorn	2006	6	26	4.48
14	Bentazon	majs	2007	5	4	72.24
14	Bentazon	majs	2007	5	15	72.24

14	Bentazon	majs	2007	6	4	72.24
14	Bentazon	vårkorn	2008	5	14	0.00
14	Propiconazol	vårkorn	2008	5	23	4.30
14	Pirimicarp	vårkorn	2008	6	10	3.87
14	Propiconazol	vårkorn	2008	6	10	4.30
14	Propiconazol	vårkorn	2008	6	17	4.30
14	Propiconazol	vårkorn	2010	5	15	1.97
14	Bentazon	vårkorn	2010	5	23	66.32
14	Propiconazol	vårkorn	2010	5	29	1.97
14	Propiconazol	vårkorn	2010	6	15	1.97
14	Pirimicarp	vårkorn	2010	6	22	0.69
14	Propiconazol	vårkorn	2011	5	10	1.98
14	Bentazon	vårkorn	2011	5	28	0.85
14	Propiconazol	vårkorn	2011	6	1	1.98
14	Propiconazol	vårkorn	2011	6	8	1.98
14	Pirimicarp	vårkorn	2011	6	16	3.29
14	Bentazon	majs	2012	5	17	12.04
14	Bentazon	majs	2012	5	24	12.04
14	Bentazon	vårkorn	2013	5	4	4.90
14	Propiconazol	vårkorn	2013	6	5	1.71
14	Pirimicarp	vårkorn	2013	6	11	7.03
14	Propiconazol	vårkorn	2013	6	18	1.71
14	Bentazon	græs	2014	5	20	17.98
14	Bentazon	vårkorn	2015	5	15	1.71
14	Propiconazol	vårkorn	2015	5	27	0.41
14	Bentazon	vårkorn	2015	6	5	1.71
14	Pirimicarp	vårkorn	2015	6	16	2.88
14	Propiconazol	vårkorn	2015	6	17	0.41
14	Propiconazol	vårkorn	2015	6	27	0.41
15	Bentazon	grønsager	2006	4	15	63.39
15	Bentazon	grønsager	2006	5	31	63.39
15	Bentazon	grønsager	2006	6	15	63.39
15	Bentazon	grønsager	2010	4	29	0.03
15	Bentazon	grønsager	2011	4	25	1.32
15	Bentazon	grønsager	2011	5	5	1.32
15	Bentazon	grønsager	2012	5	3	123.59
15	Bentazon	grønsager	2012	5	20	123.59
15	Bentazon	grønsager	2012	6	6	123.59
15	Bentazon	grønsager	2013	5	19	134.45
15	Bentazon	grønsager	2014	4	8	7.74
15	Bentazon	grønsager	2015	6	23	52.03
frugt/bær	Pirimicarp	frugt/bær	2006	5	12	31.15
frugt/bær	Pirimicarp	frugt/bær	2006	5	31	31.15
frugt/bær	Pirimicarp	frugt/bær	2007	5	12	36.99
frugt/bær	Pirimicarp	frugt/bær	2007	5	20	36.99
frugt/bær	Pirimicarp	frugt/bær	2008	5	7	100.21

frugt/bær	Pirimicarp	frugt/bær	2008	5	15	100.21
frugt/bær	Pirimicarp	frugt/bær	2008	6	5	100.21
frugt/bær	Pirimicarp	frugt/bær	2009	7	27	71.11
frugt/bær	Pirimicarp	frugt/bær	2011	4	20	91.01
frugt/bær	Pirimicarp	frugt/bær	2013	5	10	92.93
frugt/bær	Pirimicarp	frugt/bær	2013	6	6	92.93
frugt/bær	Pirimicarp	frugt/bær	2014	4	25	31.59
frugt/bær	Pirimicarp	frugt/bær	2015	8	16	9.35
grøntsager	Pirimicarp	grønsager	2006	4	5	31.76
grøntsager	Pirimicarp	grønsager	2006	5	10	31.76
grøntsager	Pirimicarp	grønsager	2007	6	10	26.61
grøntsager	Pirimicarp	grønsager	2008	6	9	13.75
grøntsager	Pirimicarp	grønsager	2009	6	22	40.14
grøntsager	Pirimicarp	grønsager	2010	6	10	178.97
grøntsager	Pirimicarp	grønsager	2012	7	2	42.85
grøntsager	Pirimicarp	grønsager	2015	7	14	51.55

Appendix 2.

Appendix 2.1 Water balance Inversion model (calibration)

```
SWAT Dec 23 2016    VER 2016/Rev 664

General Input/Output section (file.cio):
5/23/2019 12:00:00 AM ARCGIS-SWAT interface AV

     AVE ANNUAL BASIN VALUES

          PRECIP =    796.8 MM
          SNOW FALL =   39.60 MM
          SNOW MELT =    39.42 MM
          SUBLIMATION =     0.18 MM
          SURFACE RUNOFF Q =    43.65 MM
          LATERAL SOIL Q =    7.64 MM
          TILE Q =    95.85 MM
          GROUNDWATER (SHAL AQ) Q =    74.98 MM
          GROUNDWATER (DEEP AQ) Q =    55.36 MM
          REVAP (SHAL AQ => SOIL/PLANTS) =   32.51 MM
          DEEP AQ RECHARGE =     0.00 MM
          TOTAL AQ RECHARGE =  161.03 MM
          TOTAL WATER YLD =   277.48 MM
          PERCOLATION OUT OF SOIL =  160.43 MM
          ET =    489.1 MM
          PET =    617.9MM
          TRANSMISSION LOSSES =     0.00 MM
          SEPTIC INFLOW =       0.00 MM
          TOTAL SEDIMENT LOADING =      0.25 T/HA
          TILE FROM IMPOUNDED WATER =     0.000 (MM)
          EVAPORATION FROM IMPOUNDED WATER =     0.000 (MM)
          SEEPAGE INTO SOIL FROM IMPOUNDED WATER =    0.000 (MM)
          OVERFLOW FROM IMPOUNDED WATER =    0.000 (MM)
```

Appendix 3.

Appendix 3.1 Water balance Inversion model (validation)

```
SWAT Dec 23 2016    VER 2016/Rev 664

General Input/Output section (file.cio):
5/23/2019 12:00:00 AM ARCGIS-SWAT interface AV

     AVE ANNUAL BASIN VALUES

          PRECIP =    814.5 MM
          SNOW FALL =   41.92 MM
          SNOW MELT =    41.72 MM
          SUBLIMATION =     0.20 MM
          SURFACE RUNOFF Q =    46.70 MM
          LATERAL SOIL Q =    8.01 MM
          TILE Q =   101.07 MM
          GROUNDWATER (SHAL AQ) Q =    80.44 MM
          GROUNDWATER (DEEP AQ) Q =    58.29 MM
          REVAP (SHAL AQ => SOIL/PLANTS) =   31.65 MM
          DEEP AQ RECHARGE =     0.00 MM
          TOTAL AQ RECHARGE =  169.61 MM
          TOTAL WATER YLD =   294.53 MM
          PERCOLATION OUT OF SOIL =  170.57 MM
          ET =    488.2 MM
          PET =    614.9MM
          TRANSMISSION LOSSES =     0.00 MM
          SEPTIC INFLOW =       0.00 MM
          TOTAL SEDIMENT LOADING =      0.29 T/HA
          TILE FROM IMPOUNDED WATER =     0.000 (MM)
          EVAPORATION FROM IMPOUNDED WATER =     0.000 (MM)
          SEEPAGE INTO SOIL FROM IMPOUNDED WATER =    0.000 (MM)
          OVERFLOW FROM IMPOUNDED WATER =    0.000 (MM)
```

Appendix 4.

Appendix 4.1 Water, nutrient, pesticide balance Forward model

```
SWAT Dec 23 2016    VER 2016/Rev 664

General Input/Output section (file.cio):
11/11/2019 12:00:00 AM ARCGIS-SWAT interface AV

     AVE ANNUAL BASIN VALUES

          PRECIP =    814.5 MM
          SNOW FALL =   40.83 MM
          SNOW MELT =    42.00 MM
          SUBLIMATION =     0.23 MM
          SURFACE RUNOFF Q =    41.30 MM
          LATERAL SOIL Q =    7.17 MM
          TILE Q =   184.87 MM
          GROUNDWATER (SHAL AQ) Q =    50.48 MM
          GROUNDWATER (DEEP AQ) Q =    18.11 MM
          REVAP (SHAL AQ => SOIL/PLANTS) =   15.49 MM
          DEEP AQ RECHARGE =     0.00 MM
          TOTAL AQ RECHARGE =   83.73 MM
          TOTAL WATER YLD =   301.93 MM
          PERCOLATION OUT OF SOIL =   86.51 MM
          ET =    495.7 MM
          PET =    626.3MM
          TRANSMISSION LOSSES =     0.00 MM
          SEPTIC INFLOW =       0.00 MM
          TOTAL SEDIMENT LOADING =      0.45 T/HA
          TILE FROM IMPOUNDED WATER =     0.000 (MM)
          EVAPORATION FROM IMPOUNDED WATER =     0.000 (MM)
          SEEPAGE INTO SOIL FROM IMPOUNDED WATER =    0.000 (MM)
          OVERFLOW FROM IMPOUNDED WATER =    0.000 (MM)
```

```
General Input/Output section (file.cio):
11/11/2019 12:00:00 AM ARCGIS-SWAT interface AV

          AVE ANNUAL BASIN VALUES


          NUTRIENTS
               ORGANIC N =      2.117 (KG/HA)
               ORGANIC P =      0.309 (KG/HA)
               NO3 YIELD (SQ) =      0.129 (KG/HA)
               NO3 YIELD (LAT) =     0.109 (KG/HA)
               NO3 YIELD (TILE) =    12.781 (KG/HA)
               SOLP YIELD (TILE) =     0.123(KG/HA)
               SOLP YIELD (SURF INLET RISER) =     0.000 (KG/HA)
               SOL P YIELD =     0.019 (KG/HA)
               NO3 LEACHED =      0.928 (KG/HA)
               P LEACHED =      0.033 (KG/HA)
               N UPTAKE =    95.682 (KG/HA)
               P UPTAKE =   26.734 (KG/HA)
               NO3 YIELD (GWQ) =      0.003 (KG/HA)
               ACTIVE TO SOLUTION P FLOW =          2.568 (KG/HA)
               ACTIVE TO STABLE P FLOW =          2.175 (KG/HA)
               N FERTILIZER APPLIED =   115.985 (KG/HA)
               P FERTILIZER APPLIED =    16.415 (KG/HA)
               N FIXATION =      0.000 (KG/HA)
               DENITRIFICATION =    46.838 (KG/HA)
               HUMUS MIN ON ACTIVE ORG N =      6.921 (KG/HA)
               ACTIVE TO STABLE ORG N =    10.138 (KG/HA)
               HUMUS MIN ON ACTIVE ORG P =    1.273 (KG/HA)
               MIN FROM FRESH ORG N =   51.331 (KG/HA)
               MIN FROM FRESH ORG P =   18.093 (KG/HA)
               NO3 IN RAINFALL =     3.244 (KG/HA)
               INITIAL NO3 IN SOIL =      67.951 (KG/HA)
               FINAL NO3 IN SOIL =         4.312 (KG/HA)
               INITIAL ORG N IN SOIL =   11943.958 (KG/HA)
               FINAL ORG N IN SOIL =     12208.704 (KG/HA)
               INITIAL MIN P IN SOIL =    2989.115 (KG/HA)
               FINAL MIN P IN SOIL =      3056.420 (KG/HA)
               INITIAL ORG P IN SOIL =    1463.130 (KG/HA)
               FINAL ORG P IN SOIL =    1582.211 (KG/HA)
               NO3 IN FERT =    63.092 (KG/HA)
               AMMONIA IN FERT =    34.238 (KG/HA)
               ORG N IN FERT =    18.668 (KG/HA)
               MINERAL P IN FERT =    12.519 (KG/HA)
               ORG P IN FERT =     3.897 (KG/HA)
               N REMOVED IN YIELD =    39.618 (KG/HA)
               P REMOVED IN YIELD =     6.008 (KG/HA)
               AMMONIA VOLATILIZATION =     5.705 (KG/HA)
               AMMONIA NITRIFICATION =     32.535 (KG/HA)
               NO3 EVAP-LAYER 2 TO 1 =   13.582
```

```
AVERAGE ANNUAL PESTICIDE SUMMARY DATA, PESTICIDE #234:          Pirimo
                   APPLIED =       1495.2070 mg/ha
                   DECAYED =       2818.2292 mg/ha
                   IN SURFACE RUNOFF ENTERING STREAM (DISSOLVED) =         6.4493 mg/ha
                   IN SURFACE RUNOFF ENTERING STREAM (SORBED) =         0.6100 mg/ha
                   LEACHED OUT OF SOIL PROFILE =         0.0064 mg/ha
                   IN LATERAL FLOW ENTERING STREAM =         0.7159 mg/ha

                   FINAL AMOUNT OF PESTICIDE ON PLANT =         0.3300 mg/ha
                   FINAL AMOUNT OF PESTICIDE IN GROUND =       441.3302 mg/ha

AVERAGE ANNUAL PESTICIDE SUMMARY DATA, PESTICIDE # 31:         Basagra
                   APPLIED =       5708.2373 mg/ha
                   DECAYED =      12585.9668 mg/ha
                   IN SURFACE RUNOFF ENTERING STREAM (DISSOLVED) =         2.3967 mg/ha
                   IN SURFACE RUNOFF ENTERING STREAM (SORBED) =         0.0696 mg/ha
                   LEACHED OUT OF SOIL PROFILE =         0.0236 mg/ha
                   IN LATERAL FLOW ENTERING STREAM =         2.2119 mg/ha

                   FINAL AMOUNT OF PESTICIDE ON PLANT =         0.0532 mg/ha
                   FINAL AMOUNT OF PESTICIDE IN GROUND =        94.7024 mg/ha

AVERAGE ANNUAL PESTICIDE SUMMARY DATA, PESTICIDE #216:             Til
                   APPLIED =       2516.8542 mg/ha
                   DECAYED =       4618.8154 mg/ha
                   IN SURFACE RUNOFF ENTERING STREAM (DISSOLVED) =         5.3062 mg/ha
                   IN SURFACE RUNOFF ENTERING STREAM (SORBED) =         0.4389 mg/ha
                   LEACHED OUT OF SOIL PROFILE =         0.0022 mg/ha
                   IN LATERAL FLOW ENTERING STREAM =         0.3039 mg/ha

                   FINAL AMOUNT OF PESTICIDE ON PLANT =         0.0000 mg/ha
                   FINAL AMOUNT OF PESTICIDE IN GROUND =       590.8820 mg/ha
```

Appendix 5.

Appendix 5.1 Time-series of pesticides in groundwater

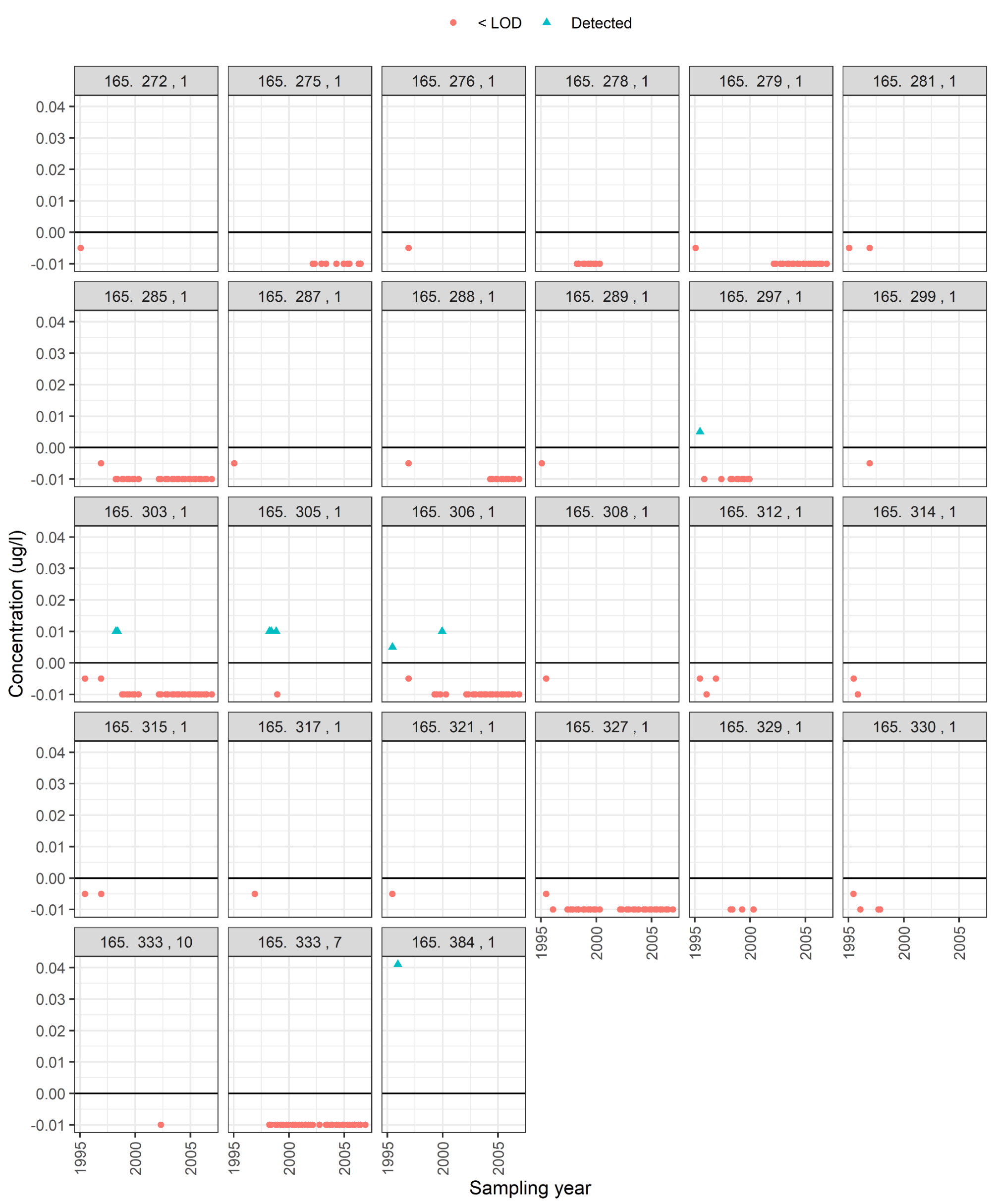

FIGURE 1. Time-series of Bentazone (µg/l) for the LOOP wells (label: DGUNR , INDTNR); below limit of detection (< LOD) are displayed with negative values (red); detections are with blue triangles.

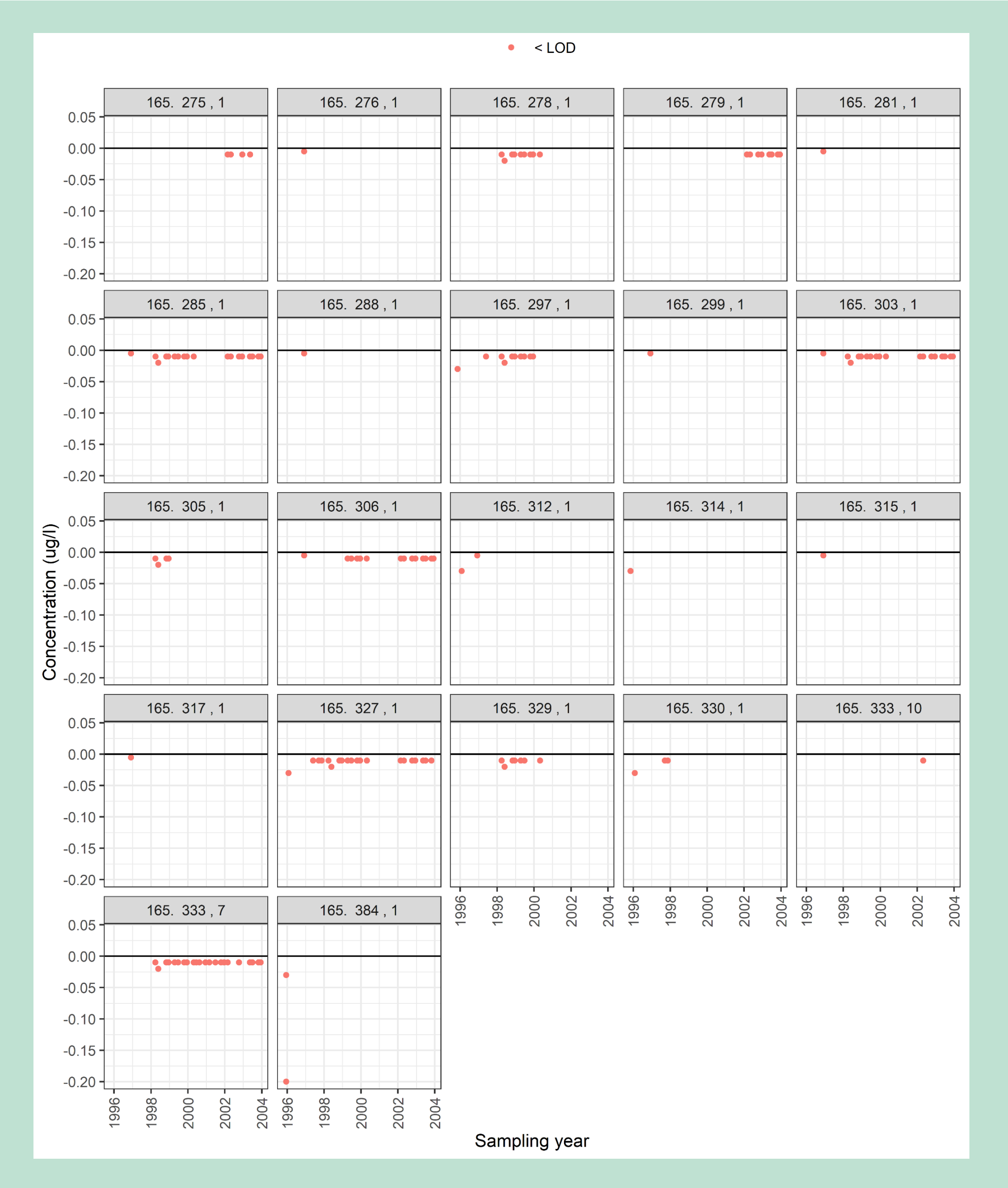

FIGURE 2. Time-series of Propiconazole (µg/l) for the LOOP wells (label: DGUNR, INDTNR); below limit of detection (< LOD) are displayed with negative values; no detections of Propiconazole in the period with analyses.

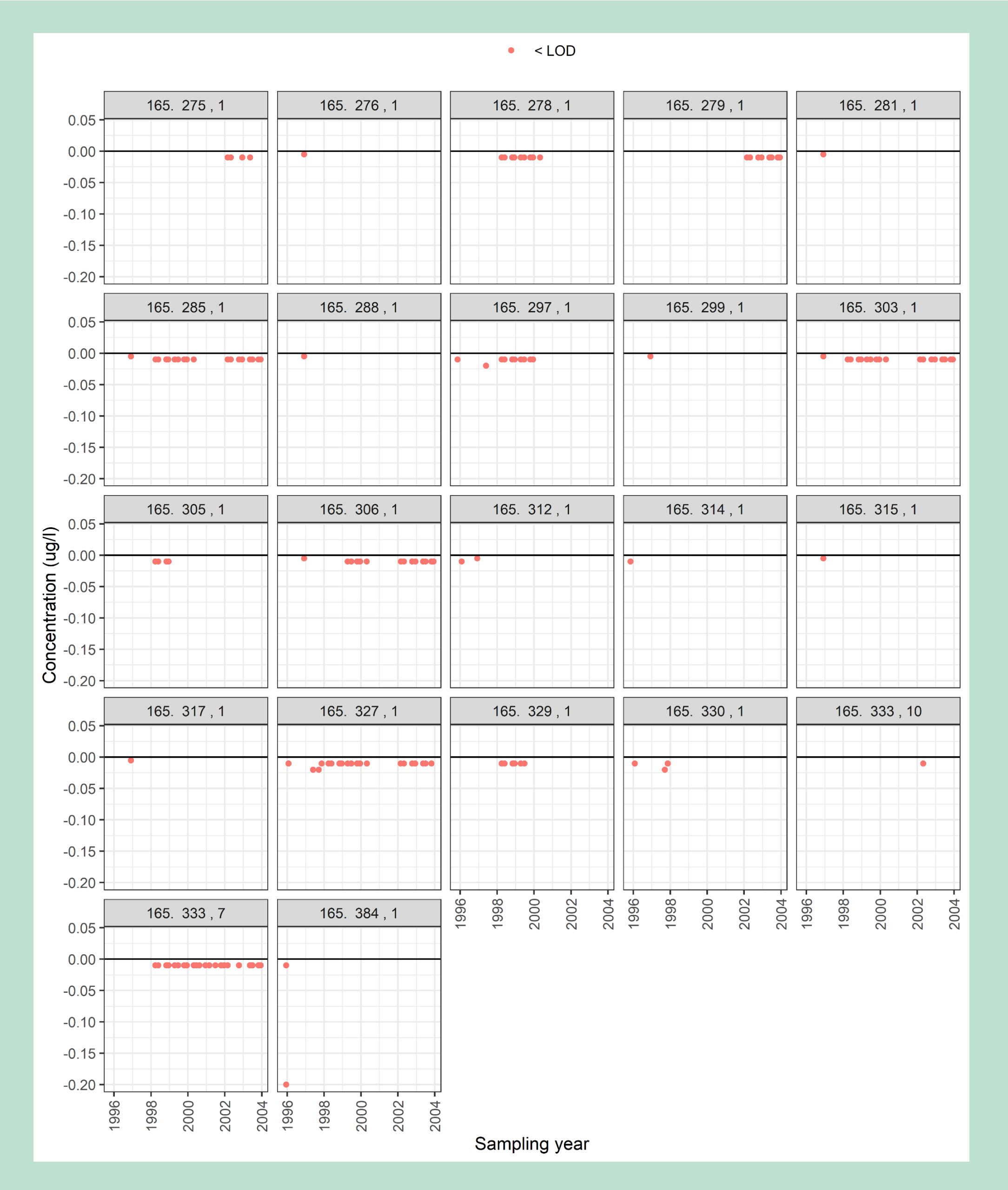

FIGURE 3. Time-series of Pirimicarb (µg/l) for the LOOP wells (label: DGUNR , INDTNR); below limit of detection (< LOD) are displayed with negative values; no detections of Pirimicarb in the period with analyses.

FIGURE 4. Bentazone time-series in GRUMO wells with at least one detection of the pesticides or metab-olites from Table 4.9 (note that DGU no. 128.155, 146.2551, 164.1484 have no detections of Bentazone, but are included because have detection(s) of the other substances); below limit of detection (< LOD) are displayed with negative values (red); detections are with blue triangles.

FIGURE 5. 1,2,4-triazole time-series in GRUMO wells with at least one detection of the pesticides or metabolites from Table 4.9; Note that only the DGU no. 128.155, 146.2551, 164.1483, 164.1484 have detected 1,2,4-triazolee, the rest are included because they had detection(s) of the other substances; below limit of detection (< LOD) are displayed with negative values (red); detections are with blue triangles.

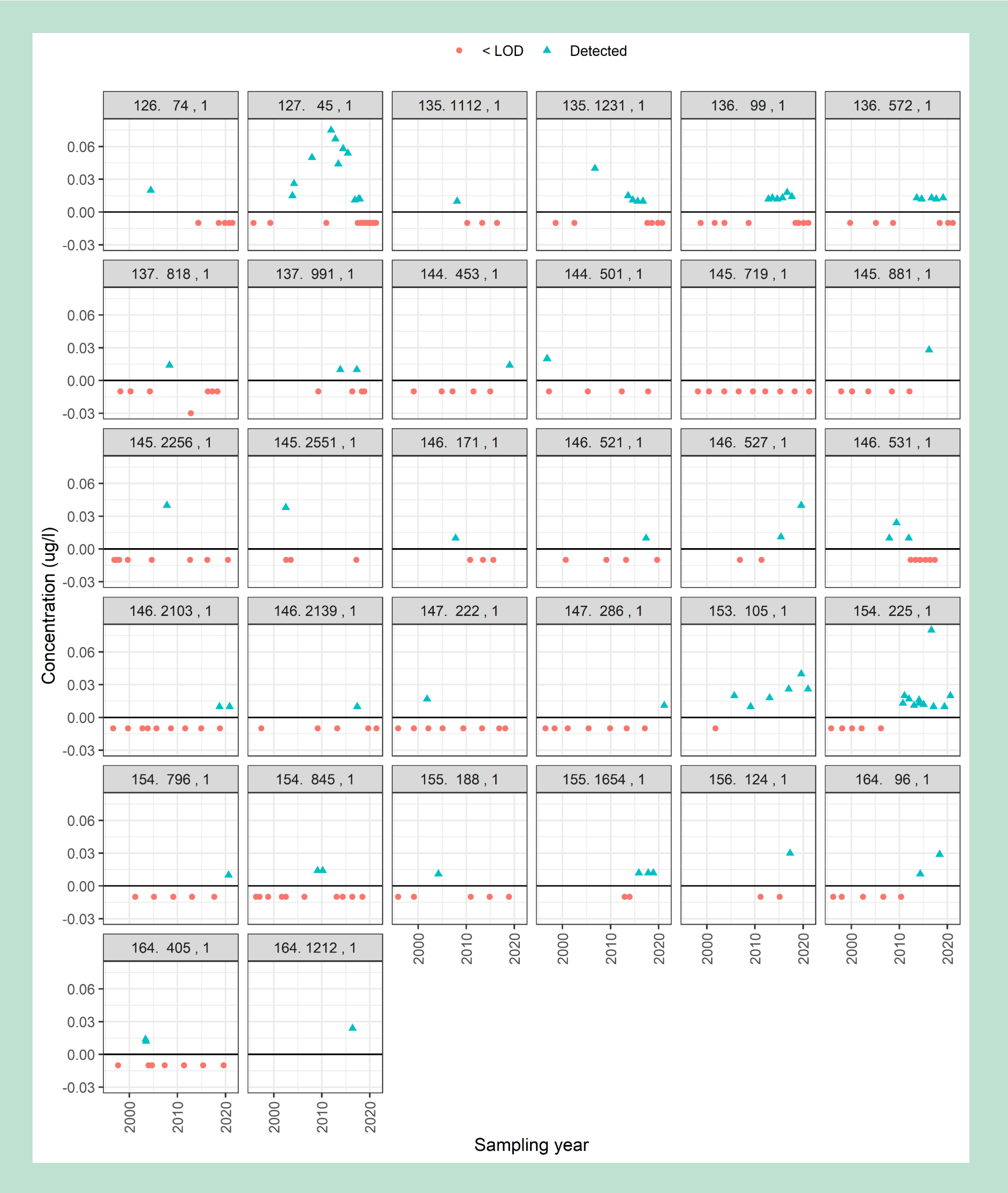

FIGURE 6. Bentazone time-series in BK wells with at least one detection of the pesticides or metabolites from Table 4.9 (note: DGU no. 145.719 has no detections of Bentazone, but is in-cluded be-cause it has detections of other substance(s)); below limit of detection (< LOD) are displayed with negative values (red); detections are with blue triangles.

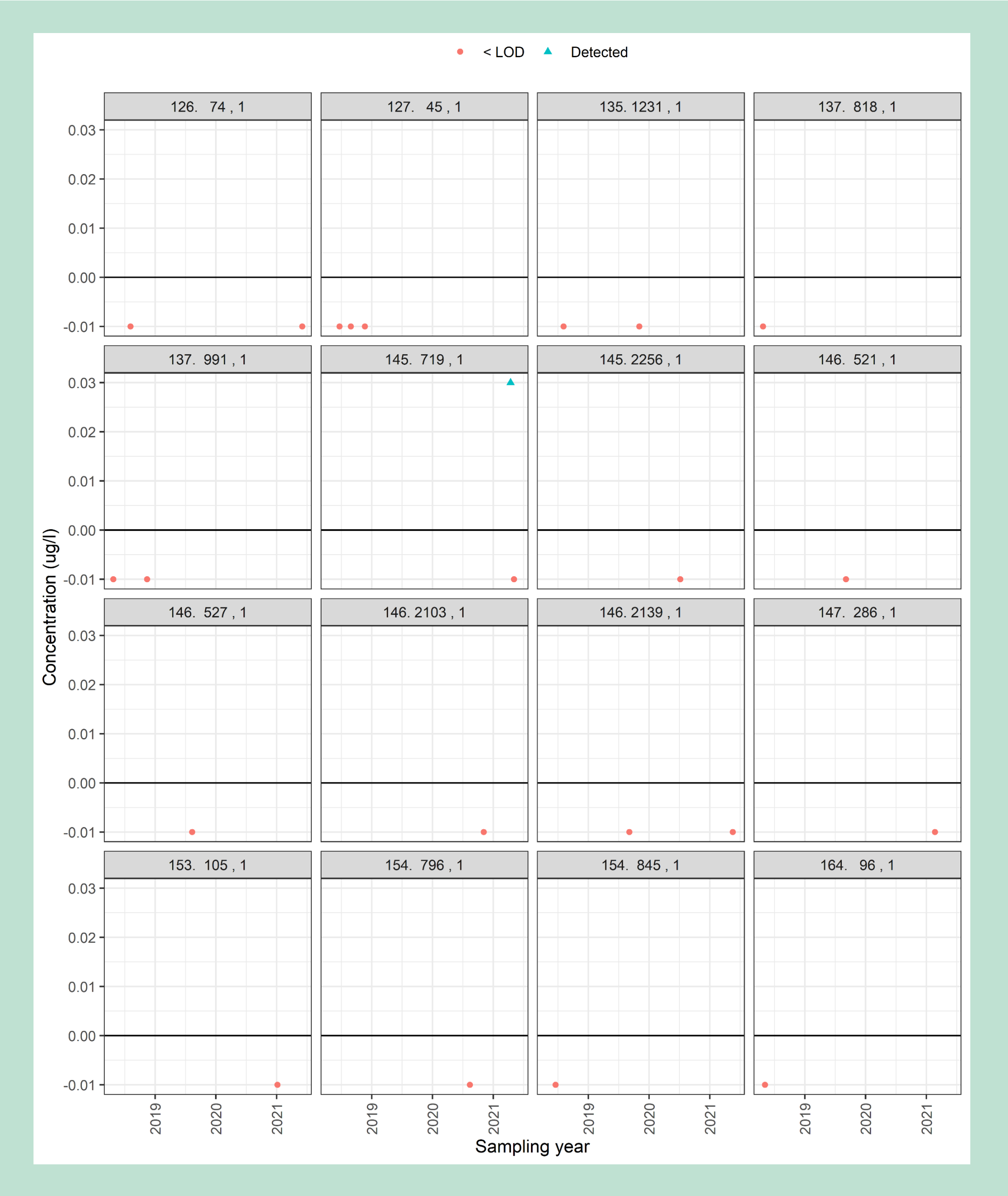

FIGURE 7. 1,2,4-triazole time-series in BK wells with at least one detection of the pesticides or metabo-lites from Table 4.9 (note: only DGU no. 145.719 has a detection for 1,2,4-triazole, the rest of the wells had detection for Bentazone); below limit of detection (< LOD) are dis-played with negative values (red); detections are with blue triangles.

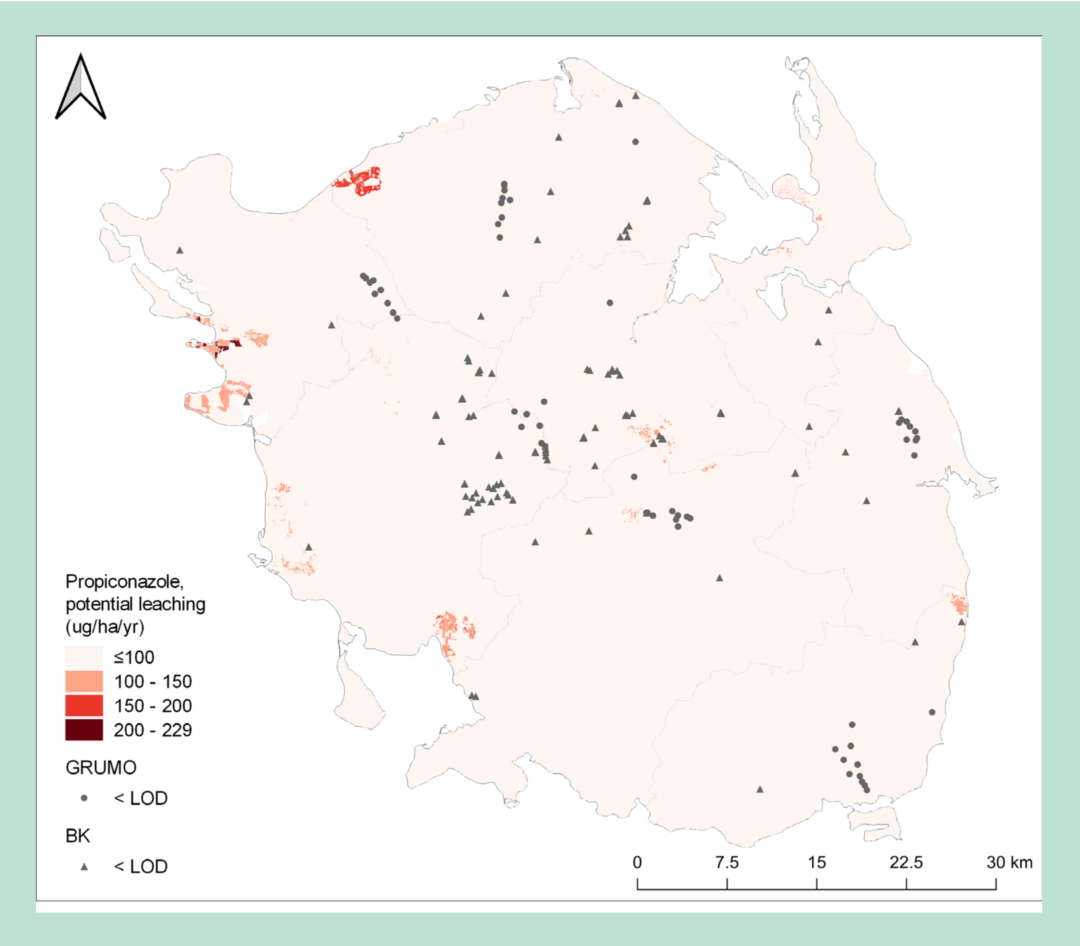

FIGURE 8. Propiconazole measurements in wells from the BK and GRUMO networks overlaying the modelled potential leaching; with grey are shown the wells where the measurements were below the limit of detection (LOD); there were no detections.

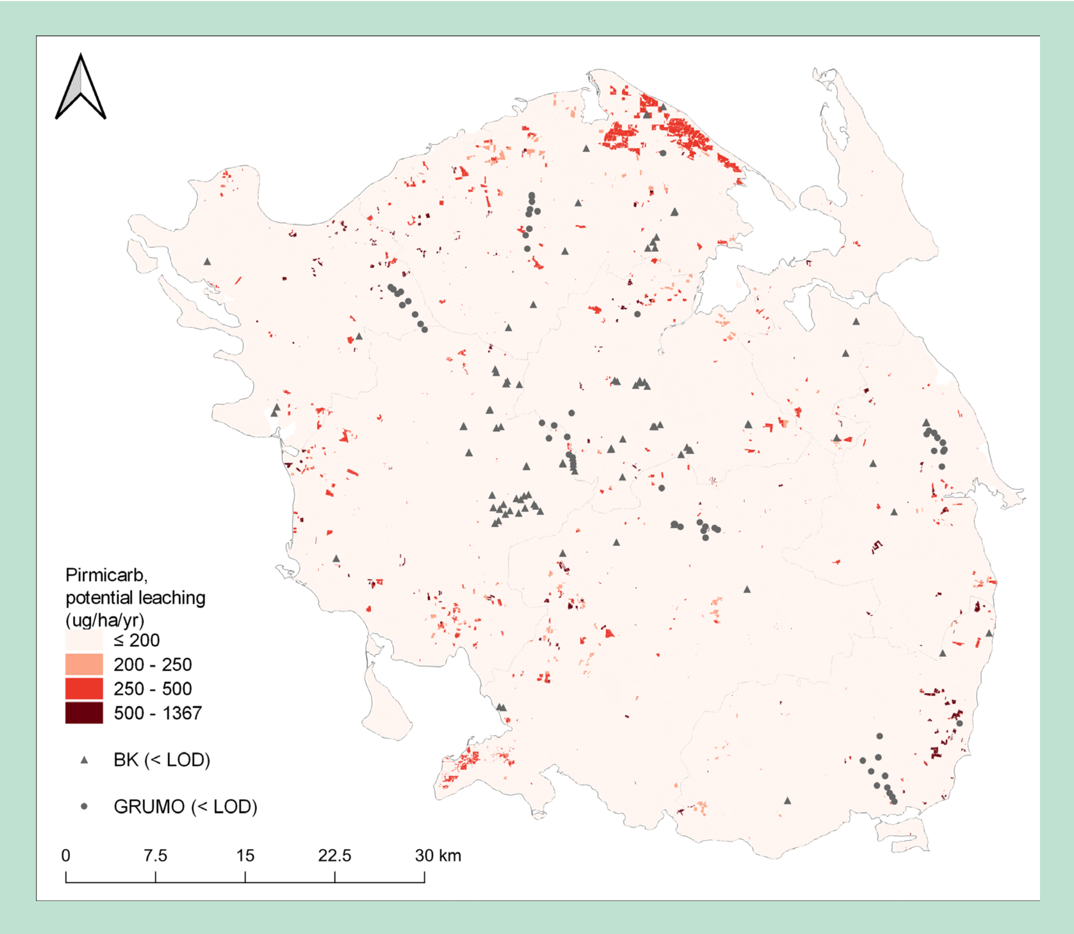

FIGURE 9. Pirimicarb measurements in wells from the BK and GRUMO networks overlaying the modelled potential leaching; with grey are shown the wells where the measurements were below the limit of detection (LOD); there were no detections

Modelling and mapping pesticide exposure risk at the catchment scale - MOMAPEST

A quantitative description of the fate of pesticides in the aquatic environments is very complex. Models are needed to give realistic evaluations of pesticide exposure of streams and groundwater at the landscape level. Complex, fully distributed models with great demands on input data have been tested in Denmark to describe transport of pesticides in streams in Denmark without satisfactory results. The project tested the ability of the semi-distributed SWAT model to quantify and visualize pesticide exposure of groundwater and surface water from small scale to landscape scale. SWAT is a freely available, open-source eco-hydrological catchment model that flexibly can be adapted to the available input data. A new module for SWAT describing the transport of dissolved and particulate bound pesticides via macro-pores to tile drains was developed. The model was used to produce maps of pesticide exposure for the island of Fyn subdivided into 102 sub-basins for the pesticides Bentazone, Primicarb and Propiconazol. Scarcity of local pesticide measurements hampered a proper validation of the modelling results. However, a comparison to all available pesticide measurements in Danish streams indicated that modelling results are in the right order of magnitude for all three test pesticides. Thus, despite the uncertainty surrounding model predictions, the SWAT model may be a useful tool for assessing the risk of pesticide exposure of surface waters at landscape level. Regarding groundwater, the project concluded that SWAT at its current development stage is not useful for decision-making or to inform policy on the risk of pesticides exposure.

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