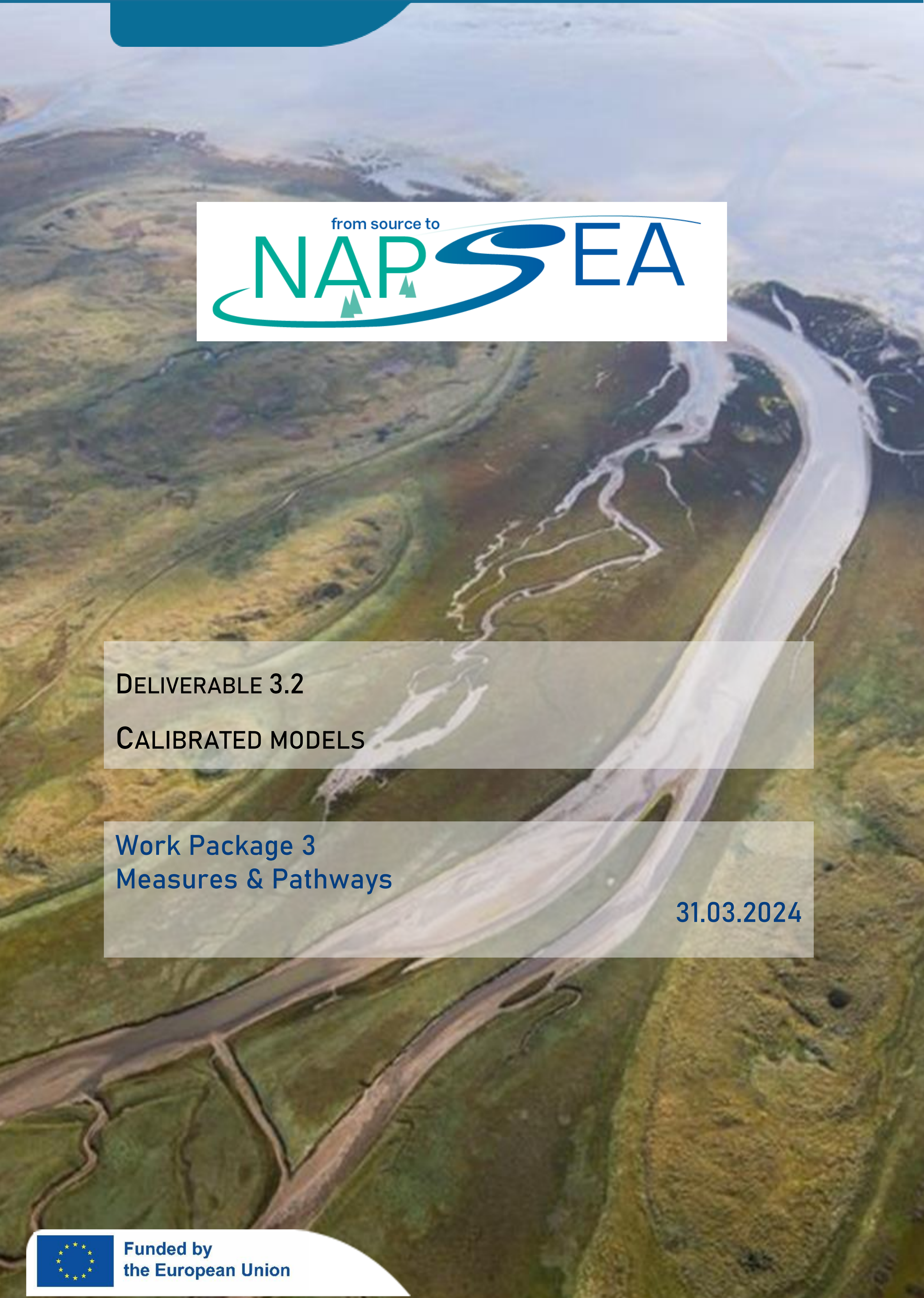

from source to NAPSEA

Deliverable 3.2

Calibrated models

Work Package 3
Measures & Pathways

31.03.2024

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Project Officer	Christel Millet
Abstract	Calibrated and validated models in demonstrator basins Rhine and Elbe, selected sub-catchments within the basins and for the Hunze catchments are presented that capture today's concentrations and exports of nitrogen and phosphorous.
Keywords	Elbe, Rhine, Hunze, mQM, CnANDY, hydrological model, water quality, Nitrogen, Phosphorus, diffuse source, point source, mitigation measure.

Contents

1. Executive summary

D3.2 reports on the implementation of the mQM model which addresses nitrogen fluxes and concentrations, and the CnANDY model, which focuses on phosphorous fluxes and concentrations. These implementations are applied to the Rhine and Elbe rivers, their selected sub-catchments and the Dutch Hunze catchments. Today`s water quality and quantity conditions serve as a foundation for the model calibration. The optimized model parameters obtained through this calibration process will be used for the upcoming tasks of scenario implementation and quantification of efficiencies. This report explains the model structure, calibration procedure, the model performance and summarizes the main modelling results.

2. Methods

2.1 mQM model description and calibration

Model description

The multiscale water quality model mQM (Nguyent et al. 2022) is a spatially lumped model for Nitrogen (N) input (soil N surplus), transport and fate considering the catchment as a single entity. The model aims at a parsimonious representation of N-cycling and legacies in the near-surface soil zone and the subsurface compartments of a given catchment with annual time step. The conceptual biogeochemical model consists of two major compartments: a soil zone and a subsurface zone where transformation processes such as denitrification occur. The subsurface zone provides an integrated representation of both the unsaturated and saturated (groundwater) zone. Transport through the subsurface is based on the principle of water travel time and by that accounts for the sometimes long time lags between N inputs to the soils and N outputs to the river network (Ehrhardt et al. 2021). In addition, an in-stream compartment is accounted for to allow for the representation of transport in the stream network and uptake reactions taking place therein.

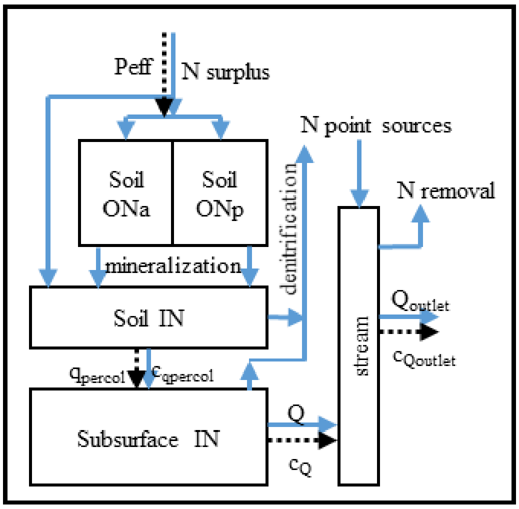

Figure 1. mQM model scheme following Ngyen et al. (2022). ON is (active (a) or passive (p) organic nitrogen, IN is mobile inorganic nitrogen.

Model calibration

For this deliverable D3.2, the model is applied to the case-studies the Elbe, Rhine, and the Hunze basins and their sub-catchments within these basins where data availability is good (see deliverable D3.1), meaning that continuous and long time series of discharge and Nitrate-N observations exist. This allows for a robust parameterization of the model. More specifically, the model uses observed annual averaged discharge as an input and the flow-weighted (WRTDS method, Hirsch et al. 2010) annual nitrate-N concentration observed at the catchment outlet as the calibration target. The calibration procedure varies all model parameters in a Monte-Carlo approach and selects the model best capturing the available annual nitrate-N observations as described in Nguyen et al. (2022). As a selection criterion we use the minimum root mean square error (RMSE) between model and observations for each catchment over time. Model output is an annual concentration time series and an individual parameter set of the best-fitting model. We note that the model is calibrated to the observed Nitrate-N concentration as this is the best available parameter for N-export across all catchments (71% of all available catchments in Germany (GER) only provide nitrate-N). By that we do not account for other species of inorganic N (nitrite, ammonia) or organic N. In the German catchments, where dissolved inorganic N and total N (TN) data were available, 92.4% of the dissolved inorganic N was present as nitrate-N. A fraction of 81.4% of the observed TN was present as nitrate-N, which means that on average our analysis misses 18.6% of the exported N loads that are present in other N forms (mainly NH4-N and organic-N). This needs to be considered in the communication of the modelling results. The WFD-targets for surface water are for TN in The Netherlands (NL) (3-year summer average concentrations) and for Nitrate-N (90th percentile within a year) and Ammonia-N (1-year average) in GER. Nitrate-N is however the dominant N-fraction in agricultural drainage and responds most directly to land use changes.

Table. 1: Parameters of mQM used for calibration and their parameter range.

Parameter	**Description**	**Range**	
beta_pc	Protection coefficient [-]	0.00E+00	7.50E-01
beta_toIN	fraction of N surplus to soil IN pool [-]	0.00E+00	0.50E+00
beta_den_soil	rate constant of denitrification in soil [1/timestep]	1.00E-01	1.00E+00
beta_min_oa	rate constants of mineralization of soil active organic N [1/timestep]	5.00E-02	7.50E-01
beta_min_op	rate constants of mineralization of soil passive organic N	6.10E-05	4.50E-04
ka	first parameter of the SAS function [-]	0.00E+00	1.00E+00
b	second parameter of the SAS function [-]	1.00E+00	1.00E+01
half_life	subsurface denitrification [1/timestep]	1.00E-02	3.00E-01
vf	stream uptake velocity [m/d]	1.00E-02	3.00E-01

2.2 CnANDY model description and calibration

Model description

The river-network model CnANDY (Yang et al. 2021) is designed to capture the competition of pelagic and benthic algae for energy (light) and one limiting nutrient (P). The model operates in river networks at high spatial resolution (100 m) and tracks diffuse and point-source inputs of P downstream on the principle of surface water travel time in the river reaches. It is able to model the build-up of algae biomass in dependence of light availability in the water and at the riverbed surface and by that models the apportionment of P inputs into total and dissolved fractions. The model does not account for temporal variability but was built to robustly capture average conditions of P fluxes in each river network. The model also does not account for P absorbed by particles (e.g., by iron(hydr)oxides.

For this deliverable the model is applied to the entire river networks of the Elbe and Rhine basins. The model builds on the spatially differentiated information of wastewater point sources and a land-use dependent diffuse flux (see deliverable D3.1) at average flow conditions. The lack of point-source data in the upstream Swiss part of the Rhine catchment needed additional data not described in D3.1. Here, we used the Swiss report BAFU (2017) that reports on annual average wastewater P-inputs into Swiss rivers. This data was spatially distributed to the input data scale of CnANDY (100 m) by weighing the data with the population density.

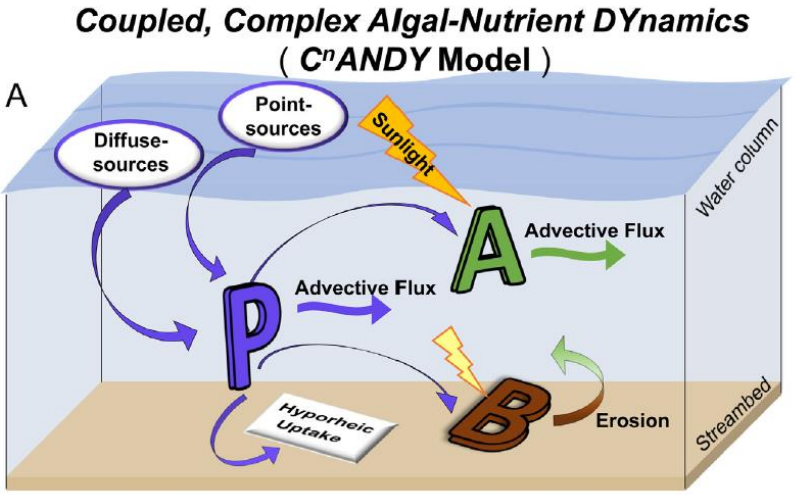

Figure 2. CnANDY model scheme Yang et al. (2021). P is dissolved phosphorous, B is benthic algae, A is pelagic algae.

Model calibration

For the model calibration averaged observational data of total P (TP) are used. More specifically, we selected parameter sets that best match the observed values splitting the data into calibration and validation stations. This calibration was done for Elbe and Rhine basin separately. The CnANDY model was built for the scale of river networks spanning multiple river orders making the application in smaller catchments with few river sections and river orders such as the Hunze critical. However, we also applied the parameterization from the Elbe and Weser basins to the stream sections in the seven sub-basins of the Hunze.

Table 2: Parameters used for the model calibration and their initial values.

Symbol	**Definition**	**Value**
c	Phosphorous to carbon quota of algae [mg P/mg C]	0.02
$v_{f,i}$	Phosphorous uptake velocity at a reach *i* [m/day]	0.17
$m_{L,B}$	Loss rate of benthic algae [day^{-1}]	0.5
$m_{L,A}$	Loss rate of pelagic algae [day^{-1}]	0.6
m_s	Scouring effect rate for benthic algae [day^{-1}]	0.01
m_p	Maximum production rate [day^{-1}]	1
m	Half saturation constant for nutrient-limited production [mg P/m^3]	5
B_K	Maximum concentration for benthic algae under neither light- nor nutrient limitations [mg C/m^2]	15000
I_o	Light intensity at the surface water [*m*mol photons m^{-2}s^{-1}]	300
h	Half saturation constant for light-limited production [*m*mol photons m^{-2}s^{-1}]	25
k	Light attenuation coefficient of algae [m^2/mg C]	0.0003
k_{bg}	Background light attenuation coefficient [m^{-1}]	2.5

3. Model results

3.1 mQM model performance and N simulations

Elbe

The model demonstrates strong performance at both the Elbe outlet and within its sub-catchments, enabling the quantification of future scenarios. The temporal dynamics of both concentrations and loads are accurately represented, and the spatial distribution aligns well with observations. The multi-year trend and the timing of the trend-reversal matches very well with the observations. The year-to-year variations are not fully captured as the observations show more variability compared to the model results. However, these year-to-year variations are likely caused by meteorological variability and are not important for multi-year scenario evaluations. Note that the year-to-year variability of the exported loads is very well captured, because mQM uses measured discharges to calculate loads. This shows that the year-to-year variation in loads depend strongly on the discharge variations.

At the outlet of the Elbe near the estuary the model performed with a RMSE of 0.65 mg/L NO3-N.

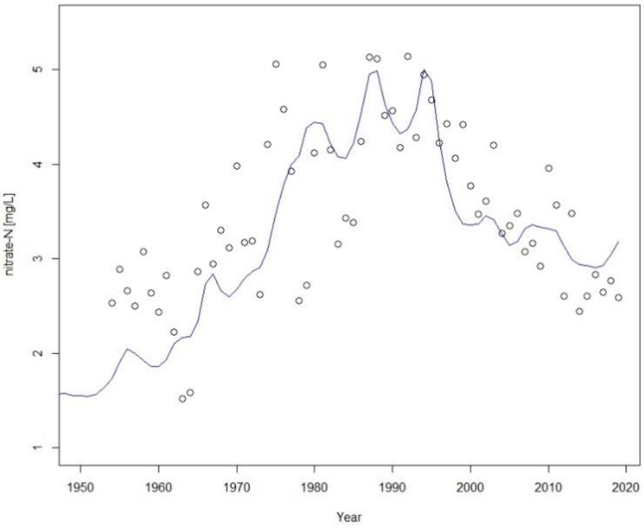

Figure 3. mQM model results for nitrate-N concentrations at the Elbe outlet, station 6340110. A comparison of observations (dots) and optimal modelling results (line).

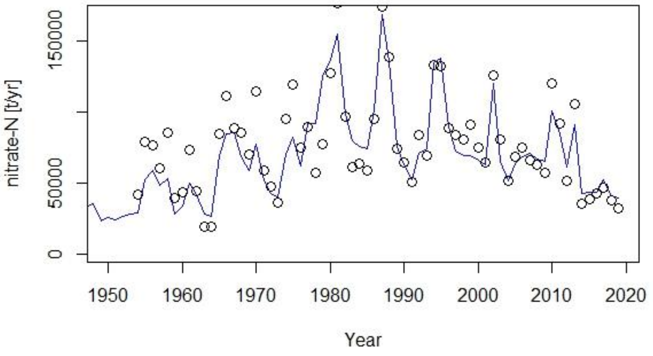

Figure 4. mQM model results for nitrate-N loads at the Elbe outlet, station 6340110. A comparison of observations (dots) and optimal modelling results (line).

Within the 66 modelled sub-catchments of the Elbe the model performed with a median RMSE of 0.51 mg/L.

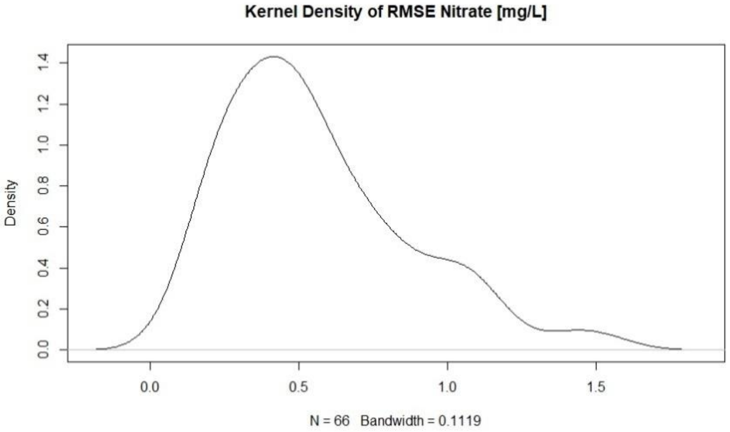

Figure 5. mQM model performance in 66 Elbe sub-catchments. Density distribution of RMSE for the nitrate concentrations.

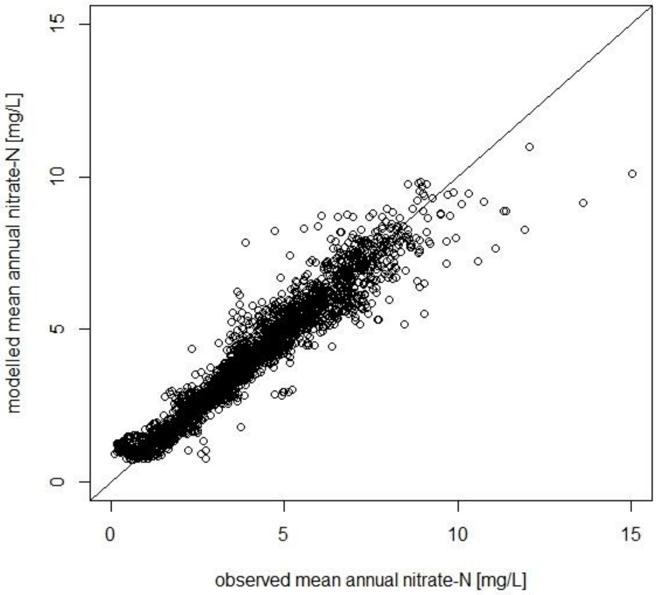

Figure 6. mQM model performance in 66 Elbe sub-catchments. A scatter plot analysis of annual observed versus modelled concentrations (n=25282).

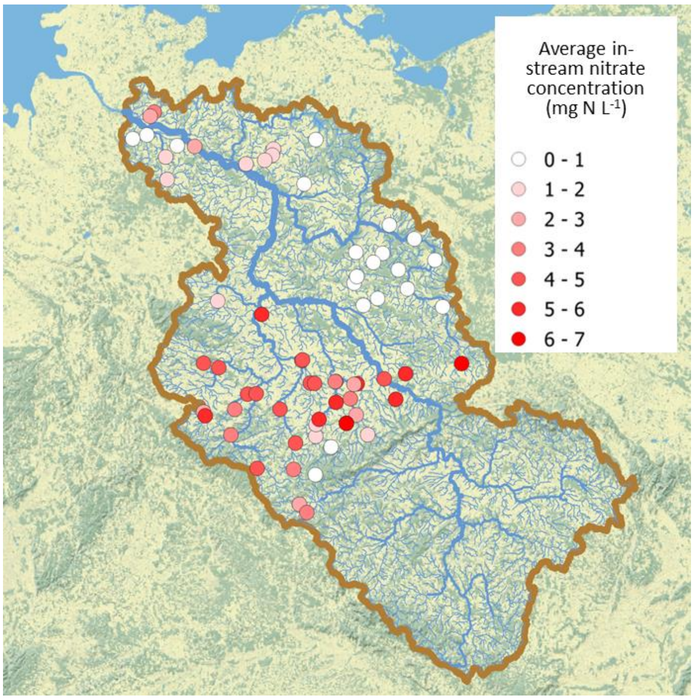

Figure 7. mQM model results in 66 Elbe sub-catchments. Averaged modelled nitrate-N concentrations at the outlet points of the sub-catchments between 2005 and 2019. Total catchment area (brown) and river network (blue) are taken from Hydrosheds (https://www.hydrosheds.org/).

Rhine

The model demonstrates strong performance at both the Rhine outlet and within its sub-catchments, enabling the quantification of future scenarios. The temporal dynamics of both concentration and loads are accurately represented, and the spatial distribution aligns well with observations. The observed year-to-year variations in nitrate concentrations are not captured by the model. Also, the downward trend is underestimated by the model (observations: ~0.2 mg/l per decade; model: ~0.1 mg/l per decade). However, the nitrate-N loads do match very well in temporal variability and trend. This shows that also for the Rhine the year-to-year variations in nitrate-N loads depend heavily on the measured discharges that were used to calculate the loads.

At the Rhine near the German-Dutch border the model performed with a RMSE of 0.33 mg/L nitrate-N.

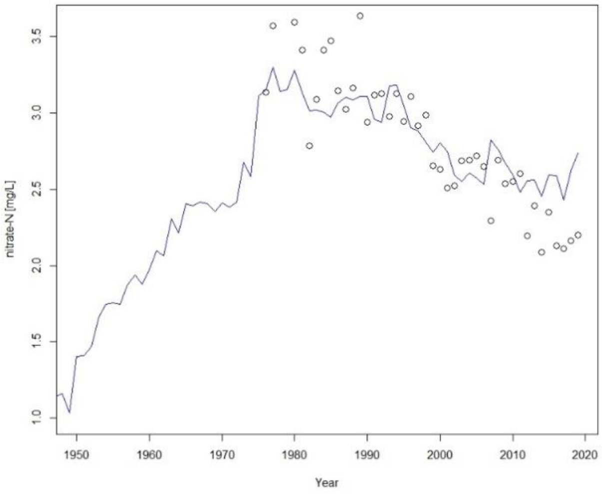

Figure 8 mQM model results for nitrate-N concentrations at the Rhine near the German-Dutch border, station 6335060. A comparison of observations (dots) and optimal modelling results (line).

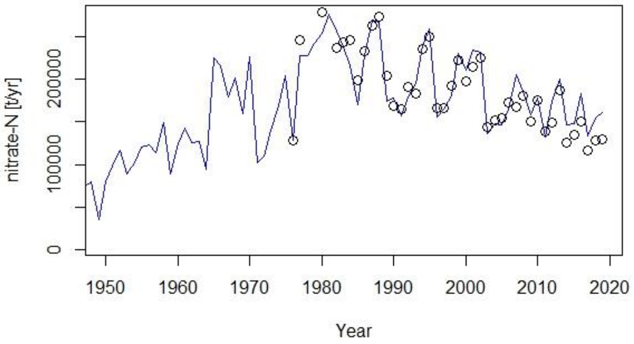

Figure 9. mQM model results for nitrate-N loads at the Rhine near the German-Dutch border, station 6335060. A comparison of observations (dots) and optimal modelling results (line). mQM model results and observations for nitrate-N loads at the Rhine catchment outlet, station 6335060. Dots depict observations, the line is the best performing modelling result.

Within the 80 modelled sub-catchments of the Rhine the model performed with a median RMSE of 0.23 mg/L.

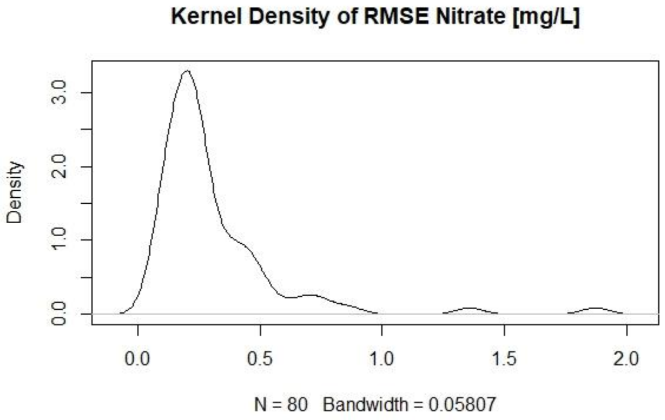

Figure 10. mQM model performance in 80 Rhine sub-catchments. Density distribution of RMSE for the nitrate concentrations.

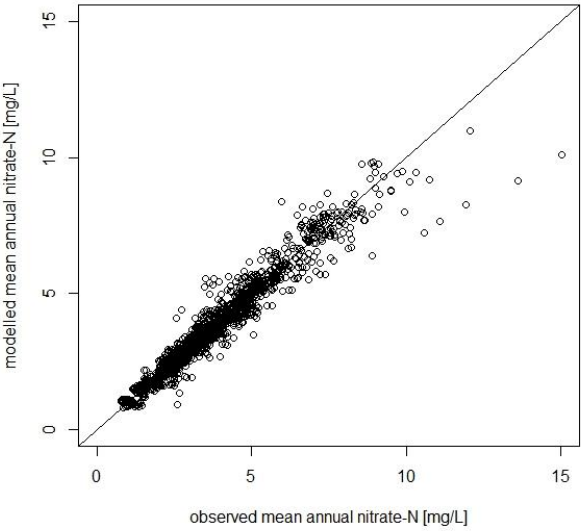

Figure 11. mQM model performance in 80 Rhine sub-catchments. A scatter plot analysis of annual observed versus modelled concentrations (n=14104).

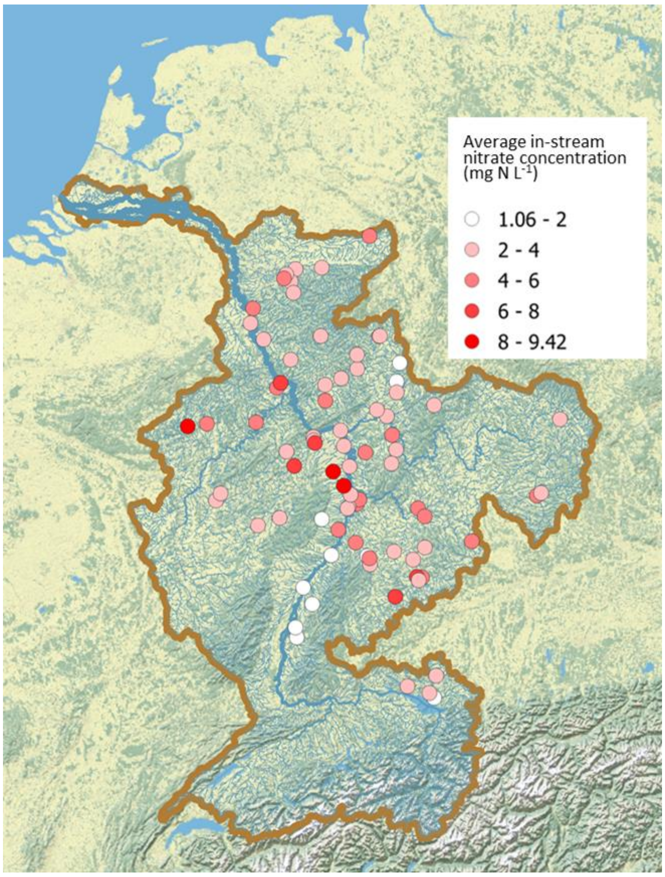

Figure 12. mQM model results in 80 Rhine sub-catchments. Averaged modelled nitrate-N concentrations at the outlet points of the sub-catchments between 2005 and 2019. Total catchment area (brown) and river network (blue) are taken from Hydrosheds (https://www.hydrosheds.org/).

Hunze

In the Hunze catchment, observed discharge is only available for four stations (4205, 4206, 4212, 4630). This may be due to active water management (water inlet and pumping) in the catchment, making modelling based on this discharge a challenging task. At the same time the estimated annual N-Surplus is high (180 kg/ha yr, Batool et al. 2022). The model cannot handle this input at the moment as water travel times are short and do not allow to remove 96-99% of that mass by time-dependent denitrification. This needs further refinement and agreement with local stakeholders.

The mQM model performs with an average RMSE of 1.89 mgN/L (range 0.81-2.27 mgN/L). Visually only the catchments 4206 (Oostermoersevaart) and 4630 (Gemaal De Bulten) perform in a sufficient way. The main contributing subcatchments 4205 (Achterste Diep) and 4212 (Voorste Diep) perform insufficiently at the moment with an average RMSE of 2.10 mgN/L.

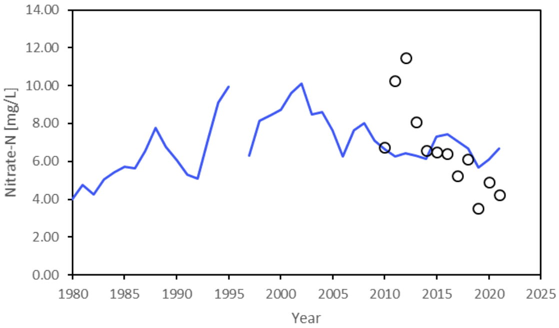

Fig. 13: Modelled annual nitrate-N concentration in the sub-catchment 4630 (Gemaal De Bulten) in the Hunze basin.

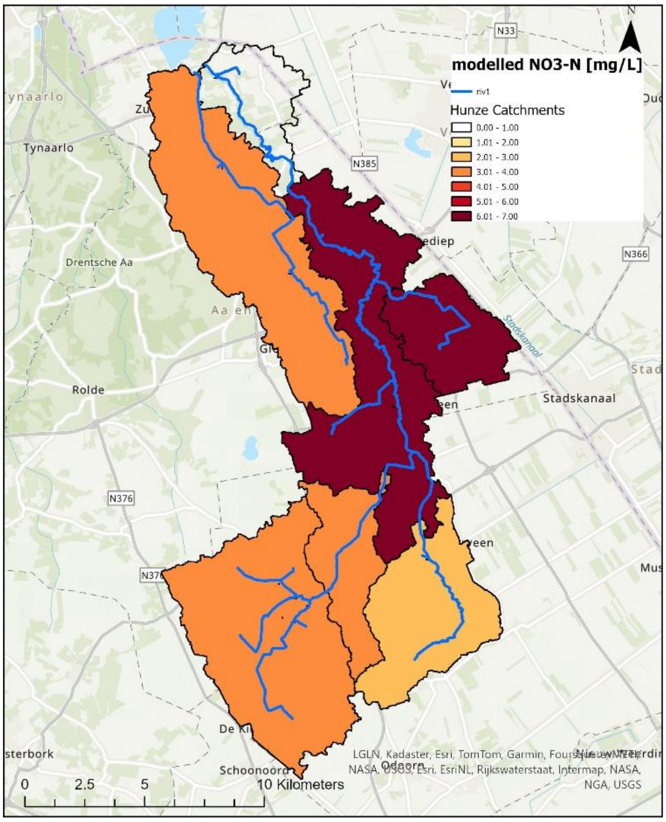

Fig. 14: Modelled Nitrate-N concentration in the sub-catchments in the Hunze basin averaged 2005-2019.

3.2 CnANDY model performance and P-simulations

<u>Elbe</u>

The CnANDY model is able to capture the spatial patterns of TP concentrations in the Elbe river network for the averaged time period of 2010 to 2020. It demonstrates close alignment with observed concentrations at 243 observation points, indicating suitability for future scenario implementations. The model performs with a RMSE of modelled TP concentrations at these stations of 61 µg/L.

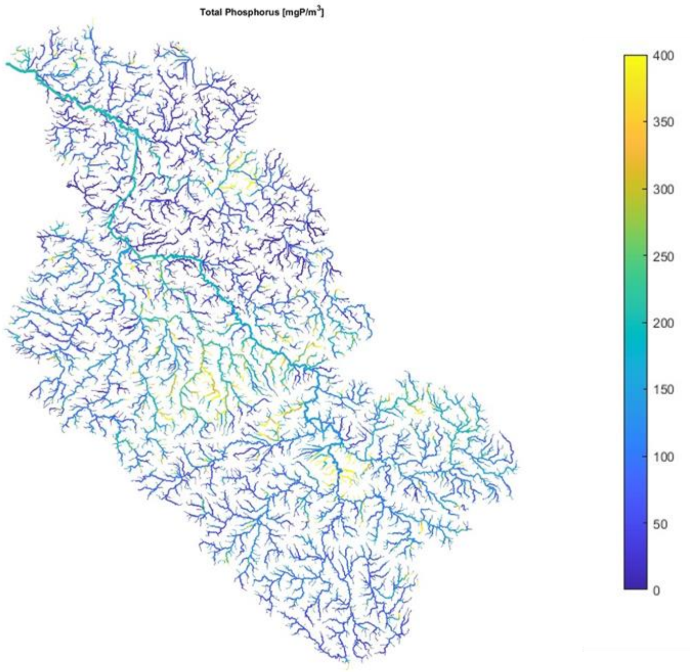

Figure 15. CnANDY model results for the spatial distribution of mean TP concentrations (2010-2020) in the Elbe river network in mgP/m^3 [µgP/L]. Legend shows the range of mean TP concentrations from 0 to 400 µP/L.

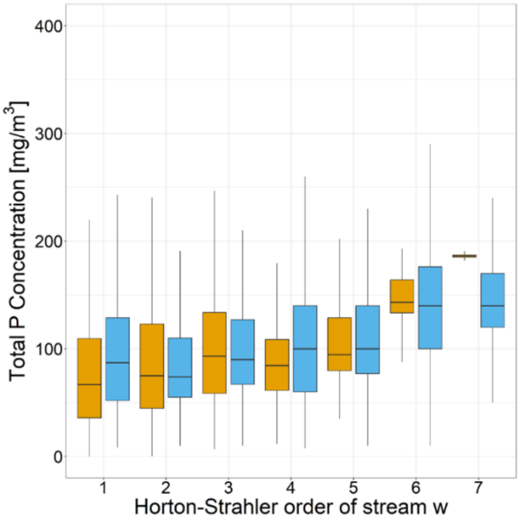

Figure 16. CnANDY model performance in the Elbe river network comparing observed (blue) and modelled TP concentrations in mgP/m^3 [µgP/L] across the different river orders.

Rhine

The CnANDY model is able to capture the spatial patterns of TP concentrations in the Rhine river network for the averaged time period of 2010 to 2020. It demonstrates close alignment with observed concentrations at 317 observation points, indicating suitability for future scenario implementations. The model performs with a RMSE of modelled TP concentrations at these stations of 86 µg/L.

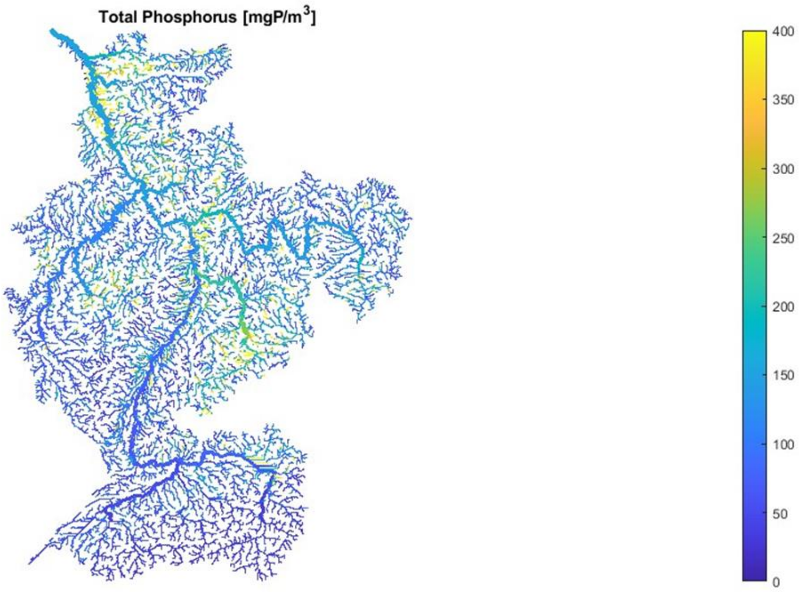

Figure 17. CnANDY model results for the spatial distribution of mean TP concentrations (2010-2020) in the Rhine river network in mgP/m^3 [µgP/L]. Legend shows the range of mean TP concentrations from 0 to 400 µP/L.

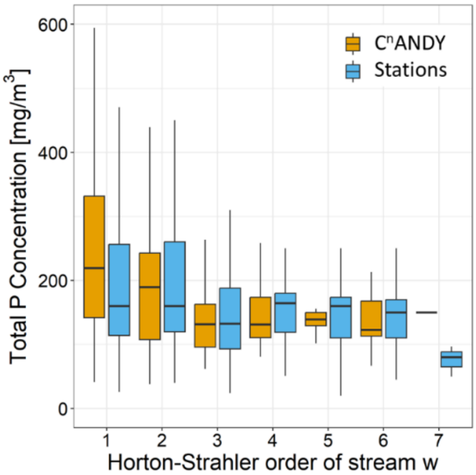

Figure 18. CnANDY model performance in the Rhine river network comparing observed (blue) and modelled TP concentrations in mgP/m^3 [µgP/L] across the different river orders.

Hunze

CnANDY performed without further calibration (see above) with a RMSE of 102 µg/L for TP. The average modelled TP concentration is 616 µg/L with highest concentration in the sub-catchment 4206 (Oostermoersevaart) receiving wastewater discharge from WWTP Gieten.

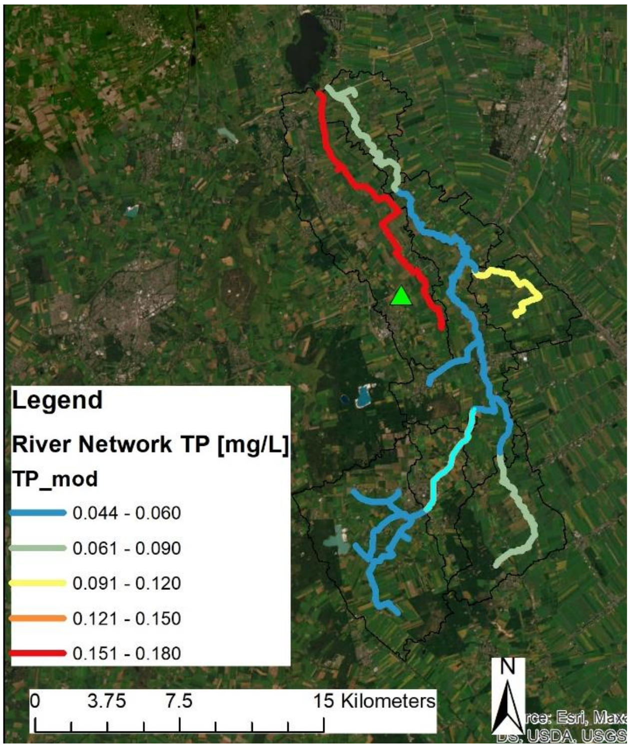

Figure 19. Map of the CnANDY model results for average TP concentrations (2000-2022) in the Hunze basin river network. Results per river section. The green triangle depicts the position of the wastewater treatment plant.

4. Next steps

The mQM model is applied to all catchments with high-quality data availability, facilitating optimal modelfitting and parameters calibration. In the subsequent phase, we aim to enlarge the set of catchments in the following manner:

- Applying the mQM model to sub-catchments that have nitrate-N but lack discharge observations, by utilizing modeled daily discharge (from the mHM-model) instead of observed discharge to derive flow-weighted annual nitrate concentrations. This approach will enlarge the number of modeled catchments approximately 500.
- Applying the mQM model to sub-catchments in The Netherlands that do not directly drain into the River Rhine, in order to accurately capture the Dutch contribution of N exports to the Wadden Sea.
- Enhancing model performance in the Hunze basin by correcting N input and discharge with the help of local knowledge.

These enlarged set of catchments will be used for the scenario evaluation in D3.5.

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