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In-stream surface water quality in China: A spatially-explicit modelling approach for nutrients

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A R T I C L E I N F O

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A B S T R A C T

Nutrient pollution is a widespread problem in rivers in China. Managing nutrient pollution requires better knowledge of in-stream processes governing the surface water quality. As current nutrient models for China mainly focus on river export of nutrients to seas, in-stream surface water quality and their contributing sources and processes are, therefore not well understood. This requires accounting for combined effects of nutrient inputs to rivers from produced waste, biochemistry of different forms of nutrients and their transport by river network. Moreover, improvements can be made in evaluating the model performance of large-scale nutrient models based on water quality measurements in China (using the surface water quality classes from 1 to 6). The objective of this study is to quantify the spatial variation in in-stream water quality for nutrients, and associated sources, for water quality classes in China. Our new Model to Assess River Inputs of Nutrients to seAs (MARINA 3.0) for in-stream water quality distinguishes different nutrient forms including dissolved inorganic (DIN, DIP) and organic (DON, DOP) nitrogen and phosphorus and was applied for the year 2012. Our model simulations compare reasonably well with measurements across 155 river sections. Results show that between 12% and 66% of the streams are highly polluted (exceeding water quality class 3) and depending on nutrient form. Diffuse sources dominate in 76% of the streams for DIN. Point sources such as direct discharges of animal manure dominate in 46%–59% of the streams for DON, DIP and DOP. The dominant sources vary considerably between rivers and nutrient forms. This indicates the need account for nutrient forms in models and national monitoring programs. Our model results could support effective management to reduce nutrient pollution in China.

1. Introduction

Chinese population accounts for 22% of the global population and suffers from water pollution (MEP, 2010–2014). Surface water accounts for 77% of total fresh water resources in China (MWR, 2014). Nutrient pollution dominates in Chinese surface water pollution (Jiacong et al., 2020). Human activities on the land such as urbanization and agriculture produce waste that pollutes Chinese surface waters with nutrients (MEE, 2019). For example, animal manure is often treated as waste and discharged to water. Efficiencies in the use of nutrients and water in agricultural production are not high enough to reduce pollution. Water pollution with nutrients contributes to eutrophication (Liu et al., 2013; Liu and Qiu, 2007; Strokal et al., 2016b) and decreases the availability of clean water for people (Jiang, 2009; Liu and Yang, 2012), potentially resulting in water scarcity (Ma et al., 2020a; van Vliet et al., 2017). Nutrient models exist to quantify nutrient pollution in water systems and their sources. Examples are the Global *NEWS*-2 (Nutrient Export from Watersheds) model on the basin scale (Mayorga et al., 2010), the family of the MARINA (Model to Assess River Inputs of Nutrients to seAs) models on the sub-basin scale for China (Strokal et al., 2016a; Wang

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et al., 2020b) and the IMAGE-GNM (Global Nutrient Model) model on a 0.5° grid scale for the world (Beusen et al., 2015; Liu et al., 2018). The MARINA model for China accounts for direct discharges of animal manure, which is ignored in many other existing nutrient models. The existing models do not quantify in-stream nutrient pollution in relation to the water quality classes used in China. This challenges the support of national policies to reduce future water pollution by nutrients.

Current large-scale nutrient pollution models generally do not account for in-stream water pollution by different nutrient forms and their sources. There is a need to combine the effects of nutrient inputs to streams, the biochemistry of nutrients in rivers (retentions) and their transport by river networks (Yu et al., 2019). Existing models often focus on river export of nutrients to coastal seas rather than in-stream nutrient pollution (Liu et al., 2018; Qu and Kroeze, 2010; Wang et al., 2020b). The Global NEWS-2 and MARINA (versions 1.0 and 2.0) models quantify river export of different nutrient forms, including dissolved organic (DON, DOP) and inorganic (DIN, DIP) N and P. However, the spatial scales of these models (basin and sub-basin) are too coarse to represent in-stream water pollution in relation to water quality classes. In contrast, IMAGE-DGNM (Dynamic Global Nutrient Model) runs at a 0.5° grid and accounts for biochemistry and transport processes of nutrients in in-streams, distinguishing different nutrient forms (Vilmin et al., 2020). However, the model was applied and validated for the Mississippi and Rhine basins, where extensive monitoring data are available. To our knowledge, the in-stream surface water quality model with balance between data requirement and detailed process descriptions for modelling water quality classes and different nutrient forms in China does not yet exist.

Large efforts have been made by the Chinese government to control water pollution. The National Environmental Monitoring Network has been set up as an important step to evaluate surface water quality status and guide the associated strategies. Surface water quality classes ranging from 1 (representing good water quality) to 6 (indicating poor water quality) are used to reflect the pollution levels of important pollutants (e.g. N, P) by the Chinese government. So far, an explicit link between the water pollution model results and these water quality classes is lacking.

Modelling studies often use nutrient observations at the river mouth to validate the model results (Liu et al., 2018; Strokal et al., 2016a; Wang et al., 2020b). However, this has not been done to a large extent for surface water quality measurements across river sections in China. Statistical analyses for surface water quality measurements and with connection to the anthropogenic drivers (e.g. livestock production) have previously been done (Ma et al., 2020b; Ouyang et al., 2006). However, these statistical studies could not explicitly address the main processes in the system, including nutrient inputs to streams, retentions of nutrients and their transport. Connecting water quality observations across river sections with integrated nutrient models will help to estimate model performances and the validated model outputs could add to the measurements with the associated source attributions for pollution management.

The main objective of this study is to quantify the spatial variation in in-stream water quality for nutrients, and associated sources, for water quality classes in China. To this end, we develop a spatially-explicit surface water quality model (MARINA 3.0) for in-stream water pollution including different nutrient forms and their associated sources. We link the model results for year 2012 with surface water quality classes across river sections in China. We assess the implication of polluted in-streams for coastal eutrophication using the Indicator for Coastal Eutrophication Potential (ICEP) (Garnier et al., 2010).

2. Methodology

2.1. Model description

We have developed a spatially-explicit nutrient model, MARINA 3.0. This model is for in-stream water quality assessment, including different nutrient forms and sources. MARINA 3.0 is developed based on the MARINA model families (Strokal et al., 2016a; Chen et al., 2019; Wang et al., 2020b). MARINA 3.0 quantifies annual flows of nutrients from land to streams (for the year 2012), followed by retentions of nutrients and their transport by river network (Fig. 1). The model is developed based on three existing modelling approaches: MARINA 1.0 and 2.0 (Strokal et al., 2016a; Wang et al., 2020b), the NUFER (Ma et al., 2010; Wang et al., 2018) county model and the VIC hydrological model (Droppers et al., 2020; van Vliet et al., 2016a; Van Vliet et al., 2016). The MARINA 1.0 and 2.0 models provide the basis for modelling nutrient inputs to rivers and their exports to seas. Outputs of NUFER and VIC are used as inputs to our model. NUFER provides model inputs for 2338 counties in China for 2012 (RESDC, 2014; Wang et al., 2018). Examples of such inputs are synthetic fertilizers and animal manure applications on land. VIC provides the total runoff on a 0.5° × 0.5° grid for quantifying the soil retention processes (van Vliet et al., 2016a; Van Vliet et al., 2016) and river discharge on a 0.5° × 0.5° grid to calculate the retentions of nutrients and concentration in streams. We used mean water temperature derived from daily simulated data with the VIC-RBM model on 0.5° × 0.5° (van Vliet et al., 2016a; Van Vliet et al., 2016).

The previous versions of the MARINA model run on the sub-basin scale and quantify the river export of nutrients at the outlets of these sub-basins (Chen et al., 2019a; Strokal et al., 2016a; Wang et al., 2020). In these earlier versions, the in-stream surface water pollution was not modelled due to their relatively coarse representations. There are three main improvements in MARINA 3.0 compared to previous versions of the model. The first improvement is in the quantification of nutrient inputs to rivers. We downscale the sub-basin approach by developing a multi-scale framework (polygon approach) to bridge the administrative scales (e.g. county) with biophysical scales (e.g. grid and sub-basin). Moreover, we distinctly improve the modelling for point sources (see Chen et al. (2019)). The second improvement is in the quantification of in-stream nutrient pollution. Based on nutrient inputs to rivers, we account for retentions of nutrients (in-stream retentions, retentions by dams and reservoirs, and consumptive water use), and transports of nutrients by the river network (upstream to downstream influences). The retention processes have been downscaled from sub-basin to grid scale, and the in-stream retention now takes a process-based modelling approach as opposed to a calibrated approach in earlier version of MARINA. Finally, we validated the model by both river sections and river mouths (while previous versions focussed validation only on river mouths). Next to this, we have made an explicit link of our model results of simulated concentrations with water quality classes for China. Below, we first summarize the approach for quantifying nutrient inputs to rivers (for details we refer to Chen et al. (2019), section 2.1.1). Next, we describe how retentions and transport of nutrients by river network are quantified (section 2.1.2).

2.1.1. Nutrient inputs to streams

Nutrient inputs to streams are quantified using the multi-scale model of Chen et al. (2019) on the basis of the modelling approaches of MARINA 1.0. The multi-scale model takes polygons as the basic intersected unit between the administrative (county) and biophysical (grid of 0.5°) scales (Fig. 1B). The model quantifies inputs of dissolved inorganic (DIN, DIP) and dissolved organic (DON, DOP) N and P to rivers by source on both biophysical (e.g. sub-basin, gird) and administrative scales (e.g. county). Inputs of N and P to Chinese streams by polygon are quantified as following (Chen et al., 2019):

$$\begin{aligned}\boldsymbol{RStotal_F} = \boldsymbol{RS_{dif_F}} + \boldsymbol{RS_{pnt_F}} + \boldsymbol{RS_{others_F}} = \left(\boldsymbol{FE_{ws,F}} \cdot \boldsymbol{WS_{dif_F}} + \boldsymbol{RSdif_{EC_F}}\right) \\ + \boldsymbol{RS_{pnt\_ma,F}} + \boldsymbol{RS_{pnt\_con,F}} + \boldsymbol{RS_{others_F}}\end{aligned} \tag{Eq.1}$$

where, $RStotal_F$ is the total inputs of nutrient form (F) from land to streams by polygon (kg year^{-1}). Nutrient forms include DIN, DIP, DON and DOP. These nutrients in river and streams result from point (RS_{pnt_F}),

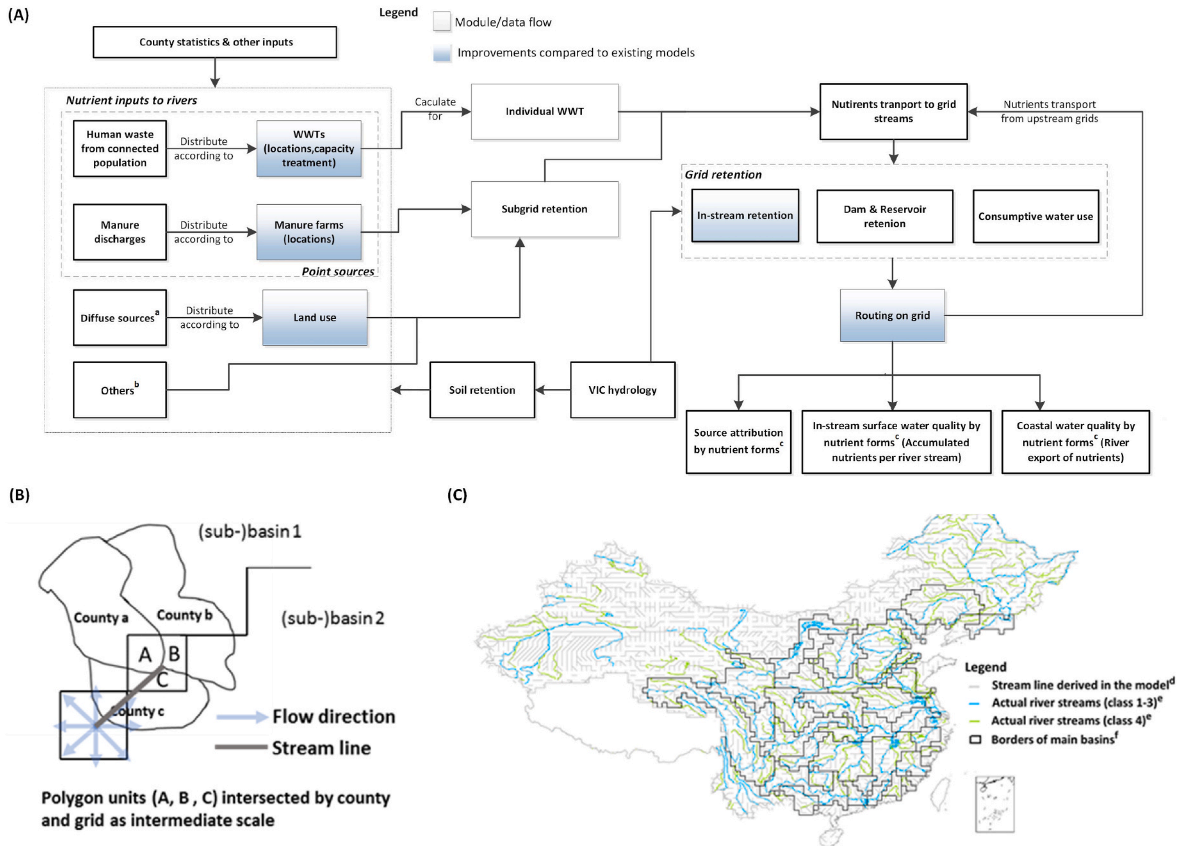


Fig. 1. Nutrient modelling framework of this study. (A) shows the connection between inputs of nutrients to rivers and their exports to seas. (B) shows the connection between polygons, grids, counties and (sub)basins in relation to the flow direction and stream network. (C) shows stream networks in the model on 0.5° grid (grey) as well as the actual Chinese river streams (green and blue). Clarifications (A): a: This box includes manure application on land, biological N_2-fixation, atmospheric N-deposition, crop export via harvesting and animal grazing, and human waste applied on land from people who are not connected to sewage systems. b: Others include human waste from unconnected population that is directly discharged to water bodies. c: Nutrient forms include dissolved inorganic (DIN, DIP) and dissolved organic (DON, DOP) nitrogen and phosphorous. d: Stream networks are derived based on the DDM30 flow direction map (Döll and Lehner, 2002). The actual Chinese river stream maps and associated river classifications are from National Geomatics Center of China (NGCC, 2018) and river channel classification standard (MWR, 1994). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

diffuse (RS_{dif_F}) and other sources (RS_{others_F}) (kg year^{-1}). Diffuse sources (RS_{dif_F}) include explicit land sources (WS_{dif_F}), which are corrected for the retentions of nutrients in soil ($FE_{ws,F}$) and parameterized export processes ($RSdif_{EC_F}$). Explicit land sources are synthetic fertilizer use, animal manure that is applied on land, human waste that is applied on land from rural and urban population disconnected to sewage systems, biological N_2 fixation, and atmospheric N-deposition. Parameterized export processes reflect inputs to streams through leaching of organic matter (DON, DOP) and weathering of P-contained minerals (DIP). Point sources (RS_{pnt_F}) include direct discharges of animal manure to streams ($\boldsymbol{RS_{pnt\_ma,F}}$) and human waste emitted from wastewater treatment plants (WWTPs) ($RS_{pnt\_con,F}$). RS_{others_F} is the direct discharges of nutrient form (F) to streams from human waste that is not connected to WWTPs in a polygon (kg year^{-1}). Model outputs at different scales (e.g., grid of 0.5°, county) are processes from polygons and here we used the 0.5°grid scale in Eq. (1) (details are in Chen et al., 2019). Both modelling of point sources (e.g. spatially-explicit WWTP database) and diffuse sources (e.g. county inputs and land-use distribution) are improved (section S2.1, SI). For a more detailed model description of nutrient inputs to streams, we refer to Chen et al. (2019). In the next section, we explain how we add retentions and routing of nutrients along the stream network in our model.

2.1.2. Nutrient retentions in streams

Nutrient inputs to rivers are retained and transported through the stream network to coastal seas. The retentions of nutrients in the stream network are quantified by two parts: the 'sub-grid' retention and the 'grid-stream' retention. The followings describe the quantifications of these two parts and the routing (i.e. transport process) of nutrients. The extended descriptions and sources of model inputs are in section S1.2 in SI.

2.1.2.1. Sub-grid retentions. Nutrient inputs to rivers are first transported by lower order streams to higher order streams (Strahler order) (Strahler, 1957). The large river presented explicitly by the stream lines (Fig. 1C) in our model is derived based on DDM30 flow direction map (Döll and Lehner, 2002) on a 0.5° × 0.5° grid. In addition to the explicit streamlines by the DDM30 (Strahler order of six or higher), there are lower order streams that are not represented by the derived streamlines. We define these lower order rivers (Strahler order from 1 to 5) which are not reflected by streamlines (Fig. 1C) as sub-grid network followed by Beusen et al. (2015). As such, 'grid-stream' refers to the derived streamlines from 0.5° × 0.5° DDM30 flow direction map and represented by grid streamlines in our model (Fig. 1C). Nutrient inputs to rivers are first entering lower order streams (from 1 to 5) and are retained before entering 'grid-stream' (Strahler order 6 or higher) represented by the grid streamline network.

Nutrient inputs to streams results from four categories including 1) diffuse sources, 2) human waste emitted from WWTPs, 3) direct discharge of animal manure and 4) direct discharge of uncollected human waste. We assume that nutrients from human waste emitted from centralized WWTPs enter directly high order streams ('grid-stream').

Nutrients from all other sources enter lower order streams and are retained and transported to the higher order streams. This results in the following equation:

$$RStotal_{F\_local} = \left(RS_{dif_F} + RS_{pnt_{ma},F} + RS_{others_F}\right) * L_{F\_subgrid} + RS_{pnt\_con,F} \tag{Eq.2}$$

where, $RStotal_{F\_local}$ is the nutrient inputs to high order streams represented in the model ('grid-stream') on 0.5° × 0.5° local cell (kg year^{-1}). These inputs are the combination of nutrient inputs from two main sources: (1) nutrient inputs to lower order streams (RS_{dif_F}, $RS_{pnt_{ma},F}$ and RS_{others_F} in Eq. (1)) where nutrients are retained ('sub-grid') and exported further to higher order streams, and (2) nutrients inputs to high order streams from WWTPs ($RS_{pnt\_con,F}$) ('grid-stream'). $L_{F\_subgrid}$ refers to nutrient retentions in lower order streams (0–1). This is based on a process-based nutrient spiralling approach (Beusen et al., 2015; Marcé and Armengol, 2009; Wollheim et al., 2008b; Workshop, 1990), which is adjusted to our study area. The parameterization of these sub-grid networks is followed by accepted geomorphic principles (Leopold et al., 1964; Wollheim et al., 2008a). The parameterization of low order streams ('sub-grid') and quantifications of in-stream retentions by sub-grid network are described in SI section S1.2.

2.1.2.2. Retentions in high order streams ('grid-stream'). After retained and transported by 'sub-grid' network, nutrient entering the 'grid-stream' and will be transported further based on flow direction to next 'grid-stream'. The main retention processes (Eq. (3)) included in the 'grid-stream' in the model follow the approach of the MARINA 1.0 model (Strokal et al., 2016a):

$$FE_{riv_F} = (1 - L_F) \cdot (1 - D_F) \cdot (1 - \mathbf{FQrem}) \tag{Eq.3}$$

where, $FEriv_F$ is the export fraction of each nutrient forms (F) on a 0.5° grid scale (0–1). L_F is in-stream retention within the river network, channels, river bed sediments, and floodplains (0–1). D_F is the nutrient retention within constructed reservoirs and behind dams (0–1). FQrem is the removal from streams through water removal for irrigation and other human needs (0–1). All these retentions are calculated on 0.5° grid.

The main differences compared to the MARINA 1.0 and 2.0 models are that: (1) the basin-scale retentions of MARINA are downscaled to a grid scale to support spatially-explicit modelling of in-stream nutrient pollution, (2) the in-stream retentions are added for all nutrient forms (previous only for DIN and DIP) and (3) L_F is quantified using the nutrient spiralling approach (Beusen et al., 2015; Marcé and Armengol, 2009; Wollheim et al., 2008c; Workshop, 1990), but adjusted to our study area. The following paragraphs explain how L_F is calculated (details are in S1.2, SI). D_F and FQrem are modified based on the approach of the Global *NEWS-2* (Mayorga et al., 2010) and MARINA 1.0 and 2.0 models (Strokal et al., 2016a; Wang et al., 2020b) and explained in the S1.2 in SI.

Retention of N (L_F) within the stream network includes three main processes: denitrification, sedimentation and uptake by aquatic plants. P is removed by sedimentation and sorption by sediment and the uptake by microorganisms and aquatic plants. The in-stream retention (L_F) is quantified following the nutrient spiralling approach (Beusen et al., 2015; Marcé and Armengol, 2009; Wollheim et al., 2008c; Workshop, 1990), but with some modifications as:

$$L_F = \left(1 - \exp\left(-\frac{V_{f,E}}{H_L}\right)\right) * F_{bio\,f} \tag{Eq.4}$$

where L_F is the fraction of the nutrient load that is removed within the stream network (0–1). $V_{f,E}$ is the net uptake velocity (m year^{-1}). F is the nutrient forms. $F_{bio,f}$ is the bioavailability coefficient that is applied only for organic forms. It is set at 0.4 and 0.7 for DON and DOP, respectively. It is assumed that organic forms of N and P are less bioavailable to bacteria and plants compared to inorganic forms. The bioavailability coefficient is derived from literature to account for lower retentions of organic forms compared to inorganic forms in rivers (section S1.2.2). H_L is the hydraulic load (m year^{-1}) representing the hydrological conditions and is quantified as:

$$\mathbf{H}_L = \frac{D}{\tau} \tag{Eq.5}$$

$$\tau = \frac{V}{Q} \tag{Eq.6}$$

$$\mathbf{V} = W \cdot L \cdot D \tag{Eq.7}$$

where D is the depth of the water body (m). τ is the residence time (year) and is calculated from the volume V (m^3) of the water body and the water discharge Q (m^3 year^{-1}). W and L (m) are the width and length of the channel, respectively. W is calculated as a function of discharge (see S1.2). Deducted from the above equations, $\mathbf{H}_L$ could be calculated as:

$$\mathbf{H}_L = \frac{Q}{W * L} \tag{Eq.8}$$

$V_{f,E}$ is the net uptake velocity (m year^{-1}) which is different for each nutrient E (N or P) and represents the biological activities. For N and P, the $V_{f,E}$ is calculated based on the constant values (m year^{-1}) that is calibrated based on the measurements across streams globally and is adjusted based on local water temperature (Wollheim et al., 2008a, 2008c):

$$\mathbf{V}_{f,N} = 35 f(t) \tag{Eq.9}$$

$$\mathbf{V}_{f,P} = 44.5 f(t) \tag{Eq.10}$$

where, t is annual mean water temperature (°C). The constants value for N and P are 35 (Wollheim et al., 2008c) and 44.5 (Marcé and Armengol, 2009), respectively.

2.1.3. Routing procedure

The routing (transport process) of nutrients is based on the flow direction network of DDM30 (Döll and Lehner, 2002) on a 0.5° × 0.5° grid scale. Each grid cell receives nutrient inputs from the local cell ($RStotal_{F\_local}$ in Eq. (2)) and from upstream grid cells ($IS_{F_{upstream}}$). Nutrients in grids are then exported (FE_{riv_F}, Eq. (3)) to the next grid. During this export, some nutrients are retained (e.g., L_F and FQrem in Eq. (3)). The same procedure holds for the next downstream grid cell. After the retentions, the in-stream nutrients are transported to the next grid cell and the same procedures applies: the local nutrient inputs from the next grid cell will be added to the nutrient accumulations from upstream cells and the local retentions (FE_{riv_F}) of this new grid will be applied. This calculation continues until nutrients reach the river mouth or until the flow in a certain grid cell does not drain to the next grid cell (i.e. inland rivers):

$$IS_F = \left(RStotal_{F\_local} + IS_{F_{upstream}}\right) \cdot FE_{riv_F} \tag{Eq.11}$$

where, IS_F refers to the in-stream nutrient accumulation load by nutrient form (F) in a grid of 0.5° (kg year^{-1}). $RStotal_{F\_local}$ refers to the total input of nutrient form from a grid of 0.5°(the local grid cell, i.e. $RStotal_F$ after correcting for sub-grid retentions that entering the higher order streamlines of the grid (kg year^{-1}). These inputs originate from activities (point and diffuse sources) in its own grid. $IS_{F_{upstream}}$ refers to the input of nutrient form F from upstream grids of 0.5° (kg year^{-1}). FE_{riv_F} refers to the export fraction of nutrient form (F) in high order streams that represented by streamlines of 0.5°grid (0–1). This export fraction accounts for retentions of nutrients in the grid during the export.

2.1.4. Surface water quality and indicator for coastal eutrophication

The in-stream water quality is expressed in our model by in-stream accumulated nutrient load in a grid cell at 0.5° × 0.5° spatial resolution (IS_F in Eq. (15)) and in-stream nutrient concentrations. The in-stream nutrient concentration is calculated by in-stream nutrient load accumulation divided by the river discharge of that grid cell. The in-stream concentrations are further converted to surface water quality classes according to the Environmental Quality Standard (MEE, 2002) for Surface Water in China (Table S4 in SI. The in-stream nutrient concentration and the converted quality class serve as an indication of annual average pollution level for each river stream, accounting for the combined effects of nutrient inputs to streams, retentions of nutrients by the network and transportation processes. We take quality class 3 as a threshold to define polluted rivers as the government reports (MWR, 2012) and other studies (Ma et al., 2020; Yu et al., 2019). The sources of in-stream nutrient loads per stream are quantified and described in S1.3 in SI. The in-stream nutrient load at the grid cell of the river mouth represents river export of nutrients to sea. We calculate an Indicator for Coastal Eutrophication Potential (ICEP) to assess the impacts of river export of nutrients on coastal eutrophication. A positive ICEP value indicates high potential for coastal eutrophication while the negative value indicates the opposite. The approach is followed Garnier et al. (2010) and is calculated with the modelled river export of nutrients. The quantifications are described in section S1.3 in SI.

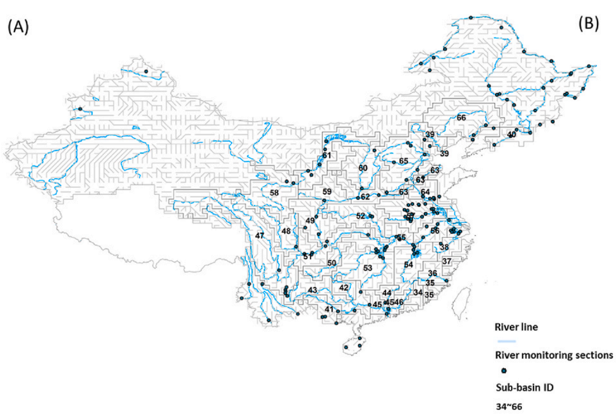
2.2. Model validation

We validate the model in two ways. First, we compare modelled river export of nutrients with measurements at the river mouth. This way is applied in many existing studies for water quality models. We collected measured concentrations of nutrients at the river mouth from available literature (Tables S3 and SI). We compared the measured values with our model values using three model performance indicators: Pearson' coefficient of determination (R^2, 0–1), the Nash-Sutcliffe efficiency (NSE, -∞ - 1) and the root mean square error to the standard deviation of measured data (RSR, 0 - +∞). The calculations and interpretation of these indicators are explained in Moriasi et al. (2007).

Second, we compare modelled in-stream nutrient pollution levels with measurements at the river sections. This way is less common in studies such as Strokal et al. (2016a), Wang et al. (2020b), Beusen et al. (2015). We collect the data and organize it in such a way to allow to use the measurements in river sections for our model validation. To this end, we create a Surface Water Quality Database (S2.3, Table S6). The database includes 155 river monitoring sections across China (Fig. 2), the weekly measurements of concentration of NH_3, COD (Chemical Oxygen Demand), DO (dissolved oxygen) and associated water quality classes (MEE, 2012). The water quality classes are determined by the government based on a so-called 'single indicator' approach (see S2.2, SI) according to the Environmental Quality Standard for Surface Water in China. We located the XY coordinates of the river sections from different sources (EPMAP, 2019; IPE, 2019).

We process the weekly measurements into two modes. The first mode is the complied annual average concentration ('average' mode). For N, we processed the weekly concentration of NH_3 to an annual average estimate for 2012. The weekly measurement data that we obtained do not include specific weekly TP concentrations. For P, we use the average annual water quality class and associate median concentration based on the thresholds of the TP standard of that class (S2.2 in SI). The second mode is to determine the most frequent occurrence of the quality classes during the year and convert it to the concentrations based on the upper limit of the thresholds of NH_3 and TP standard of that class ('frequent' mode, see S2.2). The derived concentrations of all river sections are multiplied with the 30 years average annual discharge (1970–2000) on 0.5° × 0.5° grid from the VIC hydrological model (van Vliet et al., 2016a; Van Vliet et al., 2016). The measured load is used to compare with the modelled in-stream nutrient load (Fig. 3). The modelled in-stream nutrient load is extracted based on XY coordinates of the river sections and converted from DIN to NH_3 and TDP to TP based on

(A)



(B)

Sub-basin ID	Name	Basin	station_number
	Other Inland River		48
34	Hanjiang		0
35	Jiulong		0
36	Menjiang		1
37	Qujiang		0
38	Fuchun		1
39	Luan		0
40	Yalu		4
41	Yujiang	Pearl River	4
42	Liujiang	Pearl River	0
43	Xijiang	Pearl River	4
44	Beijiang	Pearl River	1
45	Delta zhujiang	Pearl River	2
46	Dongjiang	Pearl River	0
47	Jinsha	Yangtze	5
48	Min	Yangtze	1
49	Jialing	Yangtze	4
50	Wu	Yangtze	0
51	Upstream Yangtze	Yangtze	5
52	Han	Yangtze	2
53	Dongting	Yangtze	3
54	Poyang	Yangtze	4
55	Middlestream Yangtze	Yangtze	9
56	Delta Yangtze	Yangtze	5
57	Downstream Yangtze	Yangtze	21
58	Lanzhou	Huang He	2
59	Wehe	Huang He	1
60	Longmen	Huang He	2
61	Toudaogual	Huang He	5
62	Huayuankou	Huang He	2
63	Delta Yellow	Huang He	1
64	Huai		6
65	Hai		8
66	Liao		2

(C)

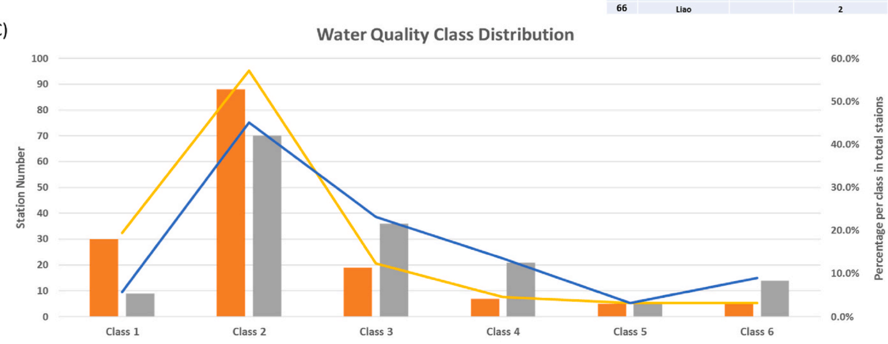


Fig. 2. Overview of surface water quality database. (A) The distribution of the river monitoring sections and the annual average water quality classes per section, processed from weekly water quality class (see details in S2.2, SI). (B) River monitoring section distribution per sub-basin. (C) Annual water quality class distribution among river monitoring sections. The 'AverageClass' refers to the annual average weekly quality class ('average' mode) and the 'FrequentClass' refers to the most frequent occurrence of the quality classes during the year ('frequent' mode). The 'percentage_avg' and 'percentage_fre' refer to the ratio of river sections of certain class in total river sections under 'average mode' and 'frequent' mode respectively. See sources in section S2.3 in SI.

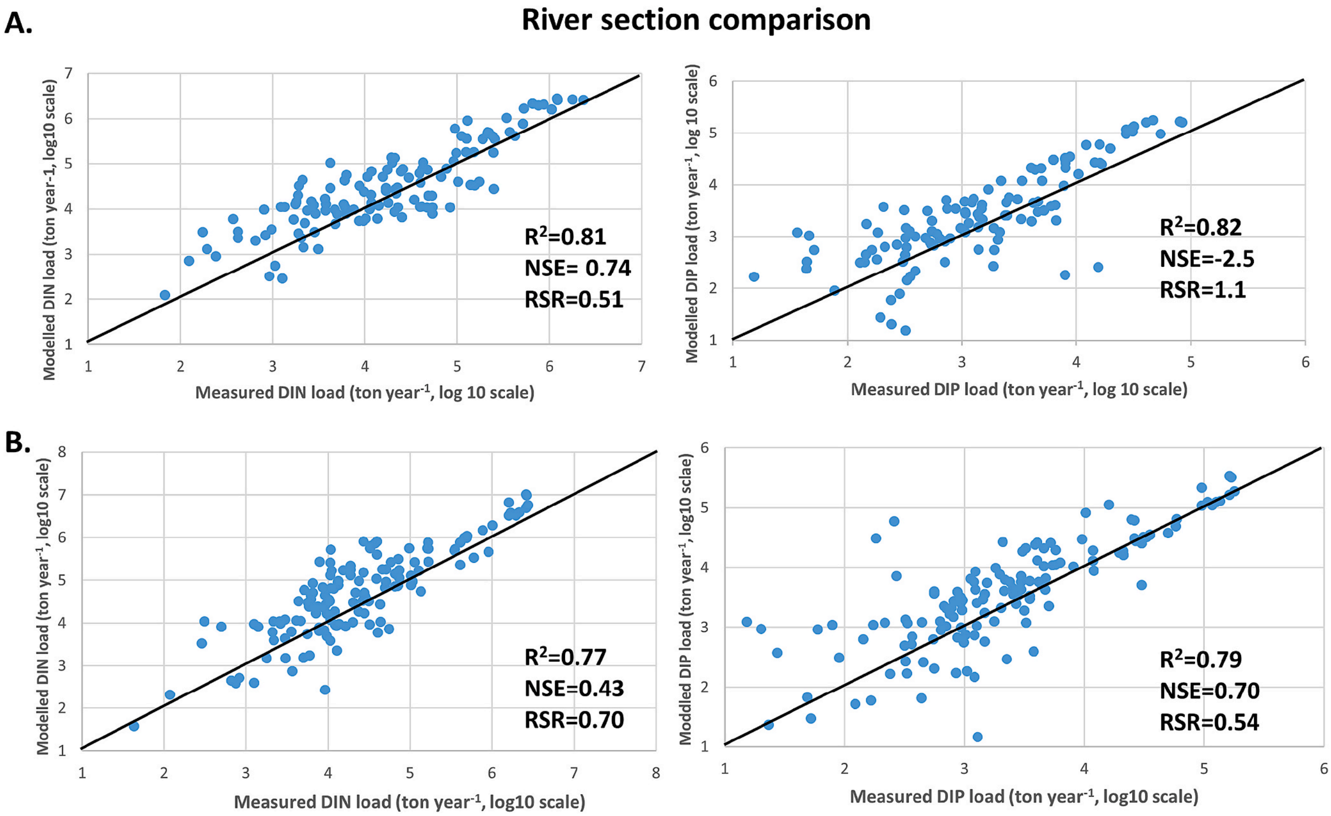


Fig. 3. Modelled versus measured loads of dissolved inorganic nitrogen (DIN, ton year^{-1}) and dissolved inorganic phosphorus (DIP, ton year^{-1}) per river monitoring section. Measured loads of DIN and DIP were converted from weekly concentrations of NH_3 and TP (see section 2.2 for the conversion method). (A) is based on 'average mode' and (B) is based on 'frequent mode' (section 2.2). R^2 is the Pearson' coefficient of determination (0–1), NSE is the Nash-Sutcliffe efficiency (-∞- 1), RSR is the root mean square error to the standard deviation of measured data (0 - +∞).

basin-specific conversion ratios derived from literature (Tables S5 and SI).

The database of measurements in river sections that we created reflects the spatial variances of pollution levels by nutrients. The spatially-explicit modelling approach is one of the strengths that we claimed and therefore would like to evaluate. We use R^2 to assess the performance of the model, because it reflects the proportion of the variance in measured data explained by the model. If the variances among different sections are captured by the model, we consider the model as appropriate to mimic the spatial distribution of the pollution level by nutrients among streams. In addition, we also calculate the NSE and RSR (Fig. 3) to get the general insights on the model performance in modelling actual in-stream loads.

3. Results

3.1. Model evaluation and validation

Model results were compared with measurements at the river sections (in-stream nutrient pollution) (Fig. 4) and measurements at the river mouths (river export of nutrients) (Fig. 3). Model validation results (Figs. 3 and 4) show that our model simulations compare reasonably well with measurements across river sections.

The main indicator R^2 for **river sections** are above 0.75 for both N and P and for both the 'average mode' and 'frequent mode' of the processed measured loads (Fig. 4). This indicates that the model is able to represent the spatial distribution of the pollution levels amongst the streams. For N, the values of NSE and RSR represent 'good' to 'satisfactory' model performance (NSE = 0.43 to 0.74; RSR = 0.51 to 0.70) (Moriasi et al., 2007). For P, a 'good' performance was found under the 'frequent' mode (NSE = 0.75; RSR = 0.50) while under 'average' mode

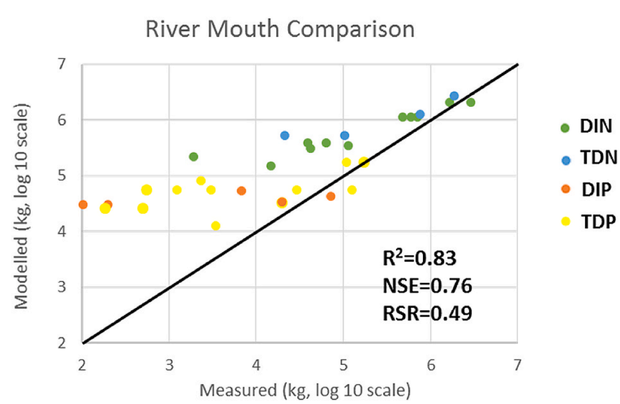


Fig. 4. Modelled versus measured river export of dissolved inorganic nitrogen (DIN, kton year^{-1}), dissolved inorganic phosphorus (DIP, kton year^{-1}), total dissolved nitrogen (TDN, kton year^{-1}) and total dissolved phosphorus (TDP, kton year^{-1}) for the Yangtze, Yellow, Pearl, Huai, Minjiang and Liao rivers. R^2 is the Pearson' coefficient of determination (0–1). NSE is the Nash-Sutcliffe efficiency (-∞- 1). RSR is the root mean square error to the standard deviation of measured data (0 - +∞). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

the model performance is lower (NSE = −2.5; RSR = 1.1). This may result from the uncertainties in the derived TP concentrations based on water quality classes (*SI, S2.2*). Nevertheless, we consider the validation results against river sections as reasonably well.

The estimates for the three model performance indicators **at the river mouth** (Fig. 3) all indicate a 'very good' performance according to the performance ratings from Moriasi et al. (2007) (R^2 = 0.83; NSE =

0.76; RSR = 0.49). Only the measurements representative for the year 2012 are included, and previous years are excluded (S2.1, Table S3). A few outlier points fall relatively far from the 1:1 line. These are results for the Yellow and Liao rivers. Our validation results indicate that the model overestimates river export of P for the Yellow river and both N and P for the Liao river. One reason for this poor agreement could be the large fluctuations in discharge, concentrations and subsequently the measured loads (Table S3) in these two river basins. The relatively large variability in the measured loads in these two basins indicates that the measured nutrient concentrations (for certain time intervals) may not represent the actual annual loads. Moreover, the overestimations in simulated loads in these two basins could be explained by underestimations of in-stream retention processes. In addition, the suspended sediment loads in the Yellow and Liao river are much higher than in other basins (Song et al., 2016; Yang et al., 2017). Previous studies have shown that higher sediment concentrations result in higher N loss by coupled 'nitrification and denitrification' and higher absorption of P in streams (Pan et al., 2013; Xia et al., 2018). The national average value of $V_{f,E}$ applied to all basins that represent the bio-chemical processes of in-stream retentions of nutrients could potentially be lower in these two basins due to the high sediment concentrations.

3.2. In-stream surface water quality

In the following, we present spatial patterns of simulated in-stream nutrient loads, surface water quality classes (nutrient concentration) and the associated source attributions. In addition, the implications of the pollutant levels and comparison of our results with other studies are discussed.

We present the modelled DIN and DON **in-stream loads** in the river sections (Fig. 5). In 84% of the streams DIN loads exceed DON loads. The spatial distribution in simulated DIN and DON in-stream loads show similar patterns and hotspots of severe pollution in the main streams. These streams are located in main river basins that drain into the seas (Figs. S1 and SI) including the main streams of the Changjiang, Yellow, Zhujiang, Hai He rivers. Next to this, the main streams of the Heilong Jiang, Songhua Jiang (north east), and Talimu He (north west) are also hotspots of high nutrient loads. This is mainly due to the increasing nutrient loads into the streams and the unbalanced retentions, resulting in large flow accumulations in these main streams. The small differences in nutrient loads between DIN and DON mainly occur in lower order streams (e.g. in Hai and Liao). For P, the inorganic form (DIP) also dominated in most streams (Fig. 6). However, the organic forms for P have a higher share compared to N, and DOP dominated for 41% of streams. The spatial distribution of in-stream P load is similar with N, showing highest pollution levels in the main streams and small variations between DIP and DOP in lower order streams.

The modelled nutrient concentration are classified into **quality classes** (class 1 to 6) according to Chinese surface water quality standards (MEE, 2002). Followed by government, the NH_3 and TP concentration is used to classify the quality classes accordingly. Results show that 12% of the streams in China are classified as highly polluted (above class 3) according to the modelled DIN concentration converted to NH_3 concentration (Fig. 6). The spatial distribution of quality classes show large variability within and between basins. The water quality of Huai, Hai, Pearl is worse than of other basins, with a quality class of 3 or higher. This is due to the combined effects of intensive nutrient inputs to rivers and relatively lower discharges (resulting in less dilution and therefore higher concentrations) in these basins. The Changjiang, Yellow river, south-west rivers and north-west rivers (Fig. S1) show better quality compared to other river basins. In these basins, more than 90% of total streams have a quality class of 1–3. Differences between spatial patterns of nutrient load and water quality class have been observed in particular for Changjiang and Yellow river. Their main streams are

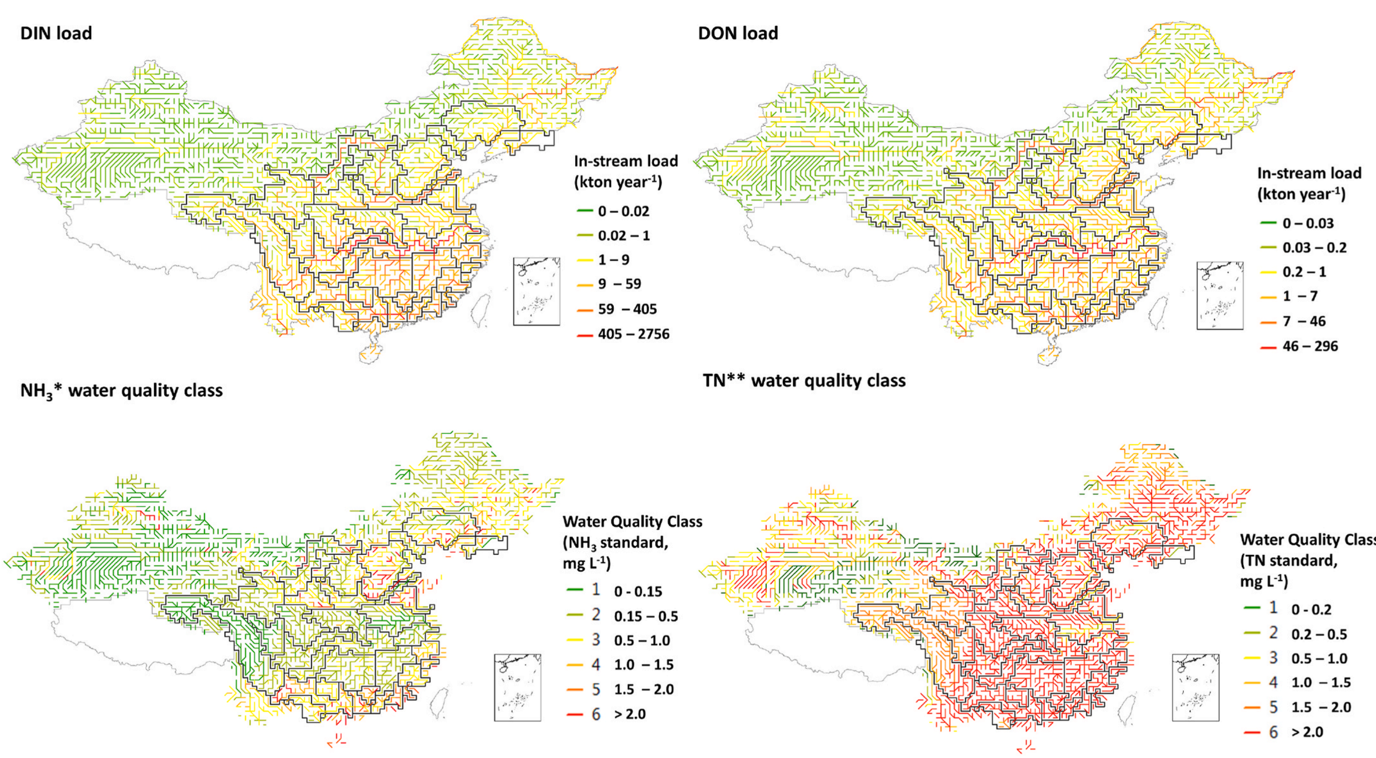


Fig. 5. Modelled in-stream loads of dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON) (kton year^{-1}) and associated water quality classes according to Chinese surface water quality standards (converted based on concentrations). The lines on the maps correspond to the streams derived based on the DDM30 flow direction. *NH_3 water quality class is converted based on modelled DIN in-stream concentration and the basin-specific conversion ratio of NH_3 and DIN (Tables S5 and SI). The range of each class is based on Chinese surface water quality standard of NH_3. **TN water quality class is the modelled TDN in-stream concentration and the range of each class is based on Chinese surface water quality standard of TN.

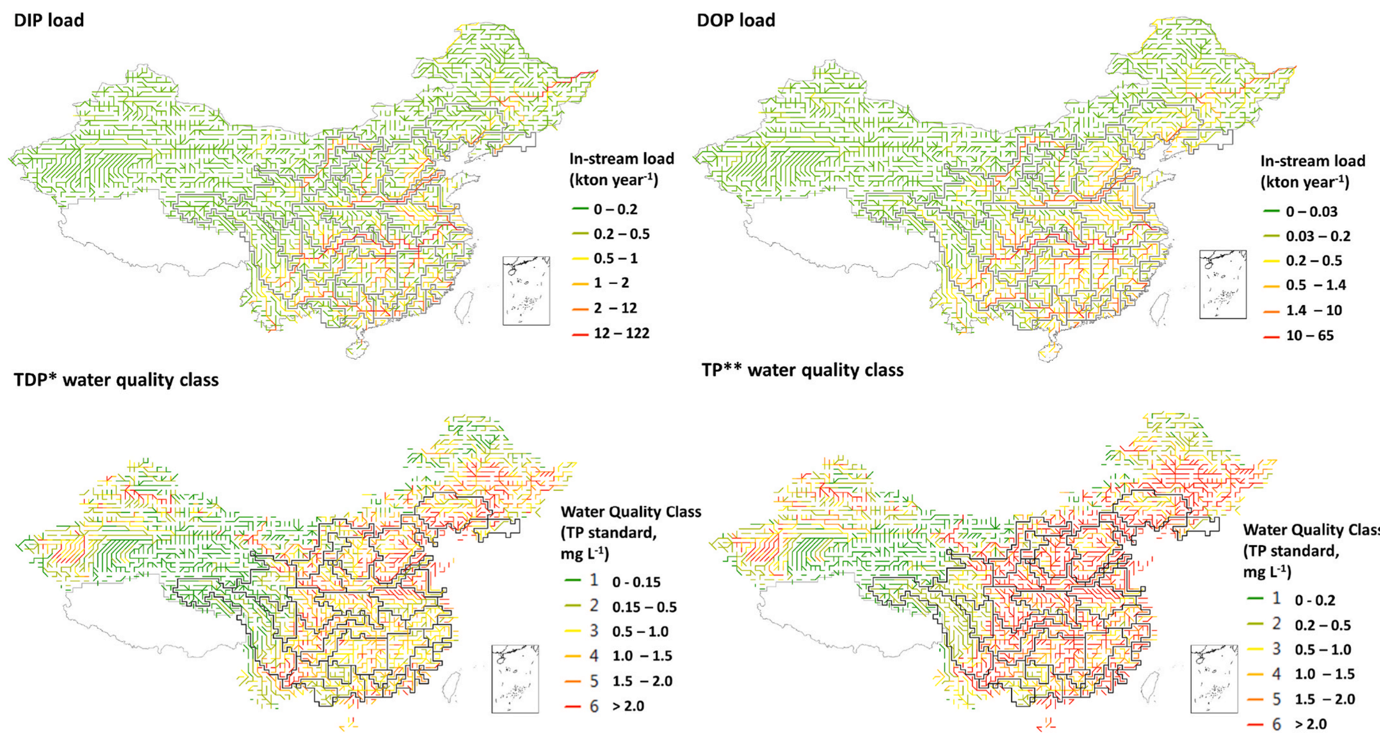


Fig. 6. Modelled in-stream loads of dissolved inorganic phosphorus (DIP) and dissolved inorganic phosphorous (DOP) (kton year^{-1}) and associated water quality classes according to Chinese surface water quality standard (converted based on concentrations). The lines on the maps correspond to the streams and are derived based on the DDM30 flow direction. *TDP water quality class is converted based on modelled TDP in-stream concentration. The range of each class is based on Chinese surface water quality standards of TP. **TP water quality class is the modelled TP concentration and the conversion is based on the basin-specific conversion ratio of TDP and TP (section SI, Table S5). The range of each class is based on Chinese surface water quality standard of TP.

hotspots of nutrient load of DIN, while they show relatively better water quality based on concentrations. This can partly be explained by the large discharges of these main stream rivers which result in high dilution and offsets high nutrient inputs. In addition, the ratio of NH_3 and DIN of these two river basins are lowest compared to other basins (Table S5), and may result in relatively lower converted NH_3 from DIN. However, monitoring of nitrogen in Chinese rivers and the associated quality classes has so far largely focussed on NH_3 concentration, rather than TN concentrations. We convert the modelled in-stream TDN load to concentration (by dividing the load by discharge) and classify them accordingly to the TN-standard of the surface water quality standard (MEE, 2002). The highly polluted streams (above class 3) increase from 12% (NH_3 concentration) to 66% (TN concentration). Also 'good quality' river basins such as Changjiang and Yellow river based on NH_3 concentration deteriorate from 'green' to 'red' (Fig. 6).

The in-stream pollution level of P (based on TP) is generally higher than that of N (based on NH_3) (Fig. 6 and Fig. 6). On national scale, 30% of the total streams in China are highly polluted (above class 3). For most river basins, TP is the dominant pollutant compared to NH_3 (i.e. the associated water quality class of streams is worse than for NH_3). Similar as for N, the Hai, Huai and Liao basins are the top 3 polluted river basins. Streams above class 3 in these basins ranging from 62% to 77%. The pollution level of South-east rivers (Hanjiang, Jiulong, Menjiang, Qujiang and Fuchun Jiang), Yellow river and Changjiang is more moderate but still with around 40% of highly polluted streams. South-west and north-west rivers (Figs. S1 and SI) show overall good quality based on TP standard, with less than 10% of polluted streams.

The **dominant sources** of surface water pollution vary among different nutrient forms. For DIN, diffuse sources dominate (Fig. 7) in 76% of rivers streams, followed by manure point sources (16%), 'others' (i.e. human waste discharges from unconnected population, 5%), and waste water treatment plants (WWTPs, 3%). For DON, manure point source dominate in 46% of the streams followed by diffuse sources in 43%, 'others' in 9% and in WWTPs in 1% of the streams. Manure point source is also the dominant source of P in most streams, dominating 53% and 59% of streams of DIP and DOP, respectively. 'Others' are the second largest pollution source of DIP dominating 24% of streams, followed by 'WWTPs' (12%) and diffuse sources (11%). For DOP, diffuse sources and 'others' are equally important, both dominating in 20% of the streams.

The spatial distribution of dominant sources shows large variability within and among different basins. Fig. 7 shows the detailed source attributions for streams. The diffuse sources are divided into several subcategories to understand the differences within the basins. **North-west rivers** and south-west rivers that are located in the Xinjiang, Gunsu and Yunan provinces (Fig. S1) are less urbanized and have lower crop and livestock production levels. The dominant sources in these regions are N-deposition (for DIN), and human waste discharges from unconnected population (for all nutrient forms). For areas with WWTPs presented (see Fig. 6 of Chen et al. (2019)), WWTPs dominated both DIN and DIP in the adjacent streams. For DON, leaching of organic matter from agricultural and non-agricultural areas dominate around 35% of the streams in these regions. **North-east rivers** that located in Jilin, Heilongjiang and Inner Mongol province have different dominant sources compared to north-west rivers. Manure point source overall dominates DIN in the Songhua river, while in other streams of north-east rivers N-deposition dominates. For other nutrient forms (DON, DIP and DOP), manure point source dominates in most streams, except for the main streams of Heilongjiang where WWTPs are the dominant source for DIP. For **main basins draining into seas**, most river and streams are dominated by manure point sources for DOP, DON and DIP. Except in upstream parts of Changjiang (Qinghai province part), Poyang and part of Delta Changjiang (Anhui province part), P-weathering and leaching of organic N-matter dominate DOP and DON. These regions have lower livestock production and are less urbanized. Therefore, natural sources seem to play a more important role than anthropogenic sources, and this

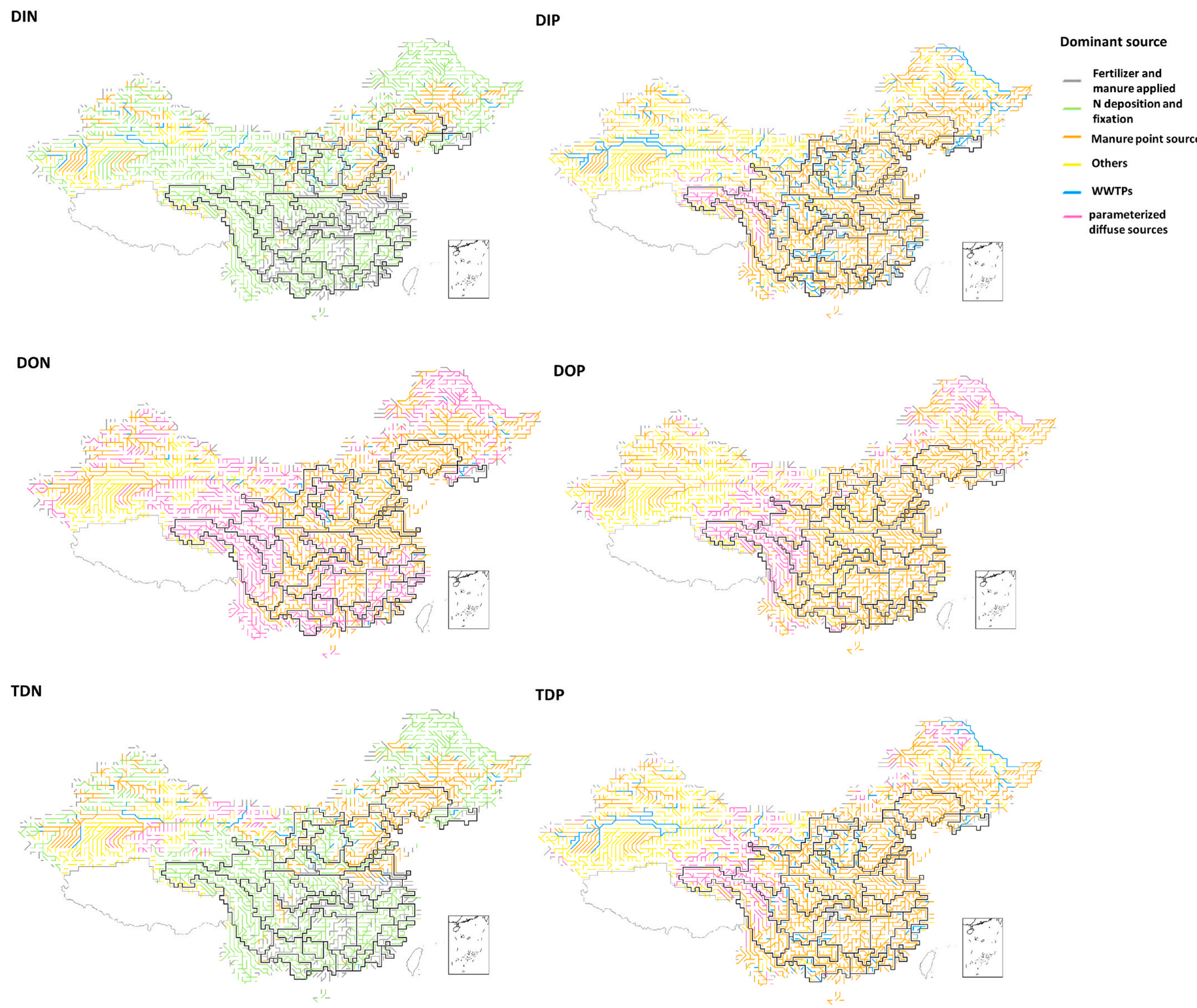


Fig. 7. Dominant sources of dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorous (DIP), dissolved organic nitrogen (DON), dissolved organic phosphorous (DOP), total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP). The lines on the maps correspond to the streams and are derived based on the DDM30 flow direction. Sources are divided into four categories. 'WWTPs' (blue) refers to nutrients in streams from human waste that is discharged from wastewater treatment plants. 'Manure point source' (orange) refers to nutrients from the direct discharges of animal manure. 'Others' refer to DIN and DIP in streams from direct discharges of the human waste from urban and rural population that are not connected to sewage systems. Diffuse sources are then divided into four sub-categories. First sub-category is fertilizer and manure applied on land (grey). Second sub-category is biological N_2-fixation by crops (for DIN) and by natural vegetation (for DIN), atmospheric N-deposition on agricultural and non-agricultural land (for DIN) (green). Third sub-category are diffuse sources including leaching of organic matter from agricultural and non-agricultural land (for DON and DIP), and weathering of P-contained minerals from agricultural and non-agricultural soils (for DIP) (purple). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

also holds for DIN and DIP in these regions. For DIP, the WWTPs are detected as the dominant sources in coastal regions, mid-stream (Longmen sub-basin) of Yellow river, mid-stream of Pearl (Yujiang sub basin). This is due to highly urbanized cities that are located along the coastal line (e.g. Shanghai, Hongkong) and less livestock productions in Longmen (Shanxi province) and Yujiang (Guangxi province) sub-basins. For DIN, manure and fertilizer applied are the dominant sources in upstream parts of the Pearl (Xijiang sub-basin), middle and downstream parts of Changjiang, and downstream of the Pearl. For highly polluted river basins (Hai and Huai) and Luan and Liao, manure point sources dominated DIN in more than 50% of streams. The atmospheric N deposition become an another important source of DIN for regions with relatively lower crop and livestock production.

3.3. Coastal water quality

The 12 Chinese rivers with basin outlets to seas () export in total 6167 kton of TDN and 449 kton of TDP to the seas. More than half of total TDN and TDP are exported to East China Sea, followed by Bohai Gulf (20%–37%), South China Sea (14%–24%)and Yellow Sea (3%–4%). About 68% of the total TDN exports originate from diffuse sources, while direct discharge of manure and human waste emitted from WWTPs are dominant sources for total TDP exports to seas. The river export of nutrients to each of the four seas and their associated sources are described below. The analyses of associated sources per river basin are presented in Fig. 9.

The Bohai Gulf received 20% and 37% of total TDN and TDP exports, respectively. Hai and Yellow are top contributors of nutrient exports,

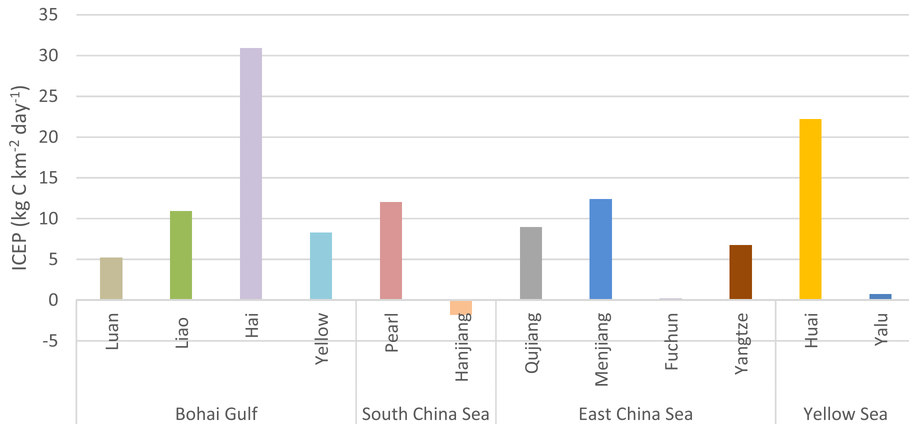


Fig. 8. The Indicator for Coastal Eutrophication Potentials (ICEP) for individual river basins in 2012 (kg C km^{-2} day^{-1}). The approach to calculate ICEP is described in SI section S1.3.2. ICEP values above zero indicate a high potential for coastal eutrophication and negative value indicates low risk for coastal eutrophication.

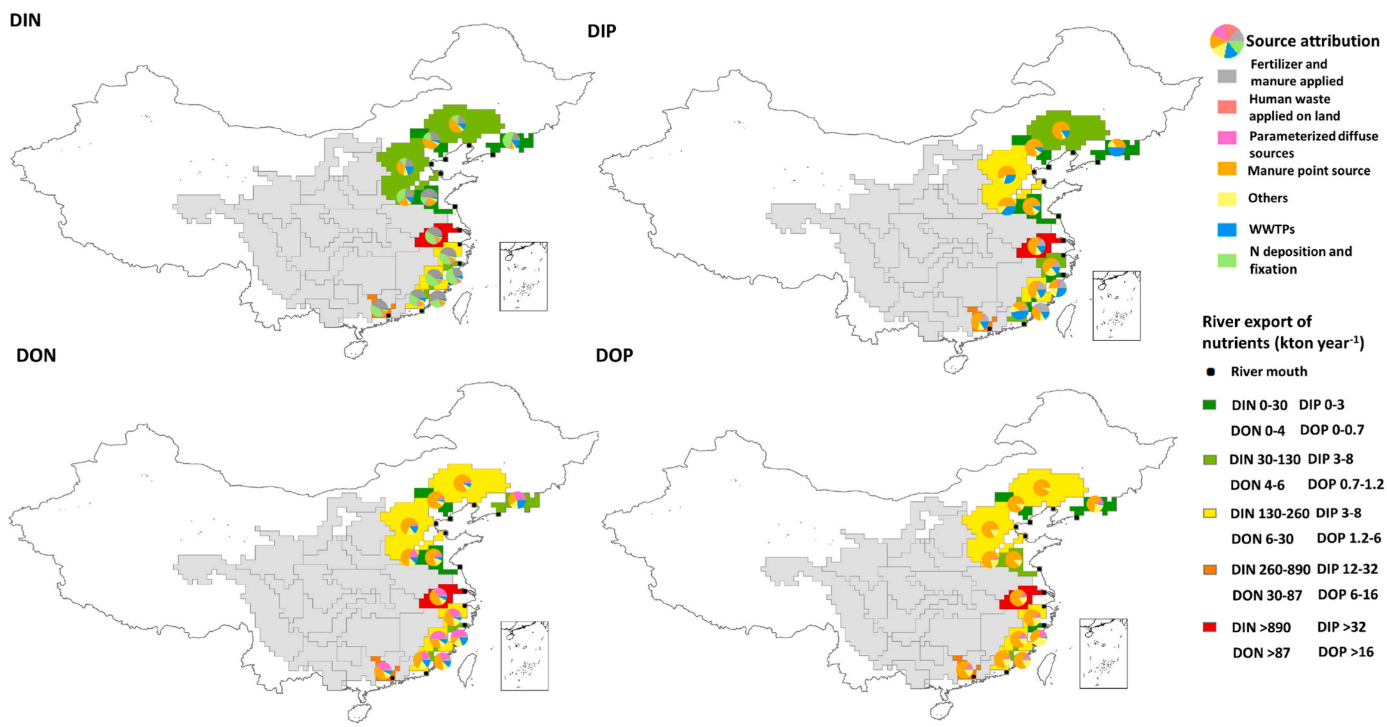


Fig. 9. River export of dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorous (DIP), dissolved organic nitrogen (DON), dissolved inorganic phosphorous (DOP) (kton year^{-1}) from 12 Chinese rivers by source in 2012. Sources are divided into four categories. 'WWTPs' (color blue) refer to nutrients in streams from human waste that are discharged from wastewater treatment plants. 'Manure point source' (color orange) refers to nutrients from the direct discharges of animal manure. 'Others' refer to DIN and DIP in streams from direct discharges of the human waste from urban and rural population that are not connected to sewage systems. Diffuse sources are then divided into four sub-categories. First sub-category is fertilizer and manure applied on land (grey). Second sub-category is biological N_2-fixation by crops (for DIN) and by natural vegetation (for DIN), atmospheric N-deposition on agricultural and non-agricultural land (for DIN) (in green). Third sub-category is parameterized diffuse sources (purple). They are leaching of organic matter from agricultural and non-agricultural land (for DON and DIP), and weathering of P-contained minerals from agricultural and non-agricultural soils (for DIP). The fourth sub-category is human waste applied on land (from total population without connections to sewage systems) (pink). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

accounting to around 80% of the TDN exports and 85% of the TDP exports. Direct discharge of animal manure dominates and is responsible for 65%–83% of DIP, DOP and DON exports to Bohai Gulf (Fig. 9). For DIN, direct discharge of animal manure, fertilizer and manure applied on land, and N-deposition and -fixation are equally important, accounting around 18%–32% exports (depending on sources). Human waste emitted from WWTPs contributes more than other sources except for manure discharges to DIP exports, accounting for 24% of DIP exports to Bohai Gulf. The South China sea receives 24% and 14% of the total river export of TDN and TDP, respectively. The Pearl river contributes to 83%–85% of nutrient export to coastal waters, while Hanjiang is responsible for the remaining part. Direct discharge of manure accounts for 42%, 50% and 71% of DON, DIP and DOP entering the South China Sea. The second largest source is the discharge of uncollected human waste for DON and DOP exports (12%–13%). For DIP, human waste emitted from WWTPs is responsible for 17% of total DIP exports. Diffuse sources include fertilizer and manure applied, N- deposition and -fixation account for 82% of DIN entering South China Sea.

The East China Sea receives most of the nutrient inputs to seas, accounting for 54%–45% of the total TDN exports and TDP exports. More than 80% of TDN and TDP are exported from the Yangtze river. The main sources of nutrient export to East China Sea are fertilizer and manure applied (for DIN), N-deposition and fixation (for DIN), direct discharge of animal manure (for DON, DIP and DOP), human waste emitted from WWTPs (for DIP). Huai and Yalu rivers are two rivers flowing into Yellow Sea, contributing to 3–4% of total TDN and TDP export to seas. Direct discharge of manure accounts for 62–83% of DON, DIP and DOP export while fertilizer and manure applied and N-fixation and -deposition are responsible for 65% of DIN entering the Yellow Sea. Human waste emitted from WWTPs contribute 18% of DIP exports.

We used the ICEP indicator to assess the potential coastal eutrophication associated with nutrient export by the 12 Chinese rivers (Figs. 8 and 9). The calculated ICEP values range from – 2 to 31 C km^{-2} year^{-1} between the different river basins. All rivers but one have positive ICEP values, indicating a high potential for coastal eutrophication along the coast of China. Among the four seas, Bohai Gulf has the highest average ICEP value (14) while South China Sea has lowest (5) (Fig. 8).

4. Discussion

Here we discuss our spatially-explicit results of surface water quality and river export of nutrients to coastal seas (4.1) and uncertainties in our newly developed model and simulation results (4.2).

4.1. Comparison of surface water quality and river export of nutrients to coastal seas

In our study we compared our spatially-explicit nutrient modelling results with official reports of the Surface Water Quality, presenting monthly and annual water quality classes (Tables S1 and SI). In general, our modelled water quality classes based on N and P are in line with the reported pollution classes based on the measurements for Chinese rivers. On the national level, the Annual Water Resource Bulletin for year 2012 reports that 33% of streams ('single indicator' approach, section S2.2 in SI) are highly polluted (above class 3), compared to our modelled results of N (NH_3) and P (TDP) based on 'single indicator' approach quantifying that 31% of streams are above quality class 3. For most rivers, TP is the main pollutant, which is in line with our model results. The spatial distribution of pollution levels and quality classes resembles with the measurements. Huai, Hai and Liao basin are the most polluted river basins, where both our modelled and the measured reported data show that more than 60% of the streams are highly polluted (i.e. above quality class 3). The south-west and north-west rivers have the best water quality, and here both our modelled and the reported data show that there are less than 10% of streams highly polluted in these regions. For the main river basins that drain into seas, the water quality of Changjiang, Zhujiang, South-east rivers are relatively better and this resembles with the measurements. For south-east rivers, we modelled relatively higher pollution level (43%–50% of the streams above class 3 based on TDP and NH_3 respectively) compared to measurements (21%). The higher percentage of polluted rivers particular for NH_3 might be due to the conversion ratio of NH_3 and DIN of these basins, which is the average value derived from all other river basins (Tables S5 and SI). The conversion ratio of Hai and Huai (up to 50%) is included while the river mouth of Changjiang and Zhujiang which is close to these river basins show less than 10% of NH_3 in total DIN. This might cause overestimates of NH_3 pollution in these rivers. For Zhujiang, we also modelled higher pollution level than measurements (56% vs. 27% of the streams above class 3 based on 'single indicator' approach). These higher estimates for NH_3 pollution for our model results compared to the reported data can be explain by the relatively higher conversion ratio of NH_3 and DIN that we derived for Zhujiang. The studies included are mostly for river mouth and downstream of Zhujiang, where the highly urbanized cities such as Hongkong and Shenzhen are located. Previous studies show that the ratio of NH_3 and DIN in highly urbanized basins are distinctly higher than in river basins with moderate or limited urban areas (Li et al., 2014; Zhang et al., 2015). For the Yellow river, our simulated and pollution levels (quality classes) correspond well with the reported classes, with the 40% (modelled) versus 45% (measured) of the streams ('single indicator' approach) above quality class 3.

We compared the modelled river export of DIN, DIP, TDN, and TDP with measurements (section 2.2). According to the model performance standards (Moriasi et al., 2007), our model shows a good performance for R^2, NSE and RSR (section 3.1). Our validation results indicate that the model overestimates river export of P for the Yellow river and both N and P for the Liao river. One reason for this lower model performance could be the large variability in measured discharge and concentrations, which directly impact the subsequently the measured loads (Table S3) in these two river basins. The relatively large variability in the measured loads indicates that the measured nutrient concentrations (for certain time intervals) may not represent the actual annual loads. Moreover, the overestimations in simulated loads in these two basins could be explained by underestimations of in-stream retention processes. In addition, the suspended sediment loads in the Yellow and Liao river are substantially higher than in other basins (Song et al., 2016; Yang et al., 2017). Previous studies have shown that higher sediment concentrations can result in higher N losses from coupled 'nitrification and denitrification' and higher absorption of P in streams (Pan et al., 2013; Xia et al., 2018). The national average value of $V_{f,E}$ that we applied to all basins and which represent the biochemical processes of in-stream retentions of nutrients could potentially be lower in the Yellow and Liao river basins due to the high sediment concentrations.

In addition, our modelled river exports are within the range reported by previous modelling studies for China. Liu et al. (2018) showed a simulated 5708 kton of TN and 371 kton of TP export with the IMAGE-GNM model for Changjiang (year 2010). Wang et al. (2020b) modelled 2373 kton of TDN and 344 kton of TDP export for Changjiang river (year 2012). Our modelled TDN export of 2625 kton is within the range of these studies. Our modelled TDP export of 173 kton is lower than the TP export from Liu et al. (2018). This might be due to the disregard of particulate P in our model, which could be up to 40% of TP (Shen and Liu, 2009). The differences between our model and MARINA 2.0 (Wang et al., 2020b) mainly results from the modelling approach of river retentions, i.e. retentions on sub-basin versus on gridded (0.5°) scale. For Pearl basin, Ti el at (2013) quantified river export of 536 kton of N for the year 2010, while we quantified 1215 kton of TDN for the year 2012. These discrepancies result both from different estimates of pollutant inputs to rivers and contributing sources, and differences in river retentions. For example, Ti et al. assumed that 22% of manure was directly discharged, while our study quantified a national average of 35% of direct manure discharge to water bodies. In addition, Ti and Yan (2013) used a constant coefficient on basin scale for river retentions while we include more processes on grid scale to represent retention, which may also partly explain the discrepancies in our results. Our source attribution of the nutrient export by Chinese rivers entering to coastal seas are in line with the results from MARINA 2.0 (Wang et al., 2020b). For three Chinese Seas, direct discharge of manure is important source of DIP, DON and DOP according to both models (57%–88% of total export from MARINA 2.0 and 45%–82% from our study). For DIN, both models agree that direct discharge of manure is the dominant source of DIN export to the Bohai Gulf, while the use of synthetic fertilizer, N-deposition and -fixation dominate DIN export to the Yellow Sea, East China Sea and South China Sea.

4.2. Model uncertainties

We recognize the impacts of uncertainties in our modelling study and address them in terms of model structure, inputs and parameters. First, the uncertainties in the model structure are mainly related to the simplifications of the 'annual steady-state' of the model. The 'steady-state' implies that: (1) the nutrients are permanently retained and lost, and do not return to river systems within the annual time-step; (2) the nutrient accumulated load and concentration (as in-stream surface water quality) represent the theoretical annual average pollution level of the river sections, ignoring the seasonal temporal variations and inter-annual memory of the soil-groundwater system (Sharpley et al., 2013). Accounting these temporal variations on such spatial scale has been hampered by data availability of nutrient inputs and measurements. We consider our approach appropriate for annual average assessment for such large scale (whole China) taking into account the balance between model complexity and data requirement.

Second, uncertainties in model inputs exist. Model uncertainties of nutrient inputs to rivers are discussed in detail in Chen et al. (2019) including uncertainties in land use data, WWTPs, manure farms. Uncertainties in estimates of source attribution differs per source. We calculated that direct discharge of manure and diffuse sources such as fertilizers and N deposition are dominant sources of nutrients in rivers. Uncertainties in direct discharge of manure, are associated with uncertainties in the discharge rates for counties, which are derived from field surveys and expert knowledge (Bai et al., 2016; Wang et al., 2018). The fertilizer applied is from Chinese county statistics, which is considered a reliable data source in China, but not without uncertainties. For N deposition, we include the dry and wet N deposition rates for the year 2012 following Wang et al. (2018), which are based on the data from a nationwide monitoring network (details in Xu el al (2015) and Liu et al. (2013)). We calculate the total N deposition as the product of deposition rate and agricultural area or natural area. For future studies, we hope to incorporate the site-specific inputs of N deposition rates. Next to this, there are uncertainties associated with the model inputs for in-stream river pollution, related to the simulated discharge. In our study we used extracted results for China from the VIC hydrological model which was run at the global scale at 0.5° (van Vliet et al., 2016a; Van Vliet et al., 2016). VIC has been validated using daily grid-based (0.5° × 0.5°) observed records of the streamflow for 1557 river monitoring stations showing a realistic representation of the observed conditions for stations globally (van Vliet et al., 2016a; Van Vliet et al., 2016). We calculated the 30-years average gridded discharge over the 1970–2000 period. Although the discharge is not changing dramatically for the current year 2012, this difference in reference year may influence the estimation of nutrient concentrations. The river network is based on the DDM30 flow direction map (Döll and Lehner, 2002), which has been validated and calibrated against rivers globally. We compare the derived streamlines with actual river flows in China (Fig. 1C) and concluded that the rivers are represented well by the modelled network. In addition, inherited uncertainties exist in the derived river section measurements database and are discussed in section S2.2 in the SI. We also realize that we do not include aquaculture as a source of nutrients. The IMAGE-GNM model indicates that aquaculture can be an important source of nutrient pollution in some regions (Chen et al., 2020; Wang et al., 2020a). In next versions of our model we could include this additional source.

Third, uncertainties exists in the model parameters we derived from existing studies. For example, we apply the global calibrated constant value in the quantifications of $V_{f,E}$ ((Eq. (4)) that represents the biological process of river in-stream retentions for Chines rivers. The recalibration for China is limited by data availability. The global constant of 35 for N (Wollheim et al., 2008c) may leads to a conservative estimate of in-stream nutrient retentions in our model. The calibrated data used in the study only accounts for denitrification while neglecting the effect of ‘coupled nitrification and denitrification’ from sediment that additionally removes N, besides the denitrification. Thus it is the conservative estimate of the in-stream retentions for N. Moreover, the calibrated value is for total N and total P (Marcé and Armengol, 2009; Wollheim et al., 2008c), while we applied the value directly to DIN and DIP and introduce the bioavailability adjustment factor (Eq. (4)) derived from literatures (Table S2) for organic forms. Existing nutrient models do not account for different nutrient forms or assume zero in-stream retentions of organic nutrient forms. However, studies have demonstrated the ability of the rivers to utilize the organic nutrient forms (Nausch and Nausch, 2007; Shi et al., 2016; Wiegner et al., 2006).

Large-scale models for nutrient pollution include full calibrated models (e.g. SWAT (Arnold et al., 2012)), and full processed based models (e.g. IMAGE-GNM (Beusen et al., 2015)). Our model is an intermediate, with a largely processed based approach and only a few calibrated parameters, in line with the earlier versions of the MARINA model and Global NEWS (Mayorga et al., 2010; Strokal et al., 2016a). A fully calibrated model at the scale of China is not preferred, because of lack of data. For future calibration of the model, the required data includes measurements and bio-geographical data, such as comprehensive measurements of in-stream concentrations by nutrient forms, nutrient export by soil on site scale, rates of nitrate uptake and denitrification in rivers, and streambed environments. The data could be used to calibrate processes such as the retentions of nutrients in soil and the in-stream retentions by Chinese rivers.

Despite these uncertainties, we consider our model approach as appropriate for analysing the in-stream water quality and associated sources. We consider our data sources as reliable (e.g. county statistics or validated modelled outputs) and include state-of-art modelling datasets (e.g. surface water quality measurements, WWTPs database). Moreover, the model is evaluated and shows that our modelling estimates correspond well with measurements of pollution levels and water quality classes. Our model and derived results can therefore provide a valuable basis in supporting effective management policies of nutrient pollution in China.

We address the novelties of our model in the context of existing nutrient models. First, our model aims quantifies pollution levels in surface waters, and the associated source attributions for different nutrient forms (DIN, DON, DIP and DOP). Other global models typically quantify total N and P, and not the different forms (Beusen et al., 2015; McCrackin et al., 2013). Second, we consider our spatial level of detail unique. Our model quantifies water quality for river sections, which differs from the basin scale in Global NEWS-2 and early versions of the MARINA model (Mayorga et al., 2010; Strokal et al., 2016a). Our multi-scale modelling framework bridges the biophysical and administrative scales, which we consider an important step towards an improved understanding of the impacts of administrative drivers/policies on water pollution. Our source attribution estimates on multiple scales support policy making. Models like SWAT and Quals are particular popular in developing countries to model in-stream water quality for specific watersheds (as summarized in Costa et al. (2019)). However, these focus on biophysical scales only, while we can provide source attributions on multiple scales, including administrative scales to support policy-making in water management. Third, our model requires less input data than some other models, as we aimed for an efficient balance between data requirement and process descriptions. This is different for, for example, an application of the IMAGE-DGNM model that calculates in-stream concentrations of TN, NH4 and NOx-for the Mississippi and Rhine basins. Our model quantifies multiple nutrient forms for whole China with moderate input requirements. This comes, however, with limitations in terms of the number of processes explicitly modelled. Compared to models such as IMAGE-DGNM (Vilmin et al., 2020) our model takes a more simple approach to model dynamics in processes within rivers and groundwater.

5. Conclusion

Our study contributes to a better understanding of the spatial variation in in-stream water pollution by nutrients, their sources and how they compare with reported water quality classes in China. For this, we developed the MARINA 3.0 model that accounts for the combined effects of nutrient inputs to rivers, retentions of nutrients and transport of nutrients by the river network. We link our modelling results for year the

2012 with measurements of in-stream water quality classes across river sections. The validation results show that the model compares reasonably well against measurements. To our knowledge, this is the first attempt to couple an integrated nutrient model with the official monitoring network of surface water quality classes on the large scale (whole China).

The modelled results could help to formulate and evaluate region-specific water management policies targeting the main sources to improve in-stream water quality in China.

Our main findings are:

- Between 12% and 66% of the streams are highly polluted (above water quality class III). The pollution is different among nutrient forms. We thus argue that water quality models and the national monitoring programs need to consider the different nutrient forms. This may not only help to better evaluate the ecological impacts of nutrient pollution but also improve the understanding of N-retention processes.
- Diffuse sources dominate in over two-thirds of the streams for DIN. Point sources dominate in around half of the streams for DON, DIP and DOP. To better understand the ecological impacts of different nutrient forms, future research should consider compound indicators accounting for both N and P to assess the environmental impact of nutrient pollution in surface water, such as the 'ICEP' indicator for coastal seas.
- Polluted streams and rivers contribute to coastal eutrophication along Chinese coasts. In particular, high potentials for coastal eutrophication are calculated for the Bohai Gulf.

CRediT authorship contribution statement

Xi Chen: Conceptualization, Methodology, Software, Writing – original draft. **Maryna Strokal:** Conceptualization, Supervision, Writing – review & editing. **Michelle T.H. van Vliet:** Conceptualization, Supervision, Writing – review & editing. **Xing Fu:** Data processing, Software. **Mengru Wang:** Data processing, Software. **Lin Ma:** Conceptualization, Supervision, Writing – review & editing. **Carolien Kroeze:** Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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