Global riverine N and P transport to ocean increased during the twentieth century despite increased retention along the aquatic continuum

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Abstract

Various human activities, including agriculture, water consumption, river damming, and aquaculture, have intensified over the last century. This has had a major impact on nitrogen (N) and phosphorus (P) cycling in global continental waters. In this study, we use a coupled nutrient-input, hydrology, in-stream nutrient retention model to quantitatively track the changes in the global freshwater N and P cycles over the 20th century. Our results suggest that, during this period, the global nutrient delivery to streams increased from 34 to 64 Tg N yr^{-1} and from 5 to 9 Tg P yr^{-1}. Furthermore, in-stream retention and removal grew from 14 to 27 Tg N yr^{-1} and 3 to 5 Tg P yr^{-1}. One of the major cause of increased retention is the growing number of reservoirs which now account for 24% and 22% of global N and P retention/removal in freshwater systems, respectively. This increase in nutrient retention could not balance the increase in nutrient delivery to rivers with the consequence that river nutrient transport to the ocean increased from 19 to 37 Tg N yr^{-1} and from 2 to 4 Tg P yr^{-1}. Human activities have also led to a global increase in the molar N:P ratio in freshwater bodies.

1. Introduction

Through ever-increasing food production, land-use change, production and application of fertilizer, discharge of human and animal waste, and combustion of fossil fuels, humans have perturbed the earth surface by the additional mobilization of essential nutrients such as nitrogen (N) and phosphorus (P) (Stumm, 1973; Galloway et al., 1995; Bouwman et al., 2013c; Morée et al., 2013). Deforestation and expanding agricultural land use have caused increasing sediment, carbon (C) and nutrient delivery to and transport through river systems (Seitzinger et al., 2010), which can influence photosynthetic and heterotrophic production and cause dramatic changes in aquatic ecosystems (Vollenweider et al., 1992; Cloern, 1996; Dodds, 2002). Eutrophication resulting from nutrient loading first manifested in lakes and rivers in the form of excessive growth of macrophytes and floating algal scums (Butcher, 1947). In serious cases, eutrophication of surface waters leads to turbid waters with decreased oxygen concentrations (hypoxia), production of toxins by algae and bacteria, and fish kills (Diaz and Rosenberg, 2008). These changes in ecosystem functioning due to elevated nutrient loading also have consequences for the efficiency of C and nutrient processing within aquatic ecosystems (Soetaert et al., 2006; Mulholland et al., 2008).

Another major human perturbation of freshwater nutrient cycling is related to human impacts on hydrology. For securing food production, humans influence the hydrology in many rivers by extracting irrigation water from the river or from constructed reservoirs; for reducing flood risks, or securing navigability, many rivers have been canalized by dam construction; for securing energy supply, humans have constructed hydropower dams (Lehner et al., 2011). These changes in hydrology have consequences for nutrient transport through and removal in aquatic ecosystems because they impact the travel time of water along the aquatic continuum (Wisser et al., 2010). Construction of the dams disconnects up- and downstream parts of rivers and the reservoirs act as filters thereby changing nutrient ratios (i.e. stoichiometry) (Billen et al., 1991).

Such human-induced changes in hydrology and nutrient delivery ~~both~~ have consequences for nutrient transport through and retention in aquatic systems conformed by the soil, groundwater, riparian zone, streams, rivers, lake, and reservoir continuum, and eventually nutrient delivery to the oceans (Bouwman et al., 2013b). International, collaborative research programs such as Global NEWS have generated estimates for the global nutrient delivery to the ocean based on lumped statistical models ignoring spatially explicit and mechanistic information (Mayorga et al., 2010; Seitzinger et al., 2010). Although providing useful data on present-day nutrient loadings and deliveries to the ocean, these statistical models do not allow hindcasting or forecasting of nutrients in freshwater systems. In order to better understand, attribute the causes of changing biogeochemistry and more accurately project future trends in riverine nutrient loadings and ratios, it is pivotal to use modelling tools that resolve spatial and temporal variability of nutrient inputs, that accommodate changes in hydrology and that include nutrient transformation and retention processes.

The objective of this study is to analyze global long-term changes in the delivery and retention of N and P during transport from land to sea using the Integrated Model to Assess the Global Environment – Global Nutrient Model (IMAGE-GNM) (Beusen et al., 2015). We analyze the relative importance, trends and spatial variability of nutrient retention in the various landscape components in different parts of the world during the 20th century, as this period encompasses dramatic changes in human population and economic ~~human~~ activities. We also investigate the temporal changes in total N versus total P, as this ratio controls the biogeochemistry and the functioning of aquatic ecosystems (Billen et al., 1991). This paper thus presents the first gridded (0.5 by 0.5 degree) approach to track and quantify N and P cycling throughout the continental aquatic system. Our model includes the interactions between human-induced changes in climate, hydrology and nutrient loading. The hydrological system incorporates a distributed river model that merges both terrestrial and aquatic aspects and includes groundwater and upland areas, wetlands, riparian zones and floodplains, and reservoirs. The data discussed in this paper are available from http://dx.doi.org/10.17026/dans-zgs-9k9m ~~<<Arthur>>~~. This includes modelled N and P river input, retention and export for all rivers in our model (grid information), as well as modelled river export per river.in table format~~xx and yy.~~

2. Data and methods

The IMAGE-Global Nutrient Model (IMAGE-GNM) (Beusen et al., 2015) is a global, spatially explicit, distributed model that couples IMAGE (Stehfest et al., 2014) with the global hydrological model PCR-GLOBWB (Van Beek et al., 2011) as the basis for describing flow and retention/removal of N and P delivery from soils to surface waters. IMAGE-GNM can study the impact of multiple environmental changes over prolonged time periods. Next to existing tools for estimating N delivery to surface water (Van Drecht et al., 2003; Bouwman et al., 2013a), IMAGE-GNM now includes models for (i) P delivery from natural and agricultural ecosystems, (ii) nutrient input from allochthonous organic material from vegetation in floodplains, (iii) N and P delivery by wastewater discharge from urban areas and aquaculture, and (iv) ~~following Wollheim et al. (2008)~~, IMAGE-GNM uses the nutrient spiraling approach (Newbold et al., 1981) to describe in-stream retention of both N and P with a yearly time step (following Wollheim et al., 2008). A detailed description of IMAGE-GNM is given in Beusen et al. (2015), with additional validations provided in Supplementary Materials.

The data flows in IMAGE-GNM including PCR-GLOBWB are presented in Figure 1a. Spatial land cover distributions for the 20th century are from HYDE (Klein Goldewijk et al., 2010) and IMAGE (1970 onwards). Global climate data are used in PCR-GLOBWB for computing the water balance, runoff and discharge for each year. For each grid cell, IMAGE-GNM provides the delivery of N and P to the surface water via diffuse sources (agriculture, natural ecosystems, aquaculture) and point sources (wastewater) (Figure 1b). Soil nutrient budgets (the difference between inputs and outputs) are calculated for each grid cell (Figure 1b). Nitrogen inputs considered are fertilizer, animal manure, atmospheric deposition and biological N fixation. Phosphorus inputs are fertilizer and animal manure. Nutrient outputs are withdrawal by agricultural crops in harvested parts and by grazing or mowing of grass and ammonia volatilization. Natural ecosystems are assumed to be mature (i.e. net withdrawal is zero), except for vegetation in floodplains where part of the litter is ~~assumed to be~~ transported by the water.

Each grid cell receives water containing N and P from upstream grid cells, and from diffuse and point sources within the grid cell. After accounting for in-stream retention, water and nutrients are transported to downstream grid cells. Discharge is routed to obtain the accumulated water and nutrient flux in each grid cell, through rivers, lakes, wetlands and reservoirs (Figure 1c). The model accounts for the “memory” of groundwater, where travel times may amount to several decades. Cumulative N storage in deep groundwater between 1900 and 2000 amounted to around 376 Tg (Bouwman et al., 2013a).~~,~~ T~~and t~~he retardation due to this ~~memory~~cumulative reservoir varies considerabl~~e~~y depending on the history of fertilizer use and manure management, as well as the geohydrological situation and climate (Van Drecht et al., 2003). In addition, the soil component has a memory, which is the change in soil P content due to accumulation in grid cells with a surplus, or loss due to surface runoff.

We compare the model sensitivity for three years (1900, 1950 and 2000) because with human acceleration of the global N and P cycles, the magnitude and relative importance of the different natural and anthropogenic nutrient sources changes. Moreover, nutrient processing within aquatic systems may change with nutrient loadings (Soetaert et al., 2006). The model sensitivity was investigated using Latin Hypercube Sampling, with uncertainty ranges for 48 model parameters for N and -34 for P (Table SI 3), respectively, and expressed using the standardized regression coefficient (SRC), to compare model output of N and P delivery, retention, and river export to the river mouth. A detailed description of the approach for the sensitivity analysis is in SI3.4.

3. Results and discussion

Before presenting and discussing model outcomes at the continental to global scale in detail, ~~it is instructive to~~we compare local model predictions with observed data. Beusen et al. (2015) compared model results with the discharge-weighed annual mean calculated from long-term time series (from 1970 onwards to most recent years, depending on the station) of observed concentrations and discharge for 125 European rivers, and for the ~~river~~ Mississippi river (11 stations), and the rivers Rhine and Meuse. In this paper ~~Here~~ we show details ~~additional~~ of the model predictions and compare those with long-term time series for stations in the Danube in Hungary, Missouri in the USA and Ångermanälven in Sweden (Figure 2). Simulated trends and interannual variability of nutrient concentrations for these stations show good agreement with reported concentrations. In general, the Root Mean Square Error (RMSE) for observed versus modelled total N and total P concentrations was less than 50%, which was considered acceptable for model predictions at the global scale (Beusen et al., 2015). There are various possible explanations ~~Where the disagreement of the~~for the larger model and observation~~s was larger~~ discrepancies (RMSE>50%), ~~there are various possible explanations~~. First, with an annual time step the model is not able to reproduce peaks in measurements. Accordingly, if these peaks were actually covering only a short period, the calculated annual aggregate from the measurements may be an overestimate, especially if the number of measurements in a year is small. Secondly, in small river basins the spatial data for both diffuse and point sources of the IMAGE model (0.5 by 0.5 degree) may not be realistic, particularly wastewater which is assumed to be discharged in all urban grid cells of the model, while in reality discharge takes place at discrete locations (e.g. wastewater treatment plants). Beusen et al. (2015) subjectively excluded river basins from the comparison with European data with a basin~~n~~ area <10,000 km^2, which is about four grid cells for our 0.5 by 0.5 degree resolution.

After this validation with long time series for a range of stations in rivers differing in size, climate and geological setting, we are confident that our model can simulate fluxes at the scale of continents or oceans with reasonable accuracy. We applied our IMAGE-GNM to calculate the changes in the continental and global nutrient flows for the twentieth century. The next sections present the temporal variation in nutrient sources (3.1), nutrient retention in rivers (3.2), nutrient export to coastal marine ecosystems (3.3), and the model sensitivity with changing anthropogenic acceleration of nutrient cycles (3.4). Finally results are put in perspective in section 3.5.

3.1. Temporal variations in nutrient sources

Expanded agricultural activity and the concomitant rise in fertilizer usage have dramatically increased the global soil N budget, even with the massive deforestation and subsequent reduction in N_2 fixation. These changes are particularly evident after 1950, especially in the basins that drain toward the Pacific Ocean, where the soil N budget saw a more than threefold increase, and for those draining in the Mediterranean Sea and the Black Sea, where they more than doubled. The rise in P has been even more dramatic. The global P soil budget in 1900 was only 5% of that in 2000 and was negative in many places (i.e. soils mining or deficit), but became positive (i.e. soil P accumulation or surplus) in the aforementioned basins by 1940

Bouwman et al., 2013c). ~~Although~~ T~~t~~he N:P ratio in fertilizers has been increasing since the 1970s (FAO, 2015).~~,~~ However, this change has been compensated by ~~N losses via volatilization coupled to~~ the expansion of livestock production, which produces high-P manure (Bouwman et al., 2013c). ~~, have led to a decrease in the N:P soil molar ratio between 1900 and 2000, with the exception of the basins draining in the Atlantic Ocean.~~ Soil P surpluses accumulate as residual soil P in many regions, especially near industrialized countries, India, and China, where it can stimulate future crop and grass production (Sattari et al., 2012).

Agriculture has grown to become the dominant nutrient source to the surface waters at a global scale. From 1900 to 2000 its contribution rose from 6 Tg N yr^{-1} (19% of total) to 33 Tg N yr^{-1} (51% of total) and from 2 Tg P yr^{-1} (35% of total) to 5 Tg P yr^{-1} (56% of total). This contrasts starkly with the contribution from natural sources, which has shown a decrease of 25 to 22 Tg N yr^{-1} (from 74% to 34% of the total N delivery), while P from natural sources was stable at 3 Tg P yr^{-1} (but its share decreased from 62% to 32% of the total P delivery), during the same time period. Global N delivery to surface water increased from 43 to 67 Tg yr^{-1}, and global P delivery from 5 to 9 Tg yr^{-1} (Figure 3). Similar to the soil budgets, the nutrient increase has been most pronounced for the basins draining into the Pacific Ocean, the Indian Ocean, and Mediterranean Sea and Black Sea. Basins draining into the Indian Ocean are close to the global average (~90% increase), while those draining in the Arctic Ocean, the Atlantic Ocean and endorheic rivers increase more slowly than the global average (Figure SI2, SI3 and Movie SI1, SI2).

While the modeled global increase of nutrient delivery was steady, similar to the Atlantic and Indian Ocean, the delivery ~~showed acceleration~~accelerates after the 1970s in the Pacific Ocean and Indian Ocean. Delivery to the Atlantic Ocean ~~,~~ ~~stabilization or slowing down of changes in the Atlantic~~ slowed down after 1970, whereas delivery ~~and a~~ decreases after 1980 in the Arctic Ocean, Mediterranean Sea and Black Sea and endorheic rivers (Movies SI1 and SI2). These patterns reflect the changes in the contribution of the various sources. Globally, the simulated contribution of natural vegetation in floodplains is large and almost constant in absolute terms, but its relative share decreased due to increases in other sources (Movie SI3 and SI4). Most increases came from diffuse sources, i.e. globally from 31 to 54 Tg N yr^{-1} and from 5 to 8 Tg P yr^{-1}. The delivery by diffuse sources ~~in~~ to the Pacific Ocean (30% for N, 29% for P) and Atlantic Ocean (43% for N and 31% for P) ~~regions both~~ contributed to a large share ~~to~~ of global diffuse delivery in 2000. Globally, the relative increase between 1900 and 2000 was more rapid for N (73%) than for P (69%), and more rapid for rivers draining into the Pacific Ocean (225% for N and 119% for P) than for all other rivers. Rivers draining into the Atlantic showed a slower increase (28% for N, 37% for P) than the global average~~, and t~~. The changes in the Indian Ocean and Mediterranean Sea and Black Sea are similar to the global average.

The contribution of agriculture (surface runoff, groundwater) increased most in the regions draining into the Pacific Ocean (1 Tg yr^{-1} or 20% of the total N delivery in 1900 to 13 Tg yr^{-1}- or 64% in 2000) and Indian Ocean (1 Tg per yr^{-1} or 32% of total delivery to 5 Tg yr^{-1} or 59%, ~~) regions (~~Figure SI2 and SI3). Agriculture is an important N source in the Mediterranean region (44% in 1900 to 57% in 2000 ~~and~~

~~peaking~~with a peak in the 1980s). ~~The Atlantic region is dominated by large rivers such as the Amazon and Congo~~Large rivers such as the Amazon and Congo dominate delivery to the Atlantic Ocean, and natural ecosystems are important sources (82% of total N delivery in 1900, decreasing to 51% in 2000). Surface runoff is a very large source of N and P globally (16% of total delivery in 1900 and 22 in 2000 for N; 51% in 1900 and 62% in 2000 for P), particularly ~~in~~ to the Mediterranean Sea, Indian Ocean and Pacific ~~region~~Ocean, ~~and~~ but less so ~~in~~ to the Atlantic Ocean.

Delivery of N and P by aquaculture showed a dramatic increase after 1950, but remains small compared to ~~the~~ diffuse and natural sources. Atmospheric deposition also increased, but its contribution also remains small. Locally, however, aquaculture and atmospheric N deposition may be important and even dominant (Movies SI3 and SI4).

The world has also experienced a remarkable increase in nutrient point sources ~~for nutrients~~ (Van Drecht et al., 2009; Moree et al., 2013)~~. (~~, Figure SI2 and SI3 and Movies SI3 and SI4). Globally, the contribution of point source delivery increased from 4-5% in 1900 to 12% in 2000 for both N and P, in absolute terms from 2 to 8 Tg N yr^{-1} (+340%) and from 0.2 to 1 Tg P yr^{-1} (+500%) between 1900 and 2000. The increase is slightly lower than the global average in most regions, but for the basins draining into the Pacific Ocean (factor of 12 for N and 17 for P) and Indian Ocean (factor of 39 for N and 50 for P) the increase is much more rapid. In most regions point sources contribute 12% or less to total N delivery except for basins draining to the Mediterranean Sea and the~~and~~ Black Sea, and also for ~~and~~ endorheic river basins~~s~~ (26% and 17%, respectively).

The molar N:P ratio of total nutrient delivery showed small variations in the course of time in most parts of the world (globally 14-16; Arctic Ocean 13-15; Atlantic Ocean 20-23; Indian Ocean 11-13; Mediterranean Sea and Black Sea 9-11; endorheic rivers 8-11~~) (~~, Figure SI4). However, the changes were much larger in the Pacific Ocean (constant at 11-13 in the first half of the century, and an increase to 17 from 1960 onwards).

3.2. N and P retention in rivers

Nutrient removal/retention (here forth referred to as retention) doubled between 1900 and 2000 (from 14 to 27 Tg yr^{-1} for N and 2.6 to 5 Tg yr^{-1} for P) at the global scale. In-stream retention increased much more in the Indian Ocean drainage basins (from 1.7 to 4.5 Tg N, or +157%; from 0.5 to 1 Tg P or +126%) and Pacific Ocean drainage basins (from 1.8 to 5.5 Tg N, or +212% for N; from 0.4 to 1.1 Tg P or +157%) regions. In ~~the~~ the regions draining into the Atlantic Ocean~~region~~ (where natural nutrient sources dominate), N removal increased from 8 to 11 Tg N yr^{-1} and that of P 0.9 to 1.5 Tg yr^{-1}. The retention fraction was rather constant (globally 41-45% of total delivery for N, and 53-58% for P) during the 20th century (Figure 4). There are large differences in the retention ~~between~~ in the regions draining into Mediterranean Sea and Black Sea (43-50% for N; 50-62% for P), Indian Ocean (37-52% for N; 53-66% for P), Pacific Ocean (28-32% for N; 37-42 for P), Atlantic Ocean (38-45% for N; 48-55% for P), with an increase in Atlantic and Indian regions in the last decades.

Total nutrient retention is the net result of ~~changes in the~~ retention in streams and rivers, lakes and reservoirs. N and P retention in streams and rivers has the largest contribution to total retention in all parts of the world, except endorheic systems. In 1900, rivers contributed 75% to total N retention of 14 Tg yr^{-1} and 82% of total P retention of 2.1 Tg yr^{-1} for P.~~;~~ I~~i~~n 2000, rivers accounted for 54% of the total N retention of 27 Tg yr^{-1}, and 63% of the total P retention of 5 Tg yr^{-1}. The global contribution of lakes decreased from 25% to 22% of total retention between 1900 and 2000, and that of P from 18% to 15%. ~~It is interesting to note that b~~Between 1900 and 2000, global retention in rivers increased from 10.7 to 14.6 Tg N (+37%) and from 2.1 to 3.2 Tg P (+51%), while the retention in lakes (3.6 to 6 Tg N yr^{-1} and 0.5 to 0.7 Tg P yr^{-1}) increased by 63% for both N and P.

Reservoirs played no role up ~~till~~ until the 1940s (retention of 1% of total retention of N and P) and strongly increased in the second half of the 20th century to 24% of total N and 22% of total P retention. In the year 2000, rivers draining into the Mediterranean Sea and Black ~~sea~~ Sea retained more N (36% of total N retention of 2 Tg yr^{-1}) and P (29% of P retention of 0.5 Tg yr^{-1}) than the global average due to the importance of retention in reservoirs.

Total N and P retention in rivers draining into the Pacific Ocean is less than the global average. Reservoirs play a smaller role in this part of the world, and also rivers and lakes retain ~~less~~fewer nutrients than elsewhere.~~;~~ T~~t~~he total N retention fraction slowly decreased due to the effect of increasing N concentrations in surface water, while the P retention fraction was less variable due to increasing retention in reservoirs, balancing the decreasing river retention (as a result of regulation of discharge downstream of dams).

3.3. N and P export to coastal marine ecosystems

In the 20th century the global river N export (19 to 37 Tg yr^{-1}, or +90%) showed a ~~more rapid~~faster increase than~~ that of P~~ P export (2 to 4 Tg yr^{-1} or +75%). The increase in export by rivers draining into the Pacific Ocean (3.7 to 14.7 Tg N yr^{-1}, increase by a factor of 4; 0.6 to 1.6 Tg P yr^{-1}, factor of 1.5) and Mediterranean Sea and Black Sea (0.9 to 2.1 Tg N yr^{-1}, +126%; 0.2 to 0.4 Tg P yr^{-1}, +80%) was much faster than in other parts of the world (Figure 5). The increase in P export was smaller than that of N in world regions. The differential increase of N and P explains the increase in the N:P ratio in rivers draining into the Pacific Ocean (13 to 20), Indian Ocean (14 to 18 since 1970), Mediterranean Sea and Black Sea (10 to 13).~~;~~ ~~there~~ There was no clear increase in the regions draining into the Atlantic ~~region~~Ocean (Figure SI5).

3.4. Model sensitivity as a function of human acceleration of nutrient cycles

A detailed discussion of the model sensitivity for the year 2000 has been presented in Beusen et al. (2015). Here we focus on the impact of the acceleration of nutrient cycles during the twentieth century on the model's sensitivity to changes in parameter values. Most parameters were varied within an interval of ±10% around the default value. We consider parameters to have an important influence ~~if their influence is~~when they are significant for global delivery, retention or river export, and in addition, they exert a variation >4% of the default model (Tables SI4 for N and SI5 for P).

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The influence of the~~ N budget in~~ natural ecosystem~~s~~ N budget on N delivery was clearly decreasing from 1900 onwards (SRC decrease from 0.38 to 0.20) and was only important (0.21) for river N export in 1900. Likewise, allochthonous organic matter input was more important for N delivery in 1900 and 1950 than in 2000. It ~~and~~ even exerts an important ~~though~~yet decreasing influence on river N export throughout the 20th century. P from allochthonous organic matter inputs was important for delivery and river export in 1900 (SRC = 0.23-0.24) while it was less important in 1950 and 2000. Weathering was important for P delivery in 1900 (SRC = 0.27) and 1950 (SRC = 0.23), and for river export in 1900 (0.21).~~;~~ P weathering is no longer important in the year 2000 due to the increasing delivery of P from fertilized fields and grazing land, and wastewater.

Met opmaak: Superscript

With a much smaller human population, less food and energy production in ~~the years~~ 1900 and 1950, the situation was different from ~~that in~~ the year 2000. Runoff had a smaller influence in the first half of the twentieth century than in the year 2000. Apparently, surface runoff was an important process for nutrient mobilization through leaching (N), surface runoff (N and P) and weathering (P) throughout the century. The influence of the agricultural N budget has been growing and became important in 2000, when its influence on N delivery to streams (SRC = 0.26) exceeded that of the N budget in natural ecosystems (SRC = 0.20). The influence of the P budget in agricultural fields has also been growing but remained an unimportant factor (SRC values < 0.20). The influence of the factors involved in the computation of P erosion (bulk density and P content of topsoil) was large in all years (SRC change from -0.54 to -0.63 for bulk density and 0.55 to 0.63 for P content between 1900 and 2000~~),~~). This influence has ~~and it seems to have~~ been ~~increasing~~ growing due to the increasing P inputs (fertilizer, manure) which partly determine P surface runoff, and due to the accumulation of P in agricultural soils in many world regions, particularly ~~in~~ during the second half of the twentieth century.

The influence of N and P discharge from wastewater on the global scale was small (SRC >0.2 only for P discharge in 2000) compared to other anthropogenic sources such as agriculture. The data show that with smaller population densities in 1900 and 1950 ~~than in~~as compared to 2000, wastewater also exerted a smaller influence on the delivery of both N and P in the first half of the twentieth century than in the year 2000. Finally, temperature has a large influence on in-stream retention (SRC values of 0.34-0.41 for N and 0.21-0.27 for P) and river N export (SRC values of 0.30-0.36~~N~~).

3.5. Results in perspective

Global estimates of current river N export vary widely, ranging from about 60 Tg N yr^{-1} (Seitzinger et al., 2005; Boyer et al., 2006) to 43 Tg N yr^{-1} (Global NEWS, Seitzinger (2010) and close to 40 Tg N yr^{-1} (Green et al., 2004). A previous version of our model with a constant global export coefficient yielded estimates of 54 Tg N yr^{-1} (Van Drecht et al., 2003) and 46 Tg N yr^{-1} (Bouwman et al., 2005). Our global river N export for 2000 of 36.5 Tg N yr^{-1} is on the low end of the range of estimates. Although the correlation of model predictions with total N concentration data for the early 1990s (Meybeck and Ragu, 1995) is better than with earlier versions of our model (Van Drecht et al., 2003), it is difficult to validate the global estimate, since the number of rivers included in this dataset is small.

Our model for N retention based on the spiraling concept is more sophisticated than earlier versions with a fixed retention rate of 30% (Van Drecht et al., 2003). Our global average N retention (43%) is larger, mainly due to the implementation of sub-grid retention in lower order streams. Moreover, our model accounts for heterogeneity due to hydrology, climate and N concentration. Our calculated N retention is less than the 53% computed with the spiraling concept globally by Wollheim et al. (2008). This disagreement may be due to differences in hydrology, N delivery and its spatial distribution. It is difficult to compare retention among models, since it also depends on the delivery to surface water. For example, Hejzlar et al. (2009) found in a model comparison that the simulated N and P retention showed larger differences among the models than between rivers.

To our knowledge, there is no global model for P river transport that includes in-stream processing~~,~~ available for comparison. Simulated global P export with our model (4 Tg P yr^{-1}) is much less than the Global NEWS estimate (9 Tg P yr^{-1}) (Seitzinger et al., 2010) and the 22 Tg P yr^{-1} estimated by Meybeck (1982) based on data for a limited number of rivers. Our model results are in fair agreement with a much larger number of ~~rivers (this paper and (Beusen et al., 2015));~~rivers. ~~given~~ Given the ~~strength~~ amount of each of the P sources and the range of uncertainty for each of them, global estimates for river P export exceeding 10 Tg yr^{-1} seem unrealistic.

In-stream biogeochemistry is simulated with separate uncoupled models for N and P, as different processes dominate N and P retention, i.e. denitrification and chemical sorption. Only in case of plant uptake and decomposition and mineralization ~~there~~ is there a close coupling of N and P (and C and Si). Simulated P retention reflects sorption of P in ~~the~~ reservoir~~sediments of reservoirs~~, lake,~~s~~ and stream,~~s~~ and rivers sediments. Nevertheless, IMAGE-GNM lacks a description of desorption processes in the case of exchange between the water column and P-saturated sediment material (Reddy et al., 1999; Richardson and Qian, 1999).

Particularly in the early 1900s, agricultural N and P soil budgets were small and for P even negative (Mediterranean and Pacific regions), P loss by surface runoff has caused a considerable depletion of soil P. Even in 2000, the delivery to streams of N and P from agricultural sources is a considerable fraction (40% for N and 34% for P) of global fertilizer use. N is very mobile in the environment, and there are various transport ways from soil to surface water (surface runoff, leaching, groundwater). P is lost primarily by surface runoff. In agricultural soils, the P loss is larger than in natural soils due to the internal manure cycle~~,~~ ~~and the primary cause of large P losses is the internal manure cycle in agriculture with~~ , such as grazing animals and manure spreading in cropland and grassland ~~which increases the mobility of P by surface runoff~~ (Smil, 2000).

About 56% of the global N retention of 27 Tg yr^{-1} in 2000 stems from agriculture. This implies that the equivalent of 17% of global fertilizer use of 81 Tg N was removed from the aquatic environment in global river basins. P retention is similarly about 20% of the global P use in 2000. ~~The equivalent of about 23% of global fertilizer N and 15% of fertilizer P are transported by rivers to the ocean~~Rivers transport the equivalent of about 23% of global fertilizer N and 15% of fertilizer P each year. Our data show that there is an enormous discrepancy ~~between~~ in the development ~~in~~ of N versus P fertilizer use. World consumption of N fertilizer rapidly increased from 10 Tg to 95 Tg N per year (increase by a factor of 10), while P fertilizer increased from 4.5 to close to 16 Tg P per year (increase by a factor of 3.5) ~~and~~. T~~t~~he molar N:P ratio increased from 5 to 13 during the 5 decades period of 1960-2010 (FAO, 2015). ~~In~~ The N:P river ratios ~~river~~ exported to the ocean the ~~N:P ratios~~ are often much larger, indicating that during processing and transport in soils, groundwater, riparian zones and streams, rivers, lakes and reservoirs, P is retained more efficiently than N.

Finally, many phytoplankton species causing harmful algal blooms take advantage from conditions of distorted nutrient conditions such as N:P away from the Redfield ratios (Glibert et al., 2014). Hence, our results point to a worldwide ongoing increase in N:P ratios in surface water, and with the simultaneous decrease in silicon export by rivers, non-siliceous harmful algae are increasingly favored in both freshwater and coastal marine ecosystems (Heisler et al., 2008;Glibert et al., 2012).

4. Concluding remarks

This paper presents the first global, spatially explicit modeling approach based on coupled hydrology, nutrient delivery to surface water, in-stream retention of N and P, that explicitly includes all major nutrient sources in aquatic ecosystems. Nutrient delivery includes diffuse sources (cultivated land and natural ecosystems, allochtonous biomass inputs in river floodplains, weathering, atmospheric deposition) and point sources (wastewater, aquaculture). Delivery is calculated for the full twentieth century to simulate river nutrient retention and transport to the oceans. Model results without specific calibration are in good agreement with time series of concentration measurements for a number of large and smaller rivers for which we could obtain measurement data.

While the regression models commonly used to estimate river nutrient export (Mayorga et al., 2010;Seitzinger et al., 2010) can provide information on the present-day transport of nutrients to the ocean, our coupled model can also be used to explore changes in various processes and interactions between them during the 20th century. We portray the dramatic changes that occurred during the 20th century in both delivery and in-stream retention due to expanding agriculture, increasing wastewater discharge, and increasing number of reservoirs..

Nutrient losses from agriculture and natural areas imply a constant flow of soil nutrients to the surface water and eventually to the oceans. The model results indicate important differences in N:P ratios in river export in different parts of the world resulting from the interplay of many processes and economic activities in different river basins. River export shows a world-wide increase in the molar N:P ratio during recent decades, primarily as a result of the stagnating P fertilizer and ever increasing N fertilizer use.

During the twentieth century, the type of parameters and their influence on the model results have changed as a consequence of the human acceleration of the global N and P cycles. In the first half of the twentieth century, natural sources (N_2 fixation, weathering, allochthonous organic matter inputs, weathering) were more important for the model sensitivity than in the second half of the century. This reflects both a decrease of natural sources in absolute terms due to deforestation, and also a decrease in relative terms due to the stark increase in N and P sources (agriculture, wastewater).

Increasing river export is responsible for eutrophication of coastal marine ecosystems leading to increased production and hypoxia (Diaz and Rosenberg, 2008~~);~~) and changing nutrient stoichiometry may lead to harmful algal blooms (Heisler et al., 2008). ~~Analysis of what the impacts of nutrients have been in the past~~Past impacts of nutrients on ecosystems, and ~~how~~ their ~~eutrophication effects will~~future effects ~~change in future scenarios~~, require~~s~~ coupling our model to coastal biogeochemistry models.

A first simple improvement of the in-stream model ~~is~~ would be to ~~by adding~~add ~~the process of~~ P saturation of sediments and desorption in case of decreasing river P loads. A next, larger step is the incorporation of a mechanistic model for describing in-stream biogeochemical processes. This will allow~~s~~ ~~to analyze~~further scrutiny of ~~the~~ individual processes and their interplay (plant uptake, sedimentation, diagenetic processes, denitrification). Simulating these processes in addition to different forms of P and N ~~, and also to simulate the different nutrient forms,~~will furthermore ~~which is important when studying~~refine our understanding of the nutrient impacts ~~such as~~on the environment, and their relation to harmful algal blooms, blue-green algae and hypoxia.

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Figure captions

Figure 1. a) Scheme of the model framework with PCR-GLOBWB and IMAGE and the data flows between the models; b) Scheme of the flows of water and nutrients, and retention processes within a grid cell; c) Scheme of the routing of water (with N and P) in a landscape with streams, rivers, lakes, wetlands and reservoirs; each type of water body within a grid cell is defined by an inflow or discharge, depth and area. Floodplains may be temporarily flooded.

Figure 2. Comparison of modeled and observed concentrations of total N (left) and P (right) at stations in the rivers Missouri in U.S.A. (at Hermann, 38° 42′ N; 91° 26′ W) (a and b), Danube in Hungary (46.8 N; 18.9 E) (c and d), and Ångermanälven in Sweden (63.17N; 17.26E) (e and f). Figure 2a is modified from Beusen et al., 2015).

Figure 3. Global N (top) and P (bottom) delivery to surface water from different sources for the 20th century

Figure 4. Retention of N and P in water delivered to surface water for rivers discharging in the Arctic Ocean, Atlantic Ocean, Indian Ocean, Pacific Ocean and Mediterranean Sea and Black Sea for the 20th century.

Figure 5. River export of N and P to coastal marine ecosystems for rivers discharging in the Arctic Ocean, Atlantic Ocean, Indian Ocean, Pacific Ocean and Mediterranean Sea and Black Sea for the 20th century.