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Invited research article

# Forms and subannual variability of nitrogen and phosphorus loading to global river networks over the 20th century

Lauriane Vilmin[a,*], José M. Mogollón[a], Arthur H.W. Beusen[a,b], Alexander F. Bouwman[a,b]

[a] Department of Earth Sciences – Geochemistry, Utrecht University, P.O. Box 80021, Utrecht 3508TA, The Netherlands
[b] PBL Netherlands Environmental Assessment Agency, P.O. Box 30314, The Hague 2500GH, The Netherlands

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ABSTRACT

Nitrogen (N) and phosphorus (P) play a major role in the biogeochemical functioning of aquatic systems. N and P transfer to surface freshwaters has amplified during the 20th century, which has led to widespread eutrophication problems. The contribution of different sources, natural and anthropogenic, to total N and P loading to river networks has recently been estimated yearly using the Integrated Model to Assess the Global Environment - Global Nutrient Model (IMAGE-GNM). However, eutrophic events generally result from a combination of physicochemical conditions governed by hydrological dynamics and the availability of specific nutrient forms that vary at subyearly timescales. In the present study, we define for each simulated nutrient source: i) its speciation, and ii) its subannual temporal pattern. Thereby, we simulate the monthly loads of different N (ammonium, nitrate + nitrite, and organic N) and P forms (dissolved and particulate inorganic P, and organic P) to global river networks over the whole 20th century at a half-degree spatial resolution. Results indicate that, together with an increase in the delivery of all nutrient forms to global rivers, the proportion of inorganic forms in total N and P inputs has risen from 30 to 43% and from 56 to 65%, respectively. The high loads originating from fertilized agricultural lands and the increasing proportion of sewage inputs have led to a greater proportion of DIN forms (ammonium and nitrate), that are usually more bioavailable. Soil loss from agricultural lands, which delivers large amounts of particle-bound inorganic P to surface freshwaters, has become the dominant P source, which is likely to lead to an increased accumulation of legacy P in slow flowing areas (*e.g.*, lakes and reservoirs). While the TN:TP ratio of the loads has remained quite stable, the DIN:DIP molar ratio, which is likely to affect algal development the most, has increased from 18 to 27 globally. Human activities have also affected the timing of nutrient delivery to surface freshwaters. Increasing wastewater emissions in growing urban areas induces constant local pressure on the quality of aquatic systems by delivering generally highly bioavailable nutrient forms, even in periods of low runoff.

## 1. Introduction

Nitrogen (N) and phosphorus (P) are key elements for the biogeochemical functioning of aquatic systems. They are essential nutrients for life and therefore play a major role in ecosystem metabolism. Both nutrients are generally available in natural freshwater systems in small amounts. Since the beginning of the industrial era, industrial $N_2$ fixation (*i.e.*, the Haber-Bosch process) and P extraction from mines has escalated, mostly to boost global food production. This transfer of mineral N and P from the atmosphere and localized formations to global agricultural soils, together with fast urbanization and the associated increase in wastewater emissions, have led to a drastic amplification and acceleration of nutrient loading to surface freshwaters (Smil, 2000; Beusen et al., 2016). The increase in anthropogenic N and P loads has fueled the massive eutrophication of these systems and increased the number of human-induced coastal hypoxia events (Smith, 2003; Neal and Heathwaite, 2005; Rabalais et al., 2014; Jenny et al., 2016). Eutrophication constitutes a threat for human and ecosystem health, and has been an important focus of water quality research and environmental policy during the past decades. In order to design efficient mitigation strategies, it is important to fully grasp the interplays between human activities, climate, and nutrient transfers to aquatic systems.

Nutrient loading to surface freshwaters is driven by global-scale climatic and socio-economic forces, such as demography and international trade of agricultural goods. Spatially explicit total N (TN) and total P (TP) loads to global surface freshwaters were estimated in a recent study by Beusen et al. (2016) at a yearly time step. In the aforementioned study, the contribution of different sources, both

* Corresponding author.
*E-mail address:* l.m.vilmin@uu.nl (L. Vilmin).

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natural and anthropogenic, to total nutrient loading was assessed using the Integrated Model to Assess the Global Environment - Global Nutrient Model (IMAGE-GNM), which simulates the interactions between the Human and Earth systems. However, eutrophic events (*i.e.*, development of algal blooms) generally respond to a combination of conditions, including temperature, light, flow, as well as nutrient form and availability that cannot be captured at low temporal resolution.

The risk of developing eutrophication is, to a greater extent, linked to soluble reactive nutrient forms, which can be directly uptaken by algal species for primary production, notably during times of ecological sensitivity (Jarvie et al., 2006). The nutrient forms entering river networks mainly depend on their origin (Jordan et al., 2003). The contribution of these sources to the total nutrient loading to aquatic systems can be highly variable over time and space, depending on their drivers (*e.g.*, population density, sewage treatment technology, hydrology, *etc.*). The intensity of these sources can show strong seasonal variations, especially for diffuse sources (Withers et al., 2009). Changes in climate patterns and variability can potentially lead to an increase in the occurrence of conditions promoting water quality deterioration (Michalak, 2016). There is thus a clear need to refine the representation of speciation and timing of nutrient fluxes in global biogeochemical models to better appraise the anthropogenic effects on water quality and eutrophication risk.

In this respect, the present work aims at assessing the forms and monthly variations of N and P loading to global river networks over the past century. We simulate the loads of different N and P forms (ammonium, nitrate + nitrite, organic N, dissolved inorganic P, particulate inorganic P and organic P) from different natural and anthropogenic sources to global river networks. We analyze the results in the context of past global changes over the 20th century, and discuss trends for regions with contrasting demography, land uses, and levels of development. By assessing the form of nutrient loading to global river systems at refined spatio-temporal scales (half-degree spatial resolution, monthly time step), these results allow for a better understanding of the potential human impacts on freshwater eutrophication.

## 2. Material and methods

### 2.1. Yearly global datasets on nutrient loads to river networks

We assess here the subannual speciation of TN and TP delivery to river networks, originating only from external sources, estimated by Beusen et al. (2016). Note that we do not study the effect of in-stream nutrient transformations (*e.g.*, pumping and release of N from/to the atmosphere *via* biological $N_2$ fixation and denitrification).

Using different modules of the Integrated Model to Assess the Global Environment (IMAGE) framework (Stehfest et al., 2014), which simulates interactions between the Human and Earth systems, Beusen et al. (2016) simulated TN and TP flows entering river networks worldwide at an annual time step. These TN and TP loads ($N_{load}$ and $P_{load}$ [$MT^{-1}$], respectively) are calculated as the sum of N and P loads from different sources:

$$N_{load} = N_{dep} + N_{aq} + N_{ww} + N_{ro} + N_{gw} + N_{veg} \quad (1)$$

$$P_{load} = P_{aq} + P_{ww} + P_{ro} + P_{weath} + P_{veg} \quad (2)$$

where the indexes *dep*, *aq*, *ww*, *ro*, *gw*, *veg* and *weath* refer to atmospheric deposition, aquaculture, wastewater, runoff, groundwater, vegetation in floodplains and chemical weathering. The groundwater exfiltration term accounts for N transfers to river networks after infiltration and transformation (*i.e.*, denitrification) in aquifers (Beusen et al., 2015). The P weathering term represents the background dissolved loads due to the chemical alteration of mineral sediments and rocks (Hartmann et al., 2014). The organic nutrient inputs due to the scouring of vegetation in floodplains are assessed with the Lund-Potsdam-Jena global dynamic vegetation model (Sitch et al., 2003). The estimation methods for all nutrient input terms are described in detail by Beusen et al. (2015).

The treatment of sewage water not only abates TN and TP emissions, but also modifies their composition. We hence distinguish between sewage water sources with different levels of treatment, using the global data gathered by Morée et al. (2013). The total input of nutrient $X$ from wastewater emissions is calculated as:

$$X_{ww} = X_{notreat} + X_{prim} + X_{sec/tert} \quad (3)$$

where *notreat* refers to untreated wastewater, *prim* to wastewater emissions after primary treatment, and *sec/tert* refers to wastewater emissions after advanced treatment (secondary or tertiary treatment processes).

As described by Beusen et al. (2015), input of nutrient $X$ through runoff is calculated as the sum of losses from recent nutrient applications in the form of fertilizer, manure or organic matter ($X_{sro}$, also called surficial runoff in the rest of the paper) and losses due to soil erosion by rainfall ($X_{soilloss}$):

$$X_{ro} = X_{sro} + X_{soilloss} \quad (4)$$

Here, we refine the description of each simulated source by defining: i) its speciation (proportions of different N forms in TN, and of different P forms in TP), based on a literature review (see Tables 1 and 2), and ii) its monthly pattern, which depends on the temporal variability of its drivers. The assumptions and characteristics we adopted to describe each nutrient source in the model are presented in the following subsections, and summarized in Tables 3 and 4.

### 2.2. Speciation of nutrient loads

We represent 3 forms of N: ammonium ($NH_4^+$), (nitrate + nitrite) ($NO_x^-$), and organic N (ON); and 3 forms of P: dissolved inorganic P (DIP), particulate inorganic P (PIP), and organic P (OP). ON and OP are the N and P contained in living and detrital organic matter. We consider ON and OP to be mainly particulate, since dissolved organic matter is typically characterized by low N and P contents (Meybeck, 1982; Pujo-Pay et al., 2011). The sum of $NH_4^+$ and $NO_x^-$ is referred to as dissolved inorganic N (DIN). DIP is the inorganic (reactive or unreactive) P in solution. In practice, it represents the inorganic P that can be measured after 0.45 μm filtration of the water sample. The PIP pool comprises different sorbed or precipitated forms of mineral P. This speciation is consistent with measured nutrient forms in rivers (*e.g.*, USGS database available at waterdata.usgs.gov). This also corresponds to the forms that are generally considered in biogeochemical river models, since they have different behaviors/impacts once in the environment (Brown and Barnwell, 1987; Billen et al., 1994; Reichert et al., 2001; Wade et al., 2002a,b; Bernot and Dodds, 2005). Appendix A provides a sensitivity analysis on the speciation of simulated sources.

#### 2.2.1. Assumptions related to point sources

Aquaculture in freshwater systems mostly consists of finfish production (Bouwman et al., 2013b). Bouwman et al. (2013a) calculated nutrient budgets for aquacultural finfish production, providing spatially explicit estimates of particulate and dissolved N and P emissions to surface freshwaters. We use these results, together with typical values from the literature on the composition of untreated finfish farm effluents to define the N and P speciations of this input term.

Although the composition of raw wastewater may depend on various factors, such as the contribution of industry to sewage effluents, population diets, *etc.*, we assume a constant global speciation for untreated sewage water. We distinguish between primary treatment, which mainly eliminates particulate forms, and advanced treatment.

**Table 1**
Percentages of different N forms in loads from various sources described in the literature.

| Reference | Description of N source | $NH_4^+$:DIN[a] | DIN:DN | $NH_4^+$:TN | $NO_x^-$:TN | ON:TN |
|---|---|---|---|---|---|---|
| *Atmospheric deposition* | | | | | | |
| Timperley et al. (1985) | Review of deposition rates in different regions of the world, and study of sites in Japan and New Zealand | | 10–89 (med = 68) | | | |
| Balestrini et al. (2000) | Deposition at prealpine/alpine sites in Italy, 1995–1997 | | | | | |
| | - dry | 40–73 | | | | |
| | - wet | 58–60 | | | | |
| Williams et al. (2001) | Precipitation in high elevation environment, Colorado Front Range, 1996–1998 | | | 32 | 52 | 16 |
| Baumgardner Jr. et al. (2002) | Deposition in the USA for 1990–1993 and 1997–2000 | | | | | |
| | - dry | 16–19 | | | | |
| | - wet | 37–41 | | | | |
| Rodà et al. (2002) | Bulk deposition in Mediterranean forests (sampling at 4 sites between 1983 and 1999) | 52–58 | | | | |
| Cornell et al. (2003) | Literature review on ON contribution to DN in rainwater | | | | | |
| | - Europe (19 data sets) | | 77 ± 8 | | | |
| | - North America (51 data sets) | | 38 ± 19 | | | |
| | - South/Central America (6 data sets) | | 29 ± 5 | | | |
| | - Southeast Asia (1 data set) | | 41 | | | |
| | - Oceania (6 data sets) | | 56 ± 27 | | | |
| | - Antarctica (1 data set) | | 11 | | | |
| | - Islands (6 data sets) | | 30 ± 32 | | | |
| Neal et al. (2003) | Rainfall in headwater catchments in mid-Wales, 1983–1999 | 54.5 | | | | |
| Neal et al. (2004) | Estimated total deposition in tributary catchments of the river Thames (largely rural to moderately intensive farming) | 78–80 | | | | |
| Holland et al. (2005) | Total deposition in the USA based on literature review | 34–45 | | | | |
| | Total deposition in Western Europe based on literature review | 38–63 | | | | |
| Welter et al. (2005) | Rainfall in an arid watershed in central Arizona, 1992–2001 | | | | | |
| | - summer | 47 | | | | |
| | - winter | 54 | | | | |
| Trebs et al. (2006) | Total deposition at tropical pasture site in Brazil, 2002 | 45–51 | | | | |
| Chen and Mulder (2007) | Annual wet deposition in 5 subtropical forested sites, South China, 2001–2003 | 54–77 | | | | |
| Duce et al. (2008) | Global estimate for deposition on open ocean in 2000 (assumed uncertainties of ± 50 %) | | | 36 | 34 | 30 |
| Lapworth et al. (2008) | Rainfall in mid-Wales moorland catchment, 2003–2004 | 53 | 81 | | | |
| Golden and Boyer (2009) | Modeled deposition on New York state for 2002–2004 | | | | | |
| | - winter | 34 | | | | |
| | - spring | 49 | | | | |
| | - summer | 50 | | | | |
| | - autumn | 41 | | | | |
| | - total | 44 | | | | |
| Liu et al. (2009) | Modeled total deposition at 6 stations in China | | | | | |
| | - summer | 67–69 | | | | |
| | - winter | 56–71 | | | | |
| Koçak et al. (2010) | Deposition at site in Erdemli, Turkey for 1999–2007 | | | | | |
| | - dry | 12 | | | | |
| | - wet | 49 | | | | |
| Zhang et al. (2012) | Modeled total deposition over the contiguous USA for 2006–2008 | 35 | | | | |
| Qi et al. (2013) | Average deposition flux in coastal region of the Yellow Sea, China, 2005–2006 | | | | | |
| | - dry | 50 | | | | |
| | - wet | 71 | | | | |
| Tu et al. (2013) | Precipitation in a subtropical bamboo forest, Sichuan, China, December 2008 | 71 | 76 | | | |
| Du et al. (2014) | Average measurements for the whole USA in 2011–2012 | 57 | | | | |
| Sickles II and Shadwick (2015) | Mean deposition for 34 eastern USA stations for 2005–2009 | | | | | |
| | - dry | 19–22 | | | | |
| | - wet | 47–54 | | | | |
| | - total | 40–45 | | | | |

(*continued on next page*)

**Table 1** (*continued*)

| Reference | Description of N source | $NH_4^+$:DIN[a] | DIN:DN | $NH_4^+$:TN | $NO_x^-$:TN | ON:TN |
|---|---|---|---|---|---|---|
| Xu et al. (2015) | Total deposition for 2010–2014, national monitoring network in China | 58 | | | | |
| Aguillaume et al. (2016) | Deposition in a Mediterranean forest | | | | | |
| | - dry, 1995–1996 | 83 | | | | |
| | - wet, 1995–1996 | 59 | | | | |
| | - dry, 2011–2013 | 47 | | | | |
| | - wet, 2011–2013 | 54 | | | | |
| Conradie et al. (2016) | Wet deposition at 4 sites in South Africa, 2009–2014 | 46–59 | | | | |
| *Aquaculture* | | | | | | |
| Boaventura et al. (1997) | Mean quality of 3 trout farm effluents in Portugal | 13–60 | | | | |
| Costa-Pierce (1998) | Nutrient levels in aquaculture ponds, LA County, USA | 71 | | | | |
| Porrello et al. (2005) | Outflow from fish farm in Italy after phytotreatment pond (% calculated on annual mean concentrations) | | 73–75 | | | |
| Bouwman et al. (2013a) | Review on finfish aquaculture | 100 | 88–93 | | | |
| Koçer et al. (2013) | Outflows from 3 trout farms in Turkey (% calculated on average concentrations) | | | 15–25 | 40–54 | 31–36 |
| Teodorowicz (2013) | Outflows from 9 fish farms in Poland (% calculated on average concentrations) | | | 3–19 (med = 8) | 14–40 (med = 26) | 51–77 (med = 66) |
| *Sewage* | | | | | | |
| Canter and Knox (1984) | Estimation of N compounds in septic tanks | | | 75 | 0 | 25 |
| Pescod (1992) | Raw wastewater, City of Davis, California | | | 82 | 0 | 18 |
| | Primary effluent, City of Davis, California | | | 76 | 0 | 24 |
| | Secondary effluent, trickling filters, California | 37–97 | | | | |
| | Secondary effluent, activated sludge, California | 22–56 | | | | |
| | Effluent quality after advanced treatment, California | | | 1–86 | 2–98 | 1–15 |
| Eiswirth and Hötzl (1997) | Mean composition of Rastatt untreated sewage water | | | 69 | 2 | 29 |
| Henze and Comeau (2008) | Typical composition of raw municipal wastewater (minor contribution of industry) | | | 75 | < 1 | 25 |
| Krasner et al. (2009) | Median water quality, survey of 23 WWTPs in the USA | | | | | |
| | - no nitrification | 99 | | | | |
| | - partial or poor nitrification | 70 | | | | |
| | - good nitrification | 95 | | | | |
| | - partial denitrification | 76 | | | | |
| | - good denitrification | 57 | | | | |
| Vilmin (2014) | WWTP effluent after treatment by nitrification-denitrification & bypass | | | 27 | 65 | 8[b] |
| *Groundwater* | | | | | | |
| Sharpley et al. (1987) | Quality of shallow groundwaters at 18 locations in Oklahoma, 1979–1986 | 0–40 (med = 3) | | | | |
| Hill (1991) | Average quality for 1986–1990 in headwater swamp area near Toronto, Ontario | | | | | |
| | - shallow groundwater | 18 | 51 | | | |
| | - deep groundwater | 19 | 21 | | | |
| DeSimone and Howes (1998) | Median ambient groundwater quality, site in Cape Cod, Massachusetts, September 1989 | 19 | 62 | | | |
| Fatta et al. (1999) | Mean characteristics of aquifer impacted by landfill leachate (6 sites) | 85–100 | | | | |
| Kroeger et al. (2006) | Aquifer in western Cape Cod, Massachusetts (median value for 870 samples at 38 points) | | 38 | | | |
| Bowen et al. (2007) | Composition of groundwater at 13 sites in New England | | | 1–67 (med = 14) | 7–86 (med = 27) | 6–78 (med = 56) |
| Lapworth et al. (2008) | Quality in 18 piezometers in mid-Wales moorland catchment, 2003–2004 | | 2–53 (med = 16) | | | |
| Shand and Edmunds (2008) | Summary statistics for major elements for European groundwaters | | | | | |
| | - proportions calculated on median values | 28 | | 15 | 38 | 47[c] |
| | - proportions calculated on mean values | 8 | | 6 | 75 | 19[c] |
| Umezawa et al. (2008) | Mean concentrations during rainy season in 2006 | | | | | |
| | - Manila, shallow groundwater | 22 | | | | |

(*continued on next page*)

**Table 1** (*continued*)

| Reference | Description of N source | $NH_4^+$:DIN[a] | DIN:DN | $NH_4^+$:TN | $NO_x^-$:TN | ON:TN |
|---|---|---|---|---|---|---|
| | - Manila, deep groundwater | 71 | | | | |
| | - Bangkok, shallow groundwater | 70 | | | | |
| | - Bangkok, deep groundwater | 96 | | | | |
| | - Jakarta, shallow groundwater | 10 | | | | |
| | - Jakarta, deep groundwater | 97 | | | | |
| Hinkle and Tesoriero (2014) | Statistics on 877 USGS ambient monitoring wells in shallow US groundwaters | 3–8 | | | | |
| Salemi et al. (2015) | Well at 3 m from stream in tropical pasture catchment in Brazil, 2007–2008 | | | 8 | 8 | 84 |
| European Environment Agency (2016) | Proportions calculated for 847 European groundwater bodies between 1982 and 2014 | 0–100 (med = 3) | | | | |
| Hao et al. (2016) | Mean concentrations at 8 wells in a rare earth mining area in China, dry season 2013 | | | 11 | 67 | |
| Stuart and Lapworth (2016) | Literature review on UK groundwaters | 0–85 (med = 1) | | | | |
| *Runoff* | | | | | | |
| Sharpley et al. (1987) | Average quality in 20 watersheds in Oklahoma & Texas, 1977–1984 | | | 1–38 (med = 27) | 5–52 | |
| Williams et al. (2001) | Snowpack meltwater in high elevation environment, Colorado Front Range, 1996–1998 | 36–44 | | | | |
| Vuorenmaa et al. (2002) | Runoff quality in 15 Finnish catchments | | | | | |
| | - forested catchments 1981–1985 | | | | | 74 |
| | - forested catchments 1986–1990 | | | | | 66 |
| | - forested catchments 1991–1995 | | | | | 70 |
| | - mixed catchments 1981–1985 | | | | | 40 |
| | - mixed catchments 1986–1990 | | | | | 46 |
| | - mixed catchments 1991–1995 | | | | | 46 |
| | - agricultural catchments 1981–1985 | | | | | 26 |
| | - agricultural catchments 1986–1990 | | | | | 37 |
| | - agricultural catchments 1991–1995 | | | | | 32 |
| Welter et al. (2005) | Sheetflow chemistry in an arid watershed in central Arizona, 1999–2001 | | | | | |
| | - summer | 38 | | | | |
| | - winter | 36 | | | | |
| Kim et al. (2007a) | Runoff quality during rainfall events in Korean watersheds (March–September 2002) | | | | | |
| | - natural forest area | 4 | | 4 | 89 | |
| | - forest and agricultural area | 11–32 | | 8–24 | 51–66 | |
| Withers et al. (2009) | Storm runoff characteristics in 3 UK microwatersheds (2005–2007), calculations done on median values | | | | | |
| | - field surface | 2 | | | | |
| | - field drains | < 1 | | | | |
| | - roads | 1 | | | | |
| | - farmyards | 11 | | | | |
| | - septic tank ditch | 12 | | | | |
| Lang et al. (2013) | Runoff after rainfall events in low-populated, headwater area in China, with human and livestock waste applied to fields, 2011–2012 | 6 | 72 | | | |
| Tu et al. (2013) | Surface runoff in a subtropical bamboo forest, Sichuan, China, December 2008 | 9 | 85 | | | |
| Salemi et al. (2015) | Surface runoff in tropical pasture catchment in Brazil, 2007–2008 | | | 20 | 20 | 60 |

TN = total N, PN = particulate N, DIN = dissolved inorganic N ($NH_4^+ + NO_x^-$), ON = organic N, WWTP = wastewater treatment plant, GW = groundwater
med = median value

[a] Calculated as ratio of measured reduced N concentrations/fluxes to reduced + oxidized N concentrations/fluxes.

[b] Estimated based on biochemical oxygen demand measurements and with a constant C:N weight ratio of 7 for organic matter.

[c] Estimated based on total organic carbon measurements and with a constant C:N weight ratio of 7 for organic matter.

**Table 2**
Percentages of different P forms in loads from various sources described in the literature.

| Reference | Description of P source | PP:TP | DIP:TP | PIP:TP | OP:TP |
|---|---|---|---|---|---|
| *Aquaculture* | | | | | |
| Porrello et al. (2005) | Outflow from fish farm in Italy after phytotreatment pond (% calculated on annual mean concentrations) | 24–29 | 58–65[a] | | |
| Bouwman et al. (2013b) | Global model results for finfish farms | 60 | | | |
| Koçer et al. (2013) | Outflows from 3 trout farms in Turkey (% calculated on average concentrations) | | 12–26 | | 62–73 |
| Teodorowicz (2013) | Outflows from 9 fish farms in Poland (% calculated on average concentrations) | | | | 21–62 (med = 42) |
| Brigolin et al. (2014) | Modeling of Mediterranean fish cage farms (*S. aurata* and *D. labrax*) | | 35–37 (urine) | | 63–65 (wasted food & faeces) |
| *Sewage* | | | | | |
| Canter and Knox (1984) | Estimation of P compounds in septic tanks | | 85 | | |
| Pescod (1992) | Primary effluent, City of Davis, California | | 100 | | |
| | Secondary effluent, activated sludge, California | | 27 | | |
| Carreira and de L. R. Wagener (1998) | Raw sewage water | 31 | | 10 | 21 |
| Cooper et al. (2002) | WWTP without P stripping | 3–6 | 94–97[a] | | |
| Neal et al. (2005) | Treated effluents, without P stripping (% calculated on average concentrations for 6 WWTPs) | 1–3 | 87–94[a] | | |
| Henze and Comeau (2008) | Typical composition of raw municipal wastewater (minor contribution of industry) | | 67 | | 33 |
| Comber et al. (2015) | WWTP effluent with no dosing for P removal | | 94 ± 1 (96[a]) | | |
| | WWTP effluent with Al dosing | | 34 ± 13 (10[a]) | | |
| | 2 WWTP effluents with Fe dosing | | 90 ± 6 (84[a]) | | |
| | | | 67 ± 12 (66[a]) | | |
| | WWTP effluent with tertiary sand filtration and Fe dosing | | 49 ± 16 (26[a]) | | |
| Vilmin et al. (2015) | WWTP effluent with tertiary P stripping & bypass | | 81 | 10 | 9 |
| Kazadi Mbamba et al. (2016) | WWTP influent (untreated) | | 56 | | |
| *Runoff* | | | | | |
| Sharpley et al. (1987) | Average runoff water quality in 20 watersheds in Oklahoma and Texas, 1977–1984 | 48–97 (med = 80) | | | |
| Kronvang (1992) | Runoff in 2 agricultural basins (~ 80% agral land use) | | 62 | 18 | 20 |
| | from Denmark in 1986–1987 (sampling in streams) | | 30 | 38 | 32 |
| Haygarth and Jarvis (1997) | Grazed grasslands in SW England in 1994 (sampling in lysimeters) | | 33[a] | | |
| Fraser et al. (1999) | Overland flow during winter rainfall events on conventionally managed arable lands in SW England in 1996–1997 | 51–76 | | | |
| Heathwaite and Dils (2000) | Surface runoff on grazed grasslands in UK during storm events in 1994–1996 | 38 | 62 (43[a]) | | |
| Cooper et al. (2002) | Estimated diffuse inputs to the Thame river basin (mainly rural) for 1995–1999 | 16–28 | | | |
| Gardner et al. (2002) | Quality in drain outlet in UK during rain event in February 2000 | 37–78 (med = 72) | | | |
| Vuorenmaa et al. (2002) | Runoff quality in 15 Finnish catchments | | | | |
| | - forested catchments 1986–1990 | | 35[a] | | |
| | - forested catchments 1991–1995 | | 30[a] | | |
| | - mixed catchments 1986–1990 | | 26[a] | | |
| | - mixed catchments 1991–1995 | | 23[a] | | |
| | - agricultural catchments 1986–1990 | | 15[a] | | |
| | - agricultural catchments 1991–1995 | | 12[a] | | |
| Hively et al. (2005) | Overland flow during simulated rainfall events under dry summer conditions around a dairy farm in the USA | | | | |
| | - grass | 33–36 | | | |
| | - pasture | 50 | | | |
| | - maize field | 82 | | | |
| | - forest | 94 | | | |
| Némery et al. (2005) | Estimated total diffuse inputs to Marne watershed (mainly losses from runoff) for 1989–1994 | 50–80 | | | |
| Kim et al. (2007a) | Runoff quality during rainfall events in Korean watersheds (March–September 2002) | | | | |
| | - natural forest area | | 32[a] | | |
| | - forest and agricultural area | | 5–31[a] | | |
| Torrent et al. (2007) | Drainage water marsh soil near estuary of river Guadalquivir | 17–39 | 45–70[a] | | |
| | Overland flow during rain events in Chromic Vertisol catchment in southern Spain in 2002 | 98–100 | | | |
| | Overland flow during rain events in Calcic Luvisol catchment in southern Spain in 2001–2002 | 72–95 | | | |
| Ulén et al. (2007) | Typical P loss from main agricultural areas in Norway | 77–91 | | | |
| | Typical P loss from main agricultural areas in Sweden | 20–80 | | | |
| | Typical P loss from main agricultural areas in UK | 40–80 | | | |
| | Typical P loss from main agricultural areas in Ireland | 20–80 | | | |
| Withers et al. (2009) | Storm runoff characteristics in 3 UK microwatersheds (2005–2007) | | | | |
| | - field surface | 46–83 (med = 72) | | | |
| | - field drains | 9–96 (med = 54) | | | |

(*continued on next page*)

**Table 2** (*continued*)

| Reference | Description of P source | PP:TP | DIP:TP | PIP:TP | OP:TP |
|---|---|---|---|---|---|
| | - roads | 8–96 (med = 76) | | | |
| | - farmyards | 2–90 (med = 50) | | | |
| | - septic tank ditch | 10–54 (med = 33) | | | |
| Eastman et al. (2010) | Study of farm fields from Quebec in 2004–2006 | | | | |
| | - subsurface drainage from field with clay-loam soil | 75–77 | | | |
| | - surface runoff on field with clay-loam soil | 81–86 | | | |
| | - subsurface drainage from field with sand-loam soil | 31–33 | | | |
| | - surface runoff on field with sand-loam soil | 15–22 | | | |

TP = total P, PP = particulate P, DIP = dissolved inorganic P, PIP = particulate inorganic P, OP = organic P, WWTP = wastewater treatment plant
med = median value

[a] Soluble reactive P values

Advanced treatment modifies N speciation due to nitrification/denitrification processes.

### 2.2.2. Assumptions related to diffuse sources

Even though ON is a significant component of atmospheric N deposition (Timperley et al., 1985; Cornell et al., 2003), large scale estimates of ON:TN for deposition over land are lacking. We thus describe the N composition of atmospheric deposition based on global estimates for oceans from Duce et al. (2008). We assume that half of the DIN is composed of $NH_4^+$, which is in agreement with most studies on deposition over land found in the literature (Table 1).

Several studies have highlighted that a significant proportion of N transferred through groundwater is organic (Kroeger et al., 2006; Bowen et al., 2007; Lapworth et al., 2008). Based on median quality data from European groundwaters (Bowen et al., 2007; Shand and Edmunds, 2008), we assume this proportion to be 50%. DIN generally occurs in groundwaters in oxidized form ($NO_x^-$, Table 1). High $NH_4^+$ concentrations have also been found in a few deep confined aquifers (Stuart and Lapworth, 2016), where anoxic conditions presumably prevents the occurrence of oxidized N compounds. These water bodies being less likely to exchange with river networks, their effect on the composition of N inputs from groundwater exfiltration is neglected. Moreover, leakage from sewage systems or waste disposal in urban areas can also constitute an important local N source to groundwater (Eiswirth and Hötzl, 1997; Foppen, 2002; Wakida and Lerner, 2005; Corniello et al., 2007; Umezawa et al., 2008; Nyenje et al., 2010), in some cases leading to higher proportions of $NH_4^+$ in underlying aquifers (Wakida and Lerner, 2005; Umezawa et al., 2008). However, urban areas represent a small proportion of the global land area, and their effect was thus neglected in the groundwater emission calculations from Beusen et al. (2015). All urban waste emissions are included in the sewage water inputs (point sources). We therefore hypothesize that $NO_x^-$ accounts for 90% of the DIN reaching surface freshwaters after transfer through aquifers.

We consider that surficial runoff does not contain any PIP. In this way, we assume that only soluble inorganic fertilizers and manure can be washed away through surficial runoff, also referred to as "incidential" or "event-specific" losses (Haygarth and Jarvis, 1999; Hart et al., 2004). We neglect the direct removal of freshly applied phosphate rock, since it was shown that its use significantly reduces the loss of P in runoff compared to other P fertilizers, and its higher density makes it less mobile (Hart et al., 2004). Moreover, directly applied phosphate rock accounts for only *ca.* 5% of the global phosphate rock production, the rest mostly being treated to make the P more soluble (Smit et al., 2009). We consider that the transfer of phosphate rock occurs through erosive processes, such as soil loss. All particulate nutrient forms (ON, PIP and OP) can be transferred to river networks through soil erosion processes during surface runoff events. For P, we further distinguish between soil loss from natural lands and from agricultural lands. We assume that soil loss from agricultural lands contains a higher proportion of PIP than soil loss from natural lands (75 *versus* 25%), due to the sorption of soluble mineral fertilizers to soil particles and/or to fertilization with phosphate rock.

**Table 3**
Adopted description of N sources: speciation (% of N forms in TN) and temporal pattern; yearly inputs to global surface freshwaters in 1900, 1950 and 2000 (TgN).

| N source | Speciation | | | Temporal pattern/Hydrological driver | Contrib. to global inputs | | |
|---|---|---|---|---|---|---|---|
| | $NH_4^+$ | $NO_x^-$ | ON | | 1900 | 1950 | 2000 |
| | % | % | % | | TgN | TgN | TgN |
| Atmospheric deposition | 35 | 35 | 30 | Uniform | 0.44 | 0.48 | 1.03 |
| Aquaculture, particulate forms | 0 | 0 | 100 | Uniform | 0 | < 0.01 | 0.12 |
| Aquaculture, dissolved forms | 30 | 70 | 0 | Uniform | 0 | 0.01 | 0.66 |
| Sewage, untreated | 65 | 0 | 35 | Uniform | 1.72 | 3.04 | 2.78 |
| Sewage, primary treatment | 90 | 0 | 10 | Uniform | 0 | 0.45 | 3.01 |
| Sewage, secondary/tertiary treatment | 60 | 30 | 10 | Uniform | 0 | 0 | 1.83 |
| Surficial runoff | 10 | 70 | 20 | Land runoff | 1.33 | 1.93 | 6.80 |
| Soil loss | 0 | 0 | 100 | Square precipitation | 3.95 | 5.13 | 7.21 |
| Groundwater exfiltration | 5 | 45 | 50 | Uniform | 15.66 | 17.02 | 32.60 |
| Vegetation in floodplains | 0 | 0 | 100 | Flooding volume | 11.94 | 12.27 | 11.77 |
| Total load | | | | | 35.04 | 40.33 | 67.81 |

**Table 4**
Adopted description of P sources: speciation (% of P forms in TP) and temporal pattern; yearly inputs to global surface freshwaters in 1900, 1950 and 2000 (TgP).

| P source | Speciation % DIP | % PIP | % OP | Temporal pattern/Hydrological driver | Contrib. to global export TgP 1900 | TgP 1950 | TgP 2000 |
|---|---|---|---|---|---|---|---|
| Aquaculture, particulate forms | 0 | 20 | 80 | Uniform | 0 | < 0.01 | 0.03 |
| Aquaculture, dissolved forms | 100 | 0 | 0 | Uniform | 0 | < 0.01 | 0.05 |
| Sewage, untreated | 15 | 30 | 55 | Uniform | 0.17 | 0.31 | 0.38 |
| Sewage, primary treatment | 80 | 10 | 10 | Uniform | 0 | 0.04 | 0.44 |
| Sewage, secondary/tertiary treatment | 80 | 10 | 10 | Uniform | 0 | 0 | 0.21 |
| Weathering | 100 | 0 | 0 | Total runoff | 1.15 | 1.20 | 1.19 |
| Surficial runoff over agricultural lands | 60 | 0 | 40 | Land runoff | 0.10 | 0.23 | 0.99 |
| Soilloss from agricultural lands | 0 | 75 | 25 | Square precipitation | 1.54 | 2.33 | 3.93 |
| Soilloss from natural lands | 0 | 25 | 75 | Square precipitation | 0.79 | 0.72 | 0.63 |
| Vegetation in floodplains | 0 | 0 | 100 | Flooding volume | 1.00 | 1.02 | 0.98 |
| Total load | | | | | 4.75 | 5.86 | 8.83 |

### 2.3. Implementation of subannual variability: hydrological drivers of nutrient sources

We assume that point sources (aquaculture and sewage water emissions), atmospheric N deposition and groundwater exfiltration are constant within a year ("uniform" temporal pattern). For all other simulated sources, we apply a monthly pattern to the previously estimated yearly loads:

$$Load_{mon,yr} = Load_{yr} \cdot \frac{d_{mon,yr}}{\overline{(d_{i,yr})_{i\in[1,12]}}} \tag{5}$$

where $Load_{mon,yr}$ is the new calculated load for the month *mon* of year *yr*, $Load_{yr}$ is the yearly load estimated by Beusen et al. (2016) for year *yr*, $d_{mon,yr}$ is the value of the identified main hydrological driver of the nutrient source for the month *mon* of year *yr*, and $\overline{(d_{i,yr})_{i\in[1,12]}}$ is the average value of this driver over the year.

The hydrological variables are estimated with the mechanistic global hydrological model PCR-GLOBWB (van Beek et al., 2011). PCR-GLOBWB, here applied at a half-degree spatial resolution, quantifies monthly water stores and fluxes in different components of the hydrosystem. It notably provides runoff estimates, and water depth and surface area in floodplains.

The total runoff ($q$ [$LT^{-1}$]) in one cell is estimated as the sum of net precipitation occurring directly on surface waters ($q_w$), and runoff in areas that are not covered in water (herein "land runoff", noted $q_{land}$):

$$q = q_w + q_{land} \tag{6}$$

$q_{land}$ [$LT^{-1}$] is the combination of the saturation-excess surface runoff that does not infiltrate (direct/surface runoff), runoff within the soil layer (interflow), and groundwater runoff (baseflow).

Chemical weathering of P is driven by total runoff (Hartmann et al., 2014). We assume that nutrient inputs due to surficial runoff are driven by land runoff, since the applied mineral fertilizer and organic matter can leach through the soil before reaching the river networks. Particle erosion from the land surface (soil loss) is known to be largely influenced by rainfall intensity (Renard and Freimund, 1994). Beusen et al. (2005) showed that the Fournier index is an important factor to describe sediment yields in rivers. We therefore consider that the soil loss nutrient inputs follow the monthly pattern of the square precipitation. Finally, we assume that nutrient inputs from vegetated floodplains depend on the volume of floodwater.

## 3. Results and discussion

Aggregated global values of the yearly nutrient compound loads to surface freshwaters are presented in the following subsections. The contributions of contrasting regions of the world and of major river basins to inputs of different N and P forms to global surface freshwaters are available online, as Supporting Information (Table S.1 and Figs. S.2–S.9). Subannual variability is discussed in terms of yearly coefficients of variation (standard deviation of the monthly loads over one year divided by the average load of the year), which provide a relative measure of the spread of the monthly values for each year. It allows for comparing the magnitudes of monthly fluctuations of the different compounds' loads, and investigating the effect of shifts in dominant nutrient sources. The coefficients of variation are assessed for 3 latitude classes — southern latitudes ($< -20°$), equatorial latitudes ($\in [-20°, 20°[$) and northern latitudes ($\geq 20°$). The equatorial latitudes are mainly characterized by tropical or desert climates. Flows are dominated by the Amazon and Congo basins. Southern and northern latitudes are subject to opposite seasonal variations. Readers interested in changes in subannual variations for specific areas of the globe can find yearly coefficients of variation of nutrient loads per region in the Supporting Information (Figs. S.10–S.17).

### 3.1. Long term nutrient inputs to global surface freshwaters

#### 3.1.1. Trends in N inputs

Beusen et al. (2016) recently estimated that global N loads to river networks have risen from 34 to 64 $Tg\,N \cdot yr^{-1}$ over the past century, with the sharpest increase between the 1960s and the 1990s. In 1900, N loads to river systems mainly originated from natural sources, *i.e.* groundwater exfiltration and vegetation in floodplains (Beusen et al., 2016). Our results therefore show that N loads were highest in tropical areas, in South America, tropical Africa and Southeast Asia, and mainly under the organic and $NO_x^-$ forms (Fig. 1). ON accounted for more than 70% of the TN inputs to river basins. The Amazon basin, which accounts for than less than 5% of the world's continental area and *ca.* 15% of the total river discharge to the global coastal ocean, generated over one quarter of this ON (Table S.1). In 1900, agriculture was already a major source of N to surface freshwaters in the USA, Western Europe and India, notably leading to relatively large $NO_x^-$ loads (Fig. 1). In these highly populated areas, untreated sewage emissions, which accounted for half of the global $NH_4^+$ inputs to surface freshwaters in 1900 (calculated from Table 3), locally constituted major N sources as well.

Natural sources have remained dominant over the entire 20th century in large areas of the Amazon basin and in tropical Africa, leading to

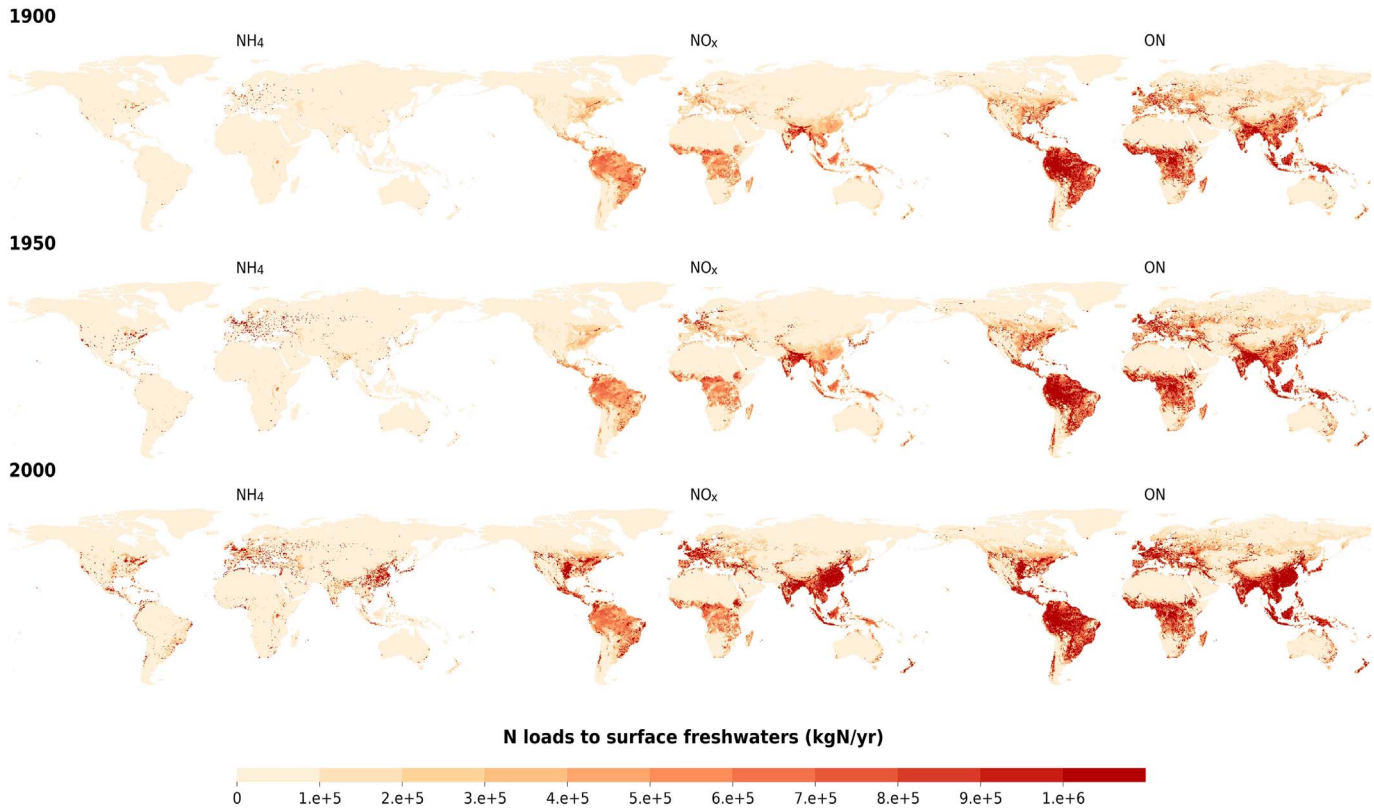


**Fig. 1.** Yearly average inputs of the different N forms to river networks in 1900, 1950, and 2000.

high loads of ON to river systems, which was shown to be the major form of N loss from natural forests (Perakis and Hedin, 2002). Howarth et al. (1996) found that the Amazon and Tocatins basins, at the end of the 20th century, were characterized by high N delivery to surface waters, with ON being the dominant form, which approaches the natural functioning of the tropical rain forest. According to our estimations, these two basins contribute to 17% of the global ON inputs to river networks in 2000 (Table S.1). Over the studied period, natural sources dominate arctic and subarctic areas (*e.g.*, Alaska, Canada and Northern Russia region) as well. However, as vegetation scouring in floodplains and groundwater flows are much lower in these regions, they contribute very little to the global N loads. Groundwater exfiltration has remained the major N source to global rivers. Its proportion in total N loading has been quite stable over the entire 20th century (42–48%, Table 3). Currently, agricultural activities dominate groundwater N emissions, leading to a large increase in $NO_x^-$ and ON loading over all continents, especially in areas of intensive agriculture such as the USA, Europe, Australia, China, India, Southern Africa and in the South of Brazil (Fig. 1). These results are in line with the common occurrence of high $NO_x^-$ concentrations in groundwater bodies in regions with intensive agriculture. For example, the proportion of groundwater bodies with mean $NO_x^-$ concentrations greater than $25\,mg{\cdot}L^{-1}$ were recently assessed to be 47% in Spain, 61% in the UK, 27% in France, 50% in Germany, and 40% in Italy (European Environmental Agency, 2012). Due to growing population and urbanization, the contribution of sewage water emissions to TN inputs into global rivers has increased from 5 to 12% (Table 3). $NH_4^+$ -rich sewage loads now constitute the dominant source of N in many densely populated areas over all continents, notably along the US coasts, in Europe, in the Middle East and Southeastern China.

The global shift in source dominance from natural to anthropogenic during the 20th century has led to a drop in the proportion of ON in the TN inputs, which decreased from 70% in 1900 down to 57% in 2000 (Fig. 3 a). N inputs have mainly shifted from ON to $NO_x^-$ that originates in a large proportion from groundwater receiving N inputs from agricultural lands. Consequently, $NO_x^-$ loads to global surface freshwaters have increased from 8 to 21 $Tg\,N{\cdot}yr^{-1}$ between 1900 and 2000. Especially due to the growing contribution of sewage water emissions, the proportion of $NH_4^+$ in TN loads has also risen, from 6 to 13%. Thereby, $NH_4^+$ loads have become larger than $NO_x^-$ loads in highly populated regions with low mineral N application to agricultural fields, such as the North African region, South Africa and the Middle East (see Supporting Information). The proportion of DIN forms, which are bioavailable for algae, reaching global surface freshwaters has hence escalated over the past century. In 2000, close to one quarter of the global DIN loads to surface freshwaters originated from the China region, which has undergone drastic increases in population, urbanization, and agricultural production over the latter part of the 20th century.

Few data exist on the forms of nutrient inputs to surface freshwaters. Most studies assess river concentrations or exports to the coasts, which are also affected by biogeochemical transformations within the river networks. However, there is strong evidence of anthropogenic activities triggering increased $NO_x^-$ and $NH_4^+$ fluvial transport (Meybeck, 1982; Smith, 2003). According to Smith (2003), human activities have increased DIN loads in rivers by more than a factor of 3 above natural fluxes. Goolsby and Battaglin (2001) found that the proportion of $NO_x^-$ in TN exports from the Mississippi river basin significantly increased at the end of the 20th century (from 50–60% prior

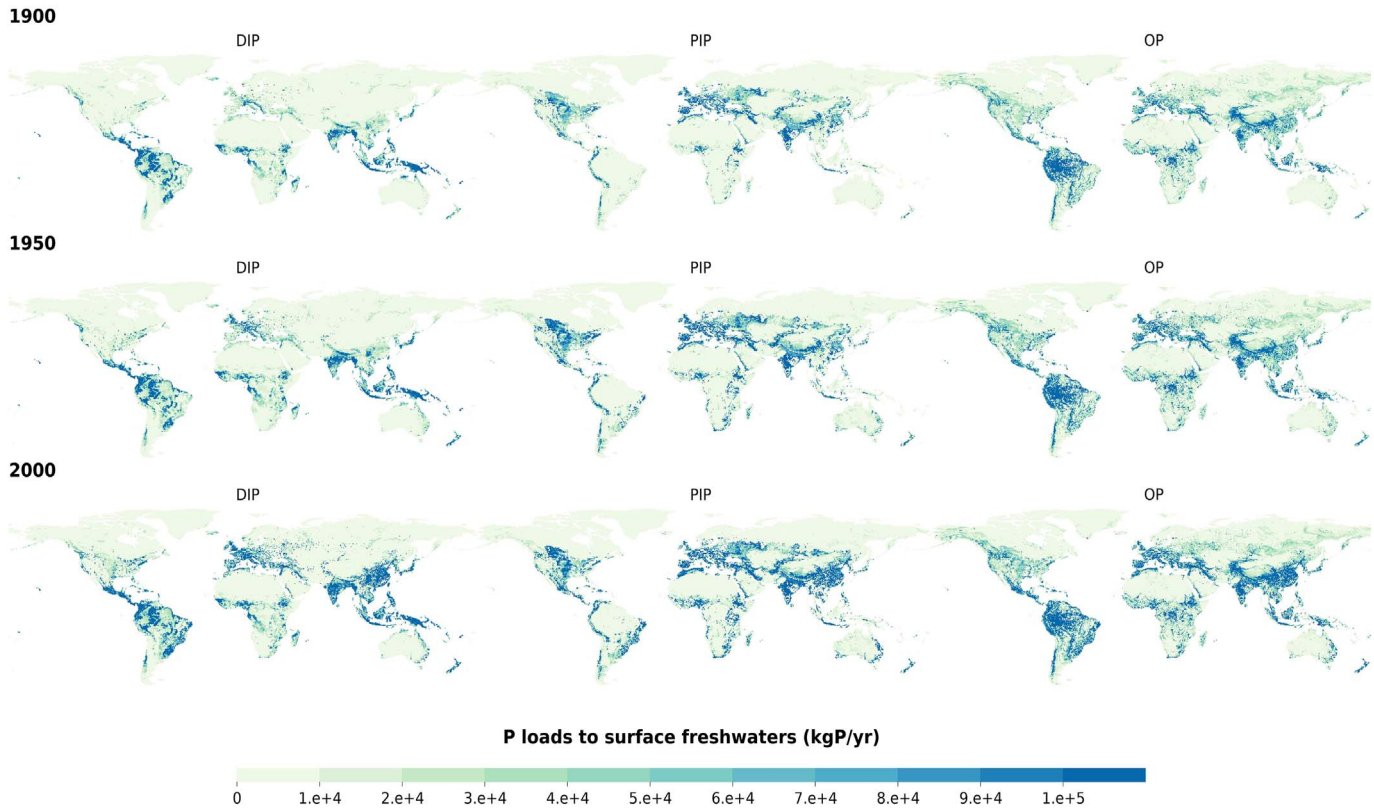


**Fig. 2.** Yearly average inputs of the different P forms to river networks in 1900, 1950, and 2000.

to 1992 up to close to 80% after). However, even in basins with high human impact, ON generally remains the dominant N pool in rivers, *e.g.* in the USA (Scott et al., 2007). Seitzinger and Harrison (2005) showed that, in the mid-1990s, global river basins exported 25 Tg N·yr$^{-1}$ of DIN and 42 Tg N·yr$^{-1}$ of PN and dissolved ON. This is consistent with our results, according to which 38 of the 66 TgN that were delivered to global river networks in 1995 were organic.

### 3.1.2. Trends in P inputs

Global TP loads to surface freshwaters have been steadily increasing over the 20th century, from 5 to 9 Tg P·yr$^{-1}$, according to Beusen et al. (2016). As with N, natural inputs dominated the global P loads to river networks (62% of total inputs) in 1900 (Table 4). This led to high OP and DIP inputs, especially in tropical regions with large productive floodplains and periods of high runoff promoting chemical weathering (Fig. 2). The Amazon River basin alone contributed to one fifth of the global OP loads to river networks. A high proportion (19%) of the DIP loads occurred in the Indonesia region, due to high weathering rates of volcanic rocks (Table S.1). In 1900, P losses from agricultural lands (principally *via* erosion) already constituted a dominant source in large areas of the USA, Europe, India, China and in the Andes region, inducing high particulate P (PP) loads.

In 2000, natural sources constitute 32% of all P inputs. They are dominant in Arctic regions (predominance of erosion), in areas of the Amazon basin and tropical Africa (predominance of weathering and vegetation scouring in floodplains), and in Indonesia that still contributes to more than 10% of the DIP inputs to global surface freshwaters due to high weathering (Fig. 2 and Table S.1). Soil loss from agricultural lands is the principal global P source (Table 4), leading to high PIP loads in the USA, Europe, Australia, China, India and Brazil. In 2000, the China region emits 19% of the global PIP loads to surface freshwaters, due to booming agriculture production, and the associated escalation of mineral fertilizer use.

The PP proportion reaching global river networks has remained stable over the 20th century (Fig. 3). Due to the growing prevalence of soil loss from agricultural lands over soil loss from natural lands and vegetation scouring in floodplains, the PP inputs have switched from mainly OP to PIP forms, with the proportion of PIP in TP inputs rising from 40 to 51% between 1900 and 2000. Sewage emissions also constitute a major P source in many densely populated areas of the world. The progressive development and improvement of sewage water treatment has led to an increase in the proportion of DIP emissions with respect to OP, locally, in many urban areas.

As with N, most studies on P forms in rivers focus on river transport and not on delivery to rivers. Comparing our results to those for river export, we can conclude that PP remains the dominant TP form throughout the watershed, regardless of PP's high retention potential within the river network (Seitzinger and Harrison, 2005; Beusen et al., 2016), and the increase in DIP loading due to human activities (Meybeck, 1982; Smith, 2003). According to our results, Asia has become the greatest contributor to DIP inputs to global watersheds by 2000 (41%, see Table S.1), which is in agreement with Harrison et al. (2010), who assessed that it contributed to 32% of the exports to the global oceans. We find that, in 2000, anthropogenic DIP sources exceeded natural weathering for 25% of the global continental area (data not shown). This is much lower than the 53% of the land area estimated by Harrison et al. (2010), for which human DIP supply had a greater contribution to DIP yields in rivers. This can be explained by the fact

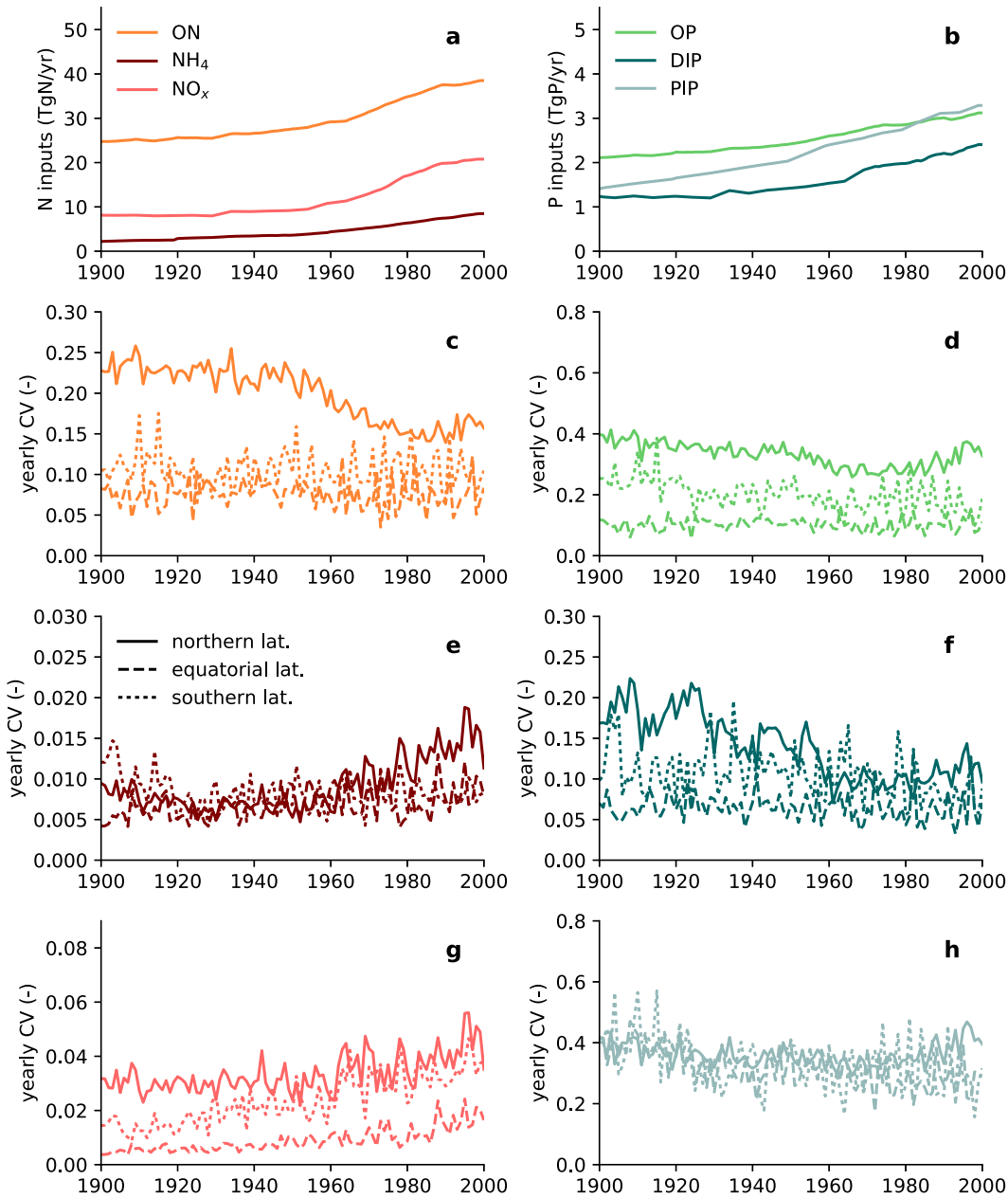


**Fig. 3.** Total global yearly average inputs a) of the different N forms and b) of the different P forms; yearly coefficients of variation of c) ON, d) OP, e) $NH_4^+$, f) DIP, g) $NO_x^-$, and h) PIP at different latitudes. northern lat. = latitudes ≥ 20°, equatorial lat. = − 20° ≤ latitudes < 20°, southern lat. = latitudes < −20°.

that the weathering term of the DIP yield from Harrison et al. (2010) was calibrated on measurements in large rivers, and hence integrates the effect of DIP retention in small headwaters and potential transfer from DIP to PP that can occur in the water column (*e.g.*, Némery et al., 2005).

### 3.1.3. Potential effect of changes in nutrient forms and ratios

Over the 20th century, the emergence of significant anthropogenic nutrient sources to surface freshwaters, with an increasing influence of agriculture and treated wastewater effluents over that of natural sources, has led to an increase in the proportion of inorganic nutrient forms. These inorganic forms are generally more bioavailable and are therefore more likely to increase eutrophication risks. The consequence of this shift can be illustrated by the example of Lake Erie, described by Jarvie et al. (2017). While the TP loads to the lake decreased during the past decades, DIP loads increased due to increased tile drainage in agricultural lands. It is believed that this, together with favorable hydrological conditions, has fueled recent large harmful algal blooms (Michalak et al., 2013; Jarvie et al., 2017). In general, the global increase in the proportion of PIP forms in TP inputs, due to the expansion of agricultural lands may lead to higher accumulation along the aquatic continuum, due to sedimentation. This accumulation most likely occurs in slow flowing areas, such as reservoirs (Seitzinger et al., 2010), and can constitute a long-term source to surface freshwaters, referred to as

nutrient legacy (Owens and Walling, 2002; Jarvie et al., 2012; Sharpley et al., 2013).

Due to the large increase in DIN inputs from agricultural lands and selective nutrient reduction measures, *i.e.*, greater focus on the reduction of P wastewater effluents through improved treatment and the progressive ban of P in detergents (Dolan, 1993; Garnier et al., 2005; Morée et al., 2013), DIN inputs have escalated at larger rates than DIP inputs. Therefore, while the yearly TN:TP molar ratio of nutrient inputs to surface freshwaters has remained stable (15–17) over the 20th century, the global DIN:DIP molar ratio has increased from 18 to 27. This is consistent with results from Paerl et al. (2006), who found a steeper increase in the DIN:DIP ratio than in the TN:TP ratio (increase by 2/3) between the mid-1980s and early 1990s in an estuarine system of the USA. These global changes in the form of nutrients reaching surface freshwaters control the development of aquatic ecosystems. The relative abundance of major nutrient elements can indeed affect ecosystem composition, and notably impact the development of algal blooms in freshwater and coastal marine systems (Anderson et al., 2002; Kim et al., 2007b; Heisler et al., 2008; Glibert and Burford, 2017). The form of the supplied nutrients is important in the relative growth of different phytoplanktonic populations, depending on their nutritive preferences, and can furthermore affect their toxicity (Glibert and Burford, 2017). Glibert and Terlizzi (1999), Li et al. (2009) and Glibert et al. (2012) showed that N:P ratios of inorganic and organic forms are important in bloom successions. For example, Glibert et al. (2012) reported that, in estuarine and coastal field studies, most *Prorocentrum* planktonic species (some of which are toxigenic, and that also have representatives in freshwaters) bloomed at DIN:DIP ratios above the Redfield molar ratio of 16:1. If combined with favorable light and flow conditions, the increase in global DIN:DIP ratios may therefore lead to a greater risk of development of harmful algae species in surface freshwaters.

### 3.2. Changes in the subannual patterns of nutrient loads to global surface freshwaters

#### 3.2.1. Subannual variability of N and P inputs

Global changes in human activities have not only intensified nutrient inputs to surface freshwaters and modified their form, but have also altered the seasonal variability of nutrient delivery.

Due to the five-fold increase in N inputs from surficial runoff over the 20th century, the proportion of $NO_x^-$ originating from seasonally-variable sources (*i.e.*, those driven by hydrology) has risen from 11 to 23% (calculated from Table 3), thus increasing the subannual variability of $NO_x^-$ inputs to surface freshwaters globally (Fig. 3 g). It has especially escalated at high rates at southern latitudes due to agricultural expansion, notably in Brazil and Australia. In these locations, the variability of ON inputs has remained quite stable between 1900 and 2000, due to the constant contribution of inputs from natural sources. However, the proportion of ON from sources with "uniform" subannual patterns has increased globally from 35 to 47% over the century. Due to the intensification of agriculture, large amounts of ON reach surface freshwaters after leaching through agricultural soils and aquifers with long retention times (Van Meter et al., 2016), which dampens the subannual variability of nutrient sources. This could also explain the ON subannual variability decrease in northern latitudes from $23{\cdot}10^{-2}$ to $16{\cdot}10^{-2}$ (Fig. 3 c). Finally, since they mainly originate from sewage effluents, $NH_4^+$ loads have little subannual variability, one order of magnitude lower than for $NO_x^-$ and ON. Yet, the proportion of $NH_4^+$ originating from surficial runoff has slightly risen (from 6 to 8% between 1900 and 2000 at the global scale), leading to a small increase in the amplitude of its monthly fluctuations (Fig. 3 e).

These results suggest that changes in monthly fluctuations in the inputs of different N compounds to surface freshwaters are mainly driven by agricultural activities at the global scale. The use of fertilizers, inducing a higher N content in land runoff water, has led to an increase in the subannual variability of the delivery of DIN forms. Concomitantly, large amounts of N inputs to agricultural soils are transferred to underlying groundwaters. This N can travel for years or decades through aquifers before reaching river networks (Böhlke, 2002). Therefore, in areas dominated by N loads from groundwater exfiltration, the variability of these inputs is attenuated, and time lags between changes in agricultural practices and delivery to aquatic systems can occur (Lindsey et al., 2003; Puckett et al., 2011; Van Meter et al., 2017). These systems are hence likely subjected to high N loads all year round, and water quality impairment may continue, even long after the introduction of mitigation strategies.

P loads are extremely variable at monthly timescales, since the major P source (*e.g.*, soil erosion, contributing to 49–52% of the global P loads, see Table 4) is driven by runoff, which depends on subseasonal weather variations. This is one of the main reasons why P export from river basins mostly occurs during periods of extreme discharge (Royer et al., 2006; Gentry et al., 2007). The subannual variabilities of the loads of PIP and OP have remained more stable over the 20th century than those of the different N forms (see Fig. 3 d, f and h). At northern latitudes, the variabilities of OP and DIP inputs have decreased (decrease in the yearly coefficient of variation from $40{\cdot}10^{-2}$ in 1900 to $33{\cdot}10^{-2}$ in 2000 and from $17{\cdot}10^{-2}$ in 1900 to $10{\cdot}10^{-2}$ in 2000, respectively). This can be explained by the increased contribution of sewage inputs (from 2 to 24% for DIP and from 4 to 9% for OP between 1900 and 2000, globally — results calculated from Table 4). The simultaneous increase in DIP loads and decrease in their subannual variability shows that there has been an escalating, continuous delivery of bioavailable P forms to global surface freshwaters over the past century.

#### 3.2.2. Effect of the increasing contribution of wastewater emissions in densely populated areas

Locally, in densely populated areas, sewage effluents can constitute major nutrient sources. In 1900, on a yearly average, sewage was the major nutrient source to surface freshwaters over less than 0.5% of the world's continental area (Fig. 4 a and b). While global population has risen more than 3-fold over the past century (from 1.7 to 6.1 billion inhabitants), population has concentrated in urban areas (urban population multiplied more than 10-fold, representing 16% in 1900 and 47% in 2000, according to Klein Goldewijk et al., 2010). This has led to extremely high localized pressures and the continental surface area, over which sewage is the dominant yearly nutrient source, has reached *ca.* 4% of the global land area at the end of the 20th century. In 2000, sewage water contributes to more than 10% of the total N and P inputs to surface freshwaters. Its contribution can reach much higher values locally. For instance, Pieterse et al. (2003) estimated that point sources contributed to 48% of TN and 81% of TP inputs to the Dommel river basin (Belgium and The Netherlands) in the early 1990s.

The forms of the nutrients originating from sewage effluents largely depends on the level of treatment (Carey and Migliaccio, 2009). In areas with large population densities and no or little treatment of sewage water, wastewater inputs substantially increase the ON and OP loads to surface freshwaters. This is notably the case in regions of Africa and Southeastern Asia (see Fig. 1 and Table S.1). In terms of N, sewage water is mainly composed of $NH_4^+$. In 2000, 66% of the global $NH_4^+$ inputs to surface freshwaters originated from wastewater (calculated

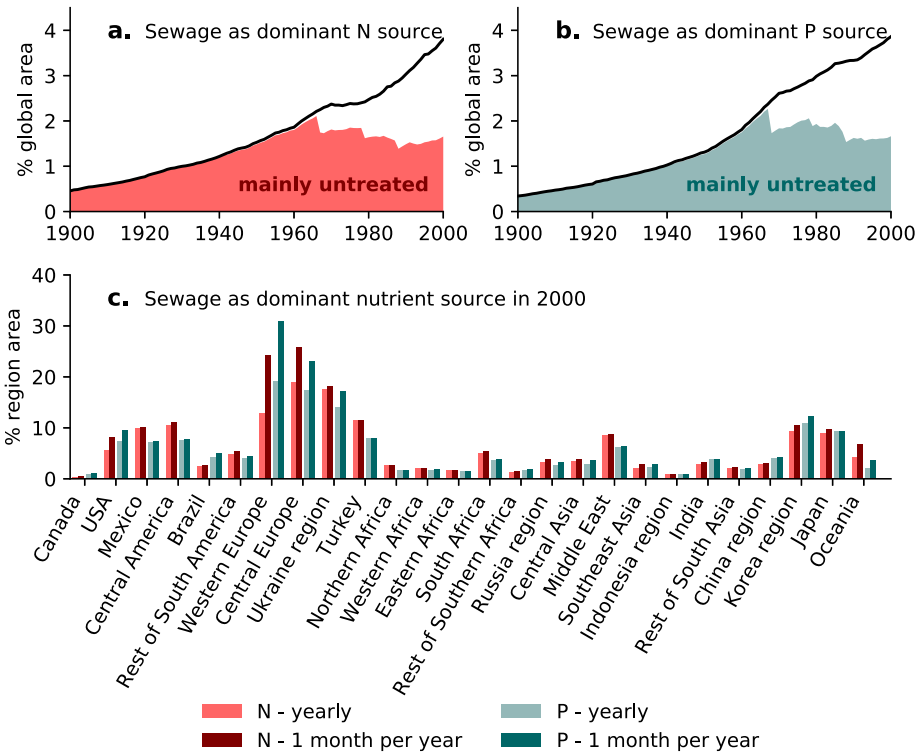


**Fig. 4.** Percentage of the global area, where sewage constitutes the major source of a) N and b) P at a yearly time scale and c) percentage of surface area, where it is the dominant nutrient source over one year/for at least one month a year for different regions of the world for the year 2000. See map Fig. S.2 for the precise delimitation of the 26 IMAGE regions.

from Table 3). The increase in sewage water emissions led to an increase in $NH_4^+$ in TN inputs from 6 to 13% over the 20th century. The level of treatment has an even greater effect on the P speciation in effluent water. Raw sewage water is mainly composed of PP forms, while after primary treatment DIP predominates (see Table 2). In 2000, over 3/5 of the global sewage water emissions have undergone treatment, which allows for the abatement of a significant proportion of TN and TP inputs from households and industry (Morée et al., 2013). Furthermore, treated sewage water generally contains large proportions of dissolved, bioavailable nutrient forms (*i.e.*, DIN and DIP) (Jarvie et al., 2006), which can control overall aquatic productivity (Carey and Migliaccio, 2009).

We assume that sewage water emissions are continuous over the year. Therefore, even in places where they do not constitute the major nutrient source on a yearly average, they can become predominant during periods of low runoff. This is particularly true for P, for which diffuse sources (*i.e.* soil loss and surficial runoff) induce a high seasonal variability. For instance, Bowes et al. (2008) showed that, in the UK, point sources could constitute the major TP load 77% of the time, even in river basins where diffuse sources constituted > 75% of the yearly TP load (*e.g.*, Leam river). Edwards and Withers (2007) gathered data from 4 Scottish rivers with contrasting land cover and population densities for the year 1974, and showed that, for all 4, the proportion of DIP in TP in the river was greater in summer (82–97% against 38–75% in winter), due to the increased relative contribution of point sources.

In 2000, wastewater effluents constituted the main P source for at least one month of the year around one third of Western Europe and one quarter of Central Europe (Fig. 4 c). In such areas, when periods of low flow coincide with periods of high biological activity (growing period), point input reductions can effectively reduce eutrophication risk (Bowes et al., 2008). New eutrophication mitigation strategies should hence incorporate the seasonal nutrient speciation in order to specifically tackle bioavailable forms (Hilton et al., 2006; Edwards and Withers, 2007).

### 3.3. Model sensitivity to source speciation and potential future improvements

The present results are based on model outputs and a number of assumptions that could be refined for future improved estimates of nutrient loading to global surface freshwaters. A sensitivity analysis on the speciation of the different nutrient sources Appendix A allows for identifying the sources that require greater refinement for a better large scale characterization.

Over the entire 20th century, N inputs to global river networks have been dominated by groundwater exfiltration. N loads are therefore most sensitive to the speciation of inflows from this source. An error of 25 percentage points on its speciation (see Appendix A for more detail) leads to coefficients of variation of the estimated yearly loads of $NH_4^+$, $NO_x^-$ and ON between 1900 and 2000 of 30–55, 19–24 and 8–11%, respectively. In 2000, coefficients of variation can locally reach 56, 32 and 27% for $NH_4^+$, $NO_x^-$ and ON, respectively (data not shown). Those high values are encountered in areas dominated by natural inputs, in the tropics, and at northernmost latitudes (> 50°). It is therefore important, for an improved assessment of the inflows of the different N forms to river networks, to focus on improving our current characterization of inputs from groundwaters. The speciation of these inputs in the present study is based on data from water sampled in wells, and we assume that N inflows from groundwater exfiltration are constant over one year. Groundwater-surface water exchanges occur at the hyporheic

zone. This zone is characterized by a possible alternation of groundwater exfiltration to river networks and surface water infiltration, depending on the variations of the groundwater table and surface water heights. The hyporheic zone can also be extremely ecologically active (Brunke and Gonser, 1997; Ingendahl et al., 2009). There are gaps in our current understanding of the functioning of the hyporheic zone, notably the fate and recycling of organic matter (Marmonier et al., 2012). It is therefore likely that we underestimate the yearly variability of N inputs and that we overestimate the ON loads from groundwater, since part of it might be mineralized before reaching the surface freshwaters. Our estimates of N inputs to surface freshwaters can be substantially refined in the future with: i) a better assessment of the biogeochemical effect of nutrient transport through the hyporheic zone and ii) large-scale hydrological simulations of subannual groundwater-surface water exchanges.

Due to the lack of data availability, we also made strong assumptions concerning the atmospheric N deposition source. Its speciation at the global scale is subject to large uncertainties ( ± 50%, according to Duce et al., 2008), since it depends on a complex combination of land use/human activities, long-distance transport of N in the air, and precipitation processes. Since atmospheric deposition accounts for a minor proportion of N inputs to global watersheds (< 2%, Table 3), the sensitivity of global $NH_4^+$, $NO_x^-$ and ON loads to its speciation is low (Appendix A). However, for some large lakes (*e.g.*, Great Lakes in North America, Lake Chad) and in desert areas, atmospheric deposition can constitute the main N source to surface freshwaters. In such areas, an error of 25 percentage points on the speciation of atmospheric N deposition can lead to coefficients of variation in the estimated yearly loads of $NH_4^+$, $NO_x^-$ and ON for the year 2000 reaching up to 37, 36 and 44%, respectively (data not shown). For these specific cases, estimates of N compound emissions to surface freshwaters would benefit from a better incorporation of anthropogenic impacts on the speciation of atmospheric N deposition, and from the differentiation between wet and dry deposition, which would allow for the identification of subannual patterns.

63% of the P inputs to surface freshwaters are brought along with runoff water. P speciation in runoff water is extremely variable (Table 2). This is due to the fact that runoff P can have many different origins, *e.g.* loss of mineral fertilizer, manure or decomposing vegetation. Furthermore, its mobilization can be the consequence of different physical processes, such as leaching, soil loss, or desorption after stormwater events (Ulén et al., 2007). P mobilization *via* runoff depends on soil characteristics and the weather. During its transfer from land to river systems, P can be retained and/or undergo transformations between PP and DIP forms through sorption processes. P can, for example, be transported as DIP along preferred hydrological pathways during storm events, when the soil has a high moisture content and becomes supersaturated with P (Heathwaite et al., 1996). In other conditions it can sorb onto soil particles and be retained as PP that may be eroded later on. In the present study, we limit uncertainties by distinguishing between different processes resulting in P transport *via* runoff: soil loss (affecting only particulate forms) and surficial runoff (losses of recently applied organic and dissolved forms, before any sorption interactions could occur in the soil). However, the partitioning between PIP and OP inputs from runoff is based on little data (see Table 2), and may contain large uncertainties. The sensitivity analysis Appendix A we performed showed that global estimated P loads are the most sensitive to the speciation of P in soil loss from agricultural soils. An error of 25 percentage points on P speciation of this source leads to coefficients of variation for PIP and OP loads between 1900 and 2000 of 16–17 and 10–18%, respectively. In areas that are not influenced by vegetation scouring in floodplains and that are subject to strong soil loss rates from agricultural lands, *i.e.*, at the Canada/USA border, in Western China, and in the southern part of the Russia region, the coefficients of variation can reach up to 19% for PIP and 59% for OP in 2000 (data not shown). As stated in Subsection 2.2, we assume that the proportion of PIP in soil loss from agricultural lands is higher than that from natural lands, due to the sorption of mineral fertilizer onto soil particles. However this proportion depends on the land use (*e.g.*, grasslands, croplands with different plant species), the type of fertilizer applied (manure, organic fertilizer or mineral fertilizer), and interactions between fertilizer and soil particles. Refining the spatial information on fertilization methods would allow for a more precise assessment of the P speciation delivered by agricultural soil loss, and thus of global P runoff.

### 3.4. Conclusion and outlook

These model results have important implications for future large scale studies on nutrient transfers and biogeochemical cycling in surface freshwaters. By using spatially explicit outputs from a global integrated assessment model, our results account for the effect of both large scale and local interactions of climate/hydrology and human activities. The fine temporal resolution of our estimates will allow for the future identification of coinciding periods of high bioavailable nutrient loading, high river biogeochemical activity and adequate climate conditions, which can drive short-term eutrophication events. The proportions, amounts and variability of the different nutrient forms can vary along the aquatic continuum, before reaching the global coasts. They can be affected by different in-stream physical and biogeochemical processes, potentially inducing time lags between nutrient loading and delivery to downstream ecosystems, inducing complex links between natural and anthropogenic inputs and water quality. To fully understand the implications of our results for long-term eutrophication risks, future investigation is therefore needed on the transformation, accumulation and re-mobilization processes of the inflowing nutrients within river networks at the global scale.

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## Appendix A. Sensitivity analysis on source speciation

The speciations of the simulated sources (Tables 3 and 4 in main text) are referred to as "reference" speciations. For each simulated source, we randomly pick 100 new speciations, where the proportions of each nutrient form stays in a range of ± 25 percentage points of the reference speciation. For example, for atmospheric deposition that has a reference speciation of 35% of $NH_4^+$, 35% of $NO_x^-$ and 30% of ON, the proportions of $NH_4^+$, $NO_x^-$ and ON (in %) are picked within the ranges [10,60], [10,60] and [5,55], respectively (with the 3 proportions summing up to 100%). The loads of the different nutrient forms to the global surface freshwaters are then calculated over the 20th century for each of these new speciations. To assess the sensitivity of the results to the speciation, for each source: i) we plot the ranges of the calculated global yearly loads of the different nutrient forms (Figs. A.5 and A.6), ii) we calculate the coefficients of variation of the 100 simulated yearly loads for all simulated nutrient forms for 1900, 1950 and 2000 (Tables A.5 and A.6).

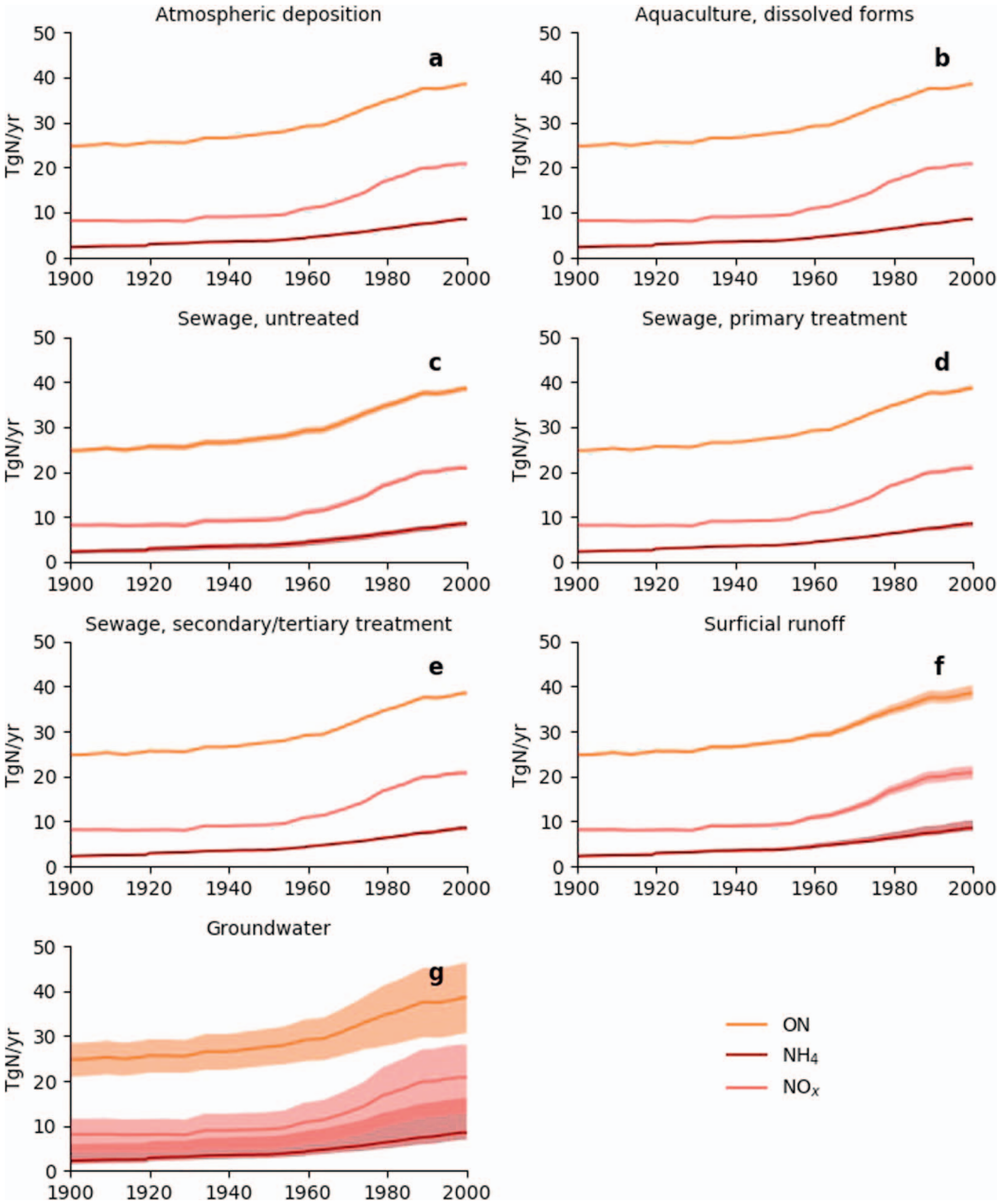


**Fig. A.5.** Effect of a variation of ± 25 percentage points in the N speciation of a) atmospheric deposition, b) aquaculture, c) untreated sewage, d) sewage with primary treatment, e) sewage with secondary/tertiary treatment, f) surficial runoff, and g) groundwater exfiltration inputs on the total yearly average loads of the different N forms to global surface freshwaters over the 20th century.

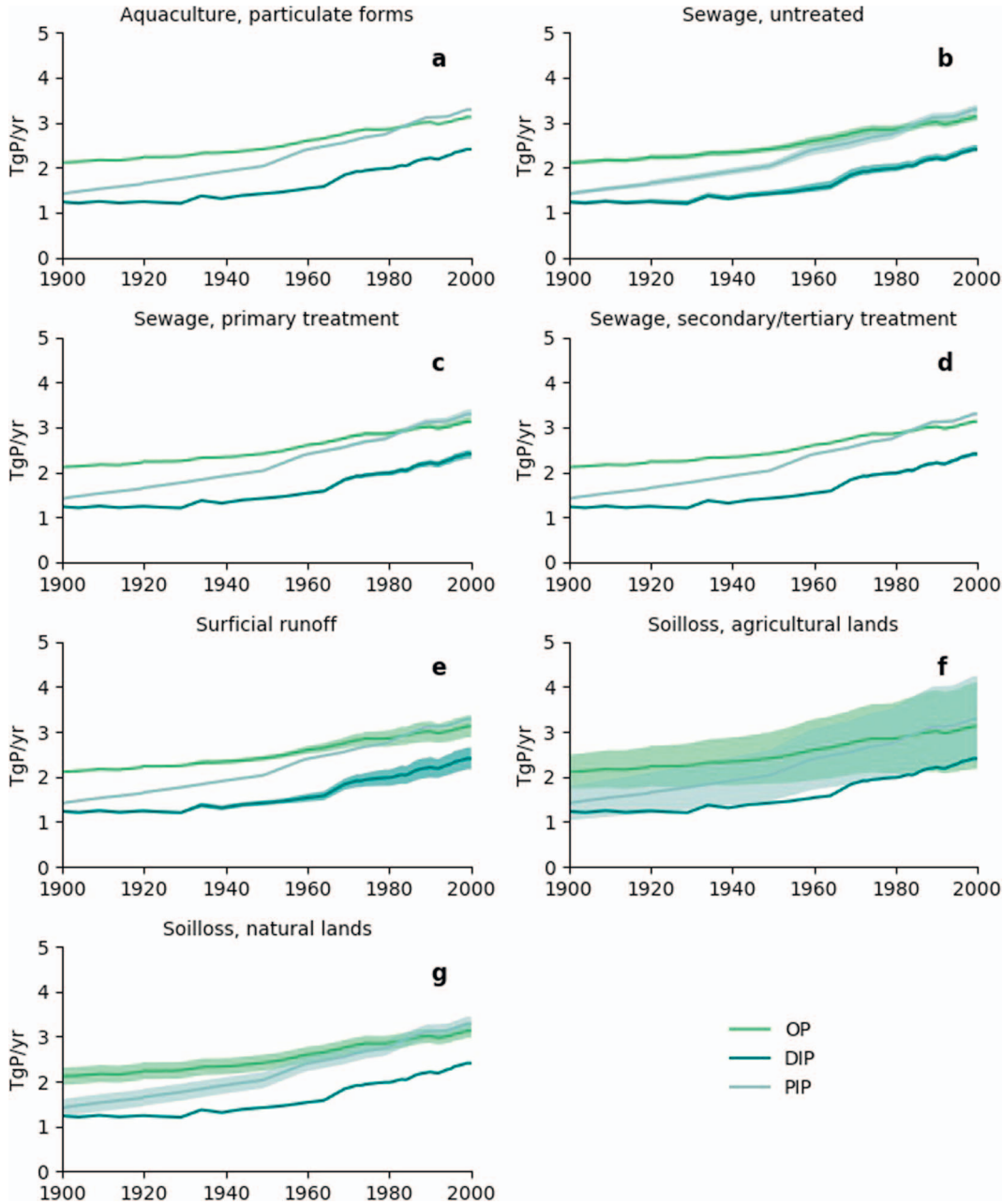


**Fig. A.6.** Effect of a variation of ± 25 percentage points in the P speciation of a) aquaculture, b) untreated sewage, c) sewage with primary treatment, d) sewage with secondary/tertiary treatment, e) surficial runoff, f) soil loss from agricultural lands, and g) soil loss from natural lands inputs on the total yearly average loads of the different P forms to global surface freshwaters over the 20th century.

Table A.5
Coefficients of variation of the estimated yearly loads for a variation of ± 25 percentage points in the N speciation of the different simulated N sources for 1900, 1950 and 2000 (in %).

| Source | $NH_4^+$ | | | $NO_x^-$ | | | ON | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1900 | 1950 | 2000 | 1900 | 1950 | 2000 | 1900 | 1950 | 2000 |
| Atmospheric deposition | 2.55 | 1.81 | 1.54 | 0.69 | 0.71 | 0.63 | 0.24 | 0.25 | 0.36 |
| Aquaculture, dissolved forms | 0 | 0.05 | 1.20 | 0 | 0.02 | 0.49 | | | |
| Sewage, untreated | 9.44 | 10.03 | 3.93 | 1.57 | 2.43 | 0.99 | 0.88 | 1.38 | 0.91 |
| Sewage, primary treatment | 0 | 1.31 | 3.65 | 0 | 0.32 | 0.91 | 0 | 0.15 | 0.72 |
| Sewage, secondary/tertiary treatment | 0 | 0 | 3.11 | 0 | 00 | 1.05 | 0 | 0 | 0.53 |
| Surficial runoff | 6.54 | 5.74 | 8.63 | 1.76 | 2.24 | 3.51 | 0.72 | 0.94 | 2.38 |
| Groundwater exfiltration | 55.01 | 36.41 | 29.56 | 24.24 | 23.32 | 19.74 | 7.91 | 7.75 | 10.57 |

Table A.6
Coefficients of variation of the estimated yearly loads for a variation of ± 25 percentage points in the P speciation of the different simulated P sources for 1900, 1950 and 2000 (in %).

| Source | DIP | | | PIP | | | OP | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1900 | 1950 | 2000 | 1900 | 1950 | 2000 | 1900 | 1950 | 2000 |
| Aquaculture, particulate forms | | | | 0 | 0.01 | 0.12 | 0 | 0.01 | 0.13 |
| Sewage, untreated | 1.37 | 2.25 | 1.57 | 1.65 | 2.13 | 1.57 | 0.92 | 1.50 | 1.37 |
| Sewage, primary treatment | 0 | 0.44 | 2.31 | 0 | 0.19 | 1.08 | 0 | 0.22 | 1.51 |
| Sewage, secondary/tertiary treatment | 0 | 0 | 1.10 | 0 | 0 | 0.51 | 0 | 0 | 0.70 |
| Surficial runoff over agricultural lands | 1.16 | 2.32 | 5.89 | | | | 0.68 | 1.36 | 4.54 |
| Soil loss from agricultural lands | | | | 15.65 | 16.43 | 17.05 | 10.44 | 13.97 | 17.97 |
| Soil loss from natural lands | | | | 7.96 | 4.93 | 2.70 | 5.31 | 4.19 | 2.84 |

## Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gloplacha.2018.02.007.

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