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Nitrogen biogeochemistry of water-agro-food systems. The example of the Seine land-to-sea continuum

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Abstract

As an illustration of the usefulness of the concept of water-agro-food systems, this paper describes the mechanisms behind the nitrogen cascade from agricultural soils to the coastal sea rivers through aquifers, riparian wetlands, rivers and streams and the estuary, for the case study of the Seine river watershed and its receiving coastal sea. It is stressed that the structure of the agro-food system, i.e. the way food production and trade, as well as consumption and waste management are organized, is the main determinant of the quality of ground- and surface water as well as of aquatic ecosystem functioning.

Key words

Nitrogen cascade, agro-food system, Seine River, denitrification, eutrophication, leaching, nitrous oxide emission.

1. Introduction

Nitrogen (N), an essential nutrient in the composition of living organisms, present in proteins and nucleic acids, and also one of the major limiting factors of primary production in terrestrial as well as in aquatic systems, has long been known to play a central role in the control of ecosystem functioning. The massive introduction of reactive nitrogen in the biosphere by human activity since the discovery of the Haber-Bosch process completely changed this control, especially since the 1950s with the intensification and modernization of agriculture to feed the increasing population (Smil, 1999; Galloway et al., 2004; Gruber & Galloway, 2008). As early as 1924, Lotka already saw that the development of the nitrogen fertilizer industry represented “*nothing less than the ushering in of a new era in the history of the human race, a new cosmic epoch. In the short span of a dozen years –geologically speaking in an instant- man has initiated transformations literally comparable in magnitude with cosmic processes*” (Lotka, 1924). Since then, the multiple environmental and societal threats created by this excessive anthropogenic introduction of reactive nitrogen (Nr) into the biospheric cycle have been underlined, at local, regional and global scales. It affects air quality and greenhouse gas balance, soil quality through acidification, and water quality through nitrate contamination and eutrophication, as well as contributing to biodiversity losses (Sutton et al., 2011).

This paradigm of the nitrogen cascade (Galloway et al., 2003) can be combined with the vision that close links exist between the biogeochemical functioning of aquatic and terrestrial systems, as well between the diverse aquatic ecosystems succeeding each other along the upstream downstream gradient of complex drainage networks. This land-to-sea continuum

view extends the river continuum concept formulated by several authors in the 1980s (Vannote et al., 1980; Ward, 1989), but places a special emphasis on the relationship with terrestrial ecosystems, hence on the importance of land cover and land use of the watershed as determinants of the biogeochemistry of rivers and streams including their discontinuities such as reservoirs, estuaries and coastal seas. This view embraces the full land sea continuum, from terrestrial to marine systems.

Another paradigm that was developed during the past decade states that food production can be considered the first determinant of land cover and land use changes, not only through agricultural practices, but also through the structure of the whole system by which food is produced to meet the dietary requirements of the population (see among other studies, the EAT-Lancet Report, Willet et al., 2019). This implies that agro-food systems should be considered as an integral part of hydrosystems for a full understanding of the interactions between human activity and water quality. This is exactly the idea behind the concept of water-agro-food systems as formulated by Garnier et al. (2015, 2019a).

The purpose of this article is to present the integrated vision we developed of the socio-ecological metabolism of the Seine watershed territory through the prism of nitrogen transformations and transfers from land to sea, from a long term perspective. We first set the stage by presenting the basic physical geographic features of the Seine basin and the long term trajectory of the agro-food system itself. We then follow the journey of nitrogen from its introduction as a limiting nutrient in cropping systems to its losses to the hydrosphere (via leaching essentially in the form of nitrate, NO_3^-), or to the atmosphere (via emissions of dinitrogen, N_2) or nitrous oxide, N_2O). We also focus on the fate of leached nitrogen through aquifers and riparian zones down to rivers, where it is joined by nitrogen originating from human excretion in urban areas, before being delivered to the sea. The issue of resulting marine eutrophication in the Seine Bay complements the integrative vision. Two contrasting scenarios of what the nitrogen cycle in this land sea continuum could look like in the next 30-50 years are finally presented.

2. The Seine watershed, its river network and the Seine Bay

The Seine watershed occupies the middle of the large Paris Basin, a sedimentary concentric rock formation, with tertiary limestone at the center, followed by a large cretaceous chalk area separated by a narrow clay band from Jurassic limestones at the periphery. These rock layers, often compared to a pile of plates, lie on an ancient massif of metamorphic and igneous rocks outcropping at the extreme north-east and south-east (Fig. 1a). The Seine River system, with a total watershed area of approximately 75 000 km², drains these geological layers via a regular network of tributaries converging to the large fluvial lower Seine River at the beginning of which Paris lies, 350 km from the outlet to the sea. In the second half of the 19th century, sluice-locks were installed on the lower Seine and its main tributaries for navigation development. The macrotidal estuarine part of the river begins at Poses, where the last of these dams is located. The estuary has also been largely managed for the purpose of navigation and harbor activities. The Seine estuary delivers its water into the Seine Bight, a rather shallow (25 m mean depth) 3775 km² open bay in the English Channel.

Land use currently comprises 50% cropland, 10% permanent grassland, 0.7% vineyard and orchard, 26% forest and 11% urban and artificialized areas (Fig. 1b). The current population is 17.5 million inhabitants, mostly concentrated in the huge Paris agglomeration and along the lower Seine River sector down to the harbors of Rouen and Le Havre (Fig 1c). The most upstream areas have a declining population.

Figure 1. a. The Seine River system and the geological formations of its watershed and surrounding areas (source: BRGM www.brgm.fr). From left to right b. Current distribution of land use (source: Corine Land Cover 2012, www.data.gouv.fr/fr/datasets/corine-land-cover-occupation-des-sols-en-france) and land cover variations in the Seine watershed since 1850 (data from Le Noë et al. subm) c. Current distribution of population density (INSEE 2017 <https://www.insee.fr/fr/information/2008354>.) and population evolution in the Seine watershed (data from Le Noë et al., 2018)

3. Long-term trajectory of the agro-food system

In the second half of the 19th century, like in most regions under temperate climate, the dominant agricultural system in the Seine watershed and in the surrounding regions was based on mixed crop and livestock farming, with crop rotations alternating between one year of forage legume and two years of cereals, and livestock manure being the major fertilizer input in addition to symbiotic fixation of atmospheric nitrogen by legumes (Fig. 2a). This system was able to sustain a rural population of approximately 50 inhabitants per km², based on a diet of 5 kgN/cap/yr with one-third animal proteins, and to still export enough surplus to feed the large Paris agglomeration (Billen et al., 2012a,b, 2019; data from Le Noë et al., 2018). Gradually during the first half of the 20th century, and then rapidly during the three decades following World War II, the region in the center of the Paris Basin specialized into stockless crop farming, replacing symbiotic fixation and manure by synthetic fertilizers as the main N inputs to arable soils. Livestock was concentrated in peripheral regions, in the eastern part of the basin (remaining in mixed crop and livestock farming system, Mignolet et al., 2007), and in the “Great-West” (where intensive livestock farming developed, highly dependent on forage import, particularly soybean grain and cakes from South America, Fig. 2b).

These trends in territorial specialization of farming systems went hand in hand with a commercial opening of agriculture. Today, the Seine basin area exports 80% of its cereal production, while it imports 70% of the animal proteins consumed by the population (Fig. 2). The share of animal-to-total protein intake in the human diet, was about 30% at the end of the 19th century, a proportion consistent with the ratio of animal to vegetal proteins produced by the mixed crop and livestock farming system. Animal protein intake has increased considerably in proportion, reaching 70% of the total protein ingestion in the beginning of the 21st century, and has slowly decreased in recent years (Le Noë et al., 2018). Human excreta in the 19th century was considered a useful fertilizing resource, collected in cesspools, and then through sewer networks (Barles, 2005; Esculier & Barles, 2019). It is currently treated in wastewater purification plants, which eliminate about 57% of N in excreta as atmospheric dinitrogen through an energetically expensive process of denitrification (using methanol as an electron donor), recover 4% as sludge, only a small part of which is recycled in agriculture, and discharge the remaining part (39%) to surface water (Esculier et al., 2018). The circularity of human excreta management, i.e. the proportion of N in human excreta that is returned to agricultural land, peaked in the 1900's to approximately 40%, and decreased since then to a negligible amount.

Figure 2. GRAFS representation of the agro-food system of the Seine watershed in the periods of 1929 and 2010-2014 (data from Le Noë et al., 2017, 2018).

4. The consequences of intensification of cropping systems

The trend described above toward territorial specialization of agriculture developed alongside the simplification of crop rotations and intensification of soil N inputs. Crop rotations alternating between forage legumes, wheat and oats, which dominated in the central region of the Paris Basin until the early 1950s, were gradually replaced by rotations alternating between rapeseed, wheat, and barley or grain maize.

Lassaletta et al. (2014) have shown that a robust relationship exists, for a given pedo-climatic context, between yield (Y in kgN/ha/yr, expressed in terms of N content of harvested products over the whole crop rotation cycle) and total N inputs to soil (F in kgN/ha/yr, including manure, symbiotic fixation, atmospheric deposition and synthetic fertilizers over the rotation cycle). This relationship can be represented by a single parameter hyperbolic function of the form: $Y = Y_{\max} F / (F + Y_{\max})$, where $Y_{\max}$ characterizes the fertility of the cropping system at maximum N availability, in a given pedo-climatic context. The data gathered from the reconstituted chronicles of crop production and fertilization in the different agricultural regions of the Seine basin over the period 1950-2015 (data from Le Noë et al., 2018) show a trajectory that describes such a relationship, with a relatively constant $Y_{\max}$, although a trend toward a slightly higher $Y_{\max}$ value (i.e. higher yields at similar or even lower rate of N inputs) is observed after the 1980's (Fig. 3). A similar relationship holds for individual crop rotations in each regions of the Seine basin documented by agronomical surveys for both conventional and organic rotations (Anglade et al., 2015a,b; Rakotovololona et al., 2018). Interestingly, the same relationship describes both systems, indicating that there is no intrinsic fertility gap inherent to organic farming practices.

Figure 3. Yield-fertilization relationships for crop rotations in the central regions of the Paris Basin (a) and in the regions of the eastern periphery of the Seine watershed (b). The ordinate is the annual average export of N imbedded in crop harvest exported over the complete rotation cycle; the abscissa is the annual average N input to the soil as manure, symbiotic fixation, atmospheric deposition and synthetic fertilizer. Gray circles refer to the reconstituted chronicles of the cropping system of Ile-de-France and Picardy (a) and Bourgogne and Lorraine (b) (Le Noë et al., 2018); red and green circles refer to data from current individual crop rotations in conventional (red) and organic (green) farming systems (Anglade et al., 2015b; Rakotovololona et al., 2018). The black curves show the theoretical Y vs F relationship for the stated values of $Y_{\max}$ (in kgN/ha/yr).

Yield-N input relationships are useful, as they allow us to predict the environmental losses of N resulting from agricultural practices. The shape of the relationship implies that these losses – defined as the N-surplus, i.e. the difference between N inputs and yield – increases with

intensification, i.e. with increasing fertilization. In other words, nitrogen use efficiency (NUE: the ratio of N yield over N total input) decreases with increasing fertilization. The agricultural N-surplus for cropland of the Seine watershed thus increased from close to 6 kgN/ha/yr in 1850 to as much as 85 kgN/ha/yr at the end of the 1980s, after which it slightly decreased to approximately 50 kgN/ha/yr in 2015 (Fig. 4).

The fate of the surplus, if not stored in the soil organic matter (OM) pool, is either to be lost to the atmosphere or to the hydrosphere. In cropland, leaching generally represents by far the largest fraction of the surplus, unless cover crops are systematically implemented in order to avoid bare soils during the wet autumn and winter season (Constantin et al 2010; Justes et al, 2012), a practice that also increases soil OM storage (Autret et al., 2016, 2019).

Le Noë et al. (2019a,b) estimated the long term dynamics of organic carbon (C) in the arable soils of France. Sequestration was shown to be mainly the result of soil inputs of humified crop residues, and only secondarily of manure application. In the Seine basin, low rates of sequestration, or even negative rates (i.e. net mineralization) were observed at the beginning of the 20th century. During the 30 years following World War II, which was marked by a rapid increase in crop productivity, higher rates of C sequestration occurred, which levelled off from the end of the 1980's. As the C:N ratio of soil OM is rather constant at around a value of 10 gC/gN (Benoit et al., 2016, Le Noë et al., 2019b), much lower than the C:N ratio of crop residues, the corresponding N sequestration in soil OM can be easily calculated (Fig. 4). As a mean for the arable land of the Seine watershed, it varied from 18 kgN/ha/yr in the 1970's to approximately 5 kgN/ha/yr in the 2010s.

Figure 4. Nitrogen budget of the Seine river watershed (limited at Poses, 69000 km²). Positive fluxes are the inputs to the water system : (1) cropland N surplus defined as the share of N soil inputs that is not exported by crop harvest; (2) N inputs to the hydrosystem from non-cropland soils (3) urban wastewater discharge to the river system after treatment. Negative fluxes refer to “retention” processes: (1) N sequestration in the soil organic matter pool, (2) soil denitrification; (3) temporary retention in vadose zone and aquifer; (4) riparian denitrification and (5) in-stream denitrification. The black curve refers to the river N delivery at the outlet of the river network: it roughly corresponds to the difference between inputs and retentions.

Another fraction of the surplus is eliminated to the atmosphere through soil denitrification, the process of anaerobic respiration of OM using nitrate as an electron acceptor, occurring in anoxic micro-zones of the soil. Wet conditions, high soil content of nitrate and OM are conditions triggering soil denitrification (Tiedje et al., 1982; Knowles, 1982; Weier et al., 1993). Although dinitrogen is the main end product of denitrification, nitrous oxide, a potent greenhouse gas, is also produced (Vilain et al., 2014; Benoit et al., 2014). For soil denitrification, $N_2O/(N_2+N_2O)$ ratios in the range of 16-40 (median 28) have been estimated (Box 1). Soil N_2O emission, although of episodic nature, is widely measured using static chambers. Garnier et al. (2019b) have proposed an empirical relationship relating soil N_2O emissions (hence soil denitrification) to climatic data and fertilization rates. Using this relationship, soil N_2O emission, as well as denitrification, in the Seine watershed was estimated for the period 1900-2015 (Fig. 4). Current values of soil denitrification range at approximately 15-20 kgN/ha/yr.

On an annual basis, leaching is the difference between surplus, N storage in soil OM and denitrification (Billen et al., 2019b). Calculations of the leaching from the surplus minus denitrification and sequestration (Fig. 4), well agrees with on-field measurements, using suction cups, which amounted to $16.2 \pm 6.3 \text{ kg N ha}^{-1}\text{yr}^{-1}$ (Benoit et al., 2016).

Box 1: $N_2O/(N_2+N_2O)$ ratio of denitrification in soils and aquatic systems.

Considerable disagreement exists in the literature concerning the relative share of N_2 and N_2O in the final products of denitrification under environmental conditions. Yet, this issue is of considerable practical importance for two reasons. First because N_2O is a potent greenhouse gas so that the use of denitrification as a way to eliminate nitrate from seepage or wastewater is potentially harmful for the climate, second, because as N_2O emission is more easy to measure than N_2 production, the former is often used as an indirect way to evaluate the latter.

Many authors report the $N_2O/(N_2+N_2O)$ ratio by denitrification under laboratory conditions where several factors, such as pH, nitrate, oxygen or organic matter concentration are manipulated (e.g. Rochester, 2003; Hénault et al., 2005, 2020). The observed effect of these factors may simply reflect the transient perturbation linked to an enzymatic or population readjustment to new conditions imposed by the experimental protocol (Simek et al., 2002a,b). On the other hand, many so called 'in situ' determinations used the acetylene block technique, based on the assumption that acetylene selectively inhibits the last step of denitrification, leaving N_2O as the sole end product. Butterbach-Bahl et al. (2013) have convincingly demonstrated that this assumption is incorrect and that the presence of acetylene modifies other microbial processes, leading to a severe overestimation of the $N_2O/(N_2+N_2O)$ ratio.

Leaving aside the values obtained with these debatable procedures, we are left with only a few direct determinations of the $N_2O/(N_2+N_2O)$ ratio which however show a consistent trend toward one order of magnitude higher ratios in soils (either agricultural or natural) than in wetlands or water bodies (Table B1). The different contribution of nitrification to N_2O emission beside denitrification can be an explanation for this observation. This also applies to the high N_2O emission ratio by wastewater treatment facilities. The values in Table B1 have been used in this study to calculate N_2O emissions from estimated denitrification in river and riparian wetlands and to calculate denitrification from estimated N_2O emissions from agricultural and forested soils.

Table B1: *In situ* determination of the $N_2O/(N_2+N_2O)$ ratio in soils, wetlands and water bodies, excluding those obtained using the acetylene block technique.

Environment	$N_2O/(N_2+N_2O)$ ratio, %	nb measurements	reference
Agricultural soils	28 ± 12	30	Schlesinger, 2009 Butterbach-Bahl et al, 2013 *
Natural soils	28 ± 17	18	ibid
Wetlands, flooded soils	4 ± 5	14	ibid
Rivers	0.9 ± 0.4	40	Beaulieu et al., 2011
Rivers and riparian zones	1.5 ± 0.5	3	Billen et al, 2020
Wastewater trtmt facilities**	17 ± 10	15	Kampschreur et al., 2009

* The data compiled by Schlesinger, 2009 (Suppl Mat) and Butterbach-Bahl et al 2013 (Suppl Mat) have been combined after deleting those in the former publication that were obtained through the acetylene block technique.

** From the data compiled by Kampschreur et al (2009), only those relating to wastewater treatment involving both nitrification and denitrification were considered.

5. Nitrogen in the hydrosystem

Nitrate leaching is the main process by which nitrate originating from soil processes is transferred to the hydrosystem. As a first approach, nitrate concentration in the total specific runoff water flux (i.e. precipitation minus evapotranspiration, expressed in mm/yr) over a cropland area can be estimated from the N soil surplus minus denitrification and N sequestration, divided by the total runoff over the same area. A part of the corresponding water flux, which we assume has the same nitrate concentration, rapidly joins surface water (surface or sub-surface rapid runoff), another part infiltrates the vadose zone and the underlying aquifer (aquifer recharge). On a pluri-annual time scale, this partition is termed the base-flow index, the ratio of groundwater (slow) to total (slow and rapid) runoff in the river annual discharge. The presence of large aquifer formations, particularly in the center of the Seine watershed, confers a rather large value to the base-flow index, varying between 0.36 and 0.85 according to the geological substratum (Gallois, pers. comm.), with an average value around 0.70. While rapid runoff reacts rapidly to changes in agricultural practices, base flow responds much more slowly, depending on the time required for groundwater composition to reach equilibrium with the composition of recharge water (Fig. 5). This delay, which varies according to the specific characteristics of the vadose zone and aquifers in the different areas of the watershed, leads to a transient retention of nitrate, which was modelled by Ledoux et al. (2007) and Beaudoin et al. (2016) (Fig. 4). Figure 5 illustrates this response by comparing the reconstituted time variations of nitrate concentration in the recharge water with the observed concentration in a number of well-documented springs in the central part of the Paris Basin. The mean nitrate concentration in the recharge water (CrNO₃, mgN/l) of the central Paris Basin (Ile-de-France region) was calculated for the period 1850-2015 from the following relationship:

$$\text{CrNO}_3 = \text{Crforest} * (1 - \text{frcropld}) + [(\text{Surpl} - \text{Denit} - \text{Nsequ}) * 10^9 / \text{Acropld}] / (\text{Runoff} * 10) * \text{frcropld} \quad (1)$$

where:

Crforest is the nitrate concentration in leaching water from forest and unmanaged grassland; it has been estimated at approximately 0.5-2 mgN/l from observations of the drainage concentration of natural areas in the Seine basin (Billen et al., 2007b),

frcropld is the fraction of land area occupied by cropland, which varies over the long term;

Surpl and Acroplnd are, respectively, the calculated N soil surplus of arable land in the considered territory expressed in ktonN/yr, and the area of cropland in ha, as estimated by Le Noë et al. (2018);

Denit is the cropland soil denitrification rate in ktonN/yr estimated from the N₂O emission calculated by Garnier et al. (2019b) taking into account an N₂O/(N₂O+N₂) ratio of 28 (Box 1);

Nsequ is the N sequestration in the soil OM pool of cropland, in ktonN/yr, estimated from the C sequestration rate calculated over the long term by Le Noë et al. (2019b), considering a constant C/N ratio of 10 gN/gC (see above);

Runoff is the mean long term value of total runoff over the considered area, estimated to be 260 mm/yr, for the whole watershed (63000 km² at Poses), based on the long term record of discharge of the Seine river at the outlet (Poses, 512 m³/s in average over the last 50 yrs).

It can be seen that the delay in the response of aquifers to the increase in nitrate concentration of recharge water is typically of approximately 10-25 years (Fig. 5). This is in good agreement with determinations of groundwater age using measurements of dissolved chloro-fluoro-carbon compounds (Vergnaud-Ayraud, et al., 2008) in several drinking water wells in the Seine basin (Anglade et al., 2017; Beaudoin et al., pers. comm.).

Figure 5. Long term trends in groundwater nitrate concentrations from data on several individual springs in the central Seine Basin (Vulaines-lez-Provins and Saint Brice, Aquibrie, pers. comm.; Melarchez, Anglade et al., 2017) with varying residence time, compared with the calculated concentration of recharge water in Ile-de-France, calculated by relation (1).

Both base flow and surface runoff, with their own differing composition, have to cross the riparian zone before reaching surface water, unless it has been by-passed by the installation of tile drains, a widespread practice in some regions of the Seine basin until the 1980s and is still the case for almost 11% of the Seine watershed area. The riparian zone generally consists of a more-or-less wide area of uncultivated wetlands, where ground- and sub-surface waters flowing from the watershed reach the upper, biogeochemically active layer of the soil (Fig. 6). The soil denitrification potential is expressed there by its capacity to reduce the nitrate loading of the water flow, before it reaches the river itself. Based on this conceptual scheme and on a basin-wide delimitation of riparian zones resting on land use and on topographic indexes (Berthier et al., 2014), Billen et al. (2018b, 2020) modeled nitrate and N_2O dynamics associated with these riparian processes (Fig. 6), and provided an estimate of their significance at the local and basin scales (Fig. 4). These data show that although riparian areas are hotspots of denitrification and N_2O emission in the sense that per area flux values are generally higher there than at other sites in the watershed, the integrated value at the watershed scale is lower, because of the small proportion of watershed area covered by active riparian wetlands (see Garnier et al., 2014). Riparian denitrification currently amounts about 15% of the diffuse flux of nitrogen at the watershed scale. This figure could have been twice higher in earlier times, before riparian wetlands were drained and/or converted to cropland.

Figure 6. Block diagram showing the transfer of nitrate from watershed soils to river channel through riparian wetlands, and the associated denitrification and N_2O emission. In-stream and reservoir denitrification processes are also represented.

The same holds true for in-stream denitrification processes which, although significant when expressed in terms of local per area values, affect nitrogen dynamics only marginally compared with soil and riparian processes. However, downstream from the largest point of wastewater discharge, microbial activity occurs, either heterotrophic mineralization of organic N into ammonium, or nitrification of ammonium, and locally affects water quality and N_2O emissions (Garnier et al., 2009). In this respect, the sector of the Seine River downstream from the discharge of the Seine-Aval wastewater purification plant treating the largest part of the Paris effluents, plays a significant role. The never-ending race between an increasing N load collected by the sewers to the wastewater plants, and the improvement of the treatments applied is reflected in the long-term series of water quality observations and modelling results of water quality along longitudinal profiles of the lower Seine River course, as shown by Aissa-Grouz et al. (2015), Romero et al. (2016) and Garnier et al. (2019c).

Denitrification, and N_2O emissions, is also significant in the large reservoirs fed by the upstream course of the Seine river and its tributaries the Aube and Marne river that were established in 1960-1990 for the purpose of discharge regulation. During the summer period of water stagnation in these reservoirs as well as in farm ponds, nitrate concentration is strongly reduced before restitution to the river network (Garnier et al., 2000; 2014; Passy et al., 2012).

6. N delivery to the coastal zone and marine eutrophication

The flux of N delivered by the Seine River at the outlet of the river network (more specifically at Poses, the entrance of the tidal estuarine sector) reflects all the diffuse and point sources distributed in the watershed area, as well as the various processes leading to the transformation, immobilization, and transfer of N loading along the land-water continuum (Garnier et al., 2019a). Figure 4 summarizes the long term trends of these sources and sinks and shows how the flux in N delivery has increased as the result of these trends. Overall, the latter currently amounts to 42-49% of net N sources to the watershed. N “retention” consists of 8% soil storage, 15% soil denitrification, 10% riparian denitrification

and 16% in stream denitrification. The largest part of 'retention' processes thus is attributable to atmospheric emission, partly under the form of N_2O contributing to climate change.

Because of the heavy morphological transformations undergone by the Seine estuary for the purpose of facilitating navigation, the N retention function of this system has been considerably reduced. The flux of N delivered to the estuary is now transferred to the Seine Bay, with only 13% (about 20 ktN/yr) being retained on an annual basis by denitrification (Romero et al., 2018).

In the Seine Bay on the other hand, the input of nitrogen, together with the other nutrients phosphorus and silica, determine the state of eutrophication of the ecosystem. Billen and Garnier (2007b) defined the N-ICEP, an indicator of the potential role of nutrient riverine delivery in promoting the growth of undesirable, non-siliceous marine phytoplankton species in coastal bights. The concept behind this indicator is that when nutrients are brought into the sea in proportions corresponding to the Redfield ratio of algal composition, they promote the development of diatom communities able to feed a linear food chain leading to fish, while if N and/or phosphorus are in excess over silica with respect to diatoms requirements, algal blooms dominated by potentially toxic or harmful species develop, including dinoflagellates or even low-silicified diatoms such as *Pseudo-nitzschia*, producing domoic acid in response to silica depletion (Garnier et al., 2019a). The long-term trend of the N-ICEP in the flow delivered to the Seine Bight is shown in Figure 7. While negative N-ICEP values would occur under pristine conditions, positive values have been calculated since 1850; they increased rapidly after 1950 and are still positive today, although a slow decreasing trend is observed since the 1980s. The ECOMARS-3D model of the Channel developed by IFREMER (<http://www.ifremer.fr/mars3d/Le-modele/Descriptif/>, Menesquen et al., 2018) is able to reasonably simulate diatom and nanoflagellate blooms (Passy et al., 2016; Romero et al., 2018; Desmit et al., 2018), including *Pseudo-nitzschia* (Garnier et al., 2019a), in response to the reconstructed riverine nutrient fluxes.

Figure 7. Long-term trends of N-ICEP in the nutrient flow delivered by the Seine River into the Seine estuarine sector (at Poses). Black circles and bars: values calculated for median, wet or dry hydrology (Billen & Garnier, 2007b); open circles: values calculated with the Seneque-Riverstrahler model for actual conditions from 2002 and 2014 (Garnier et al., 2019a)

7. Two contrasting scenarios for the future

To a large extent, the current knowledge on nutrient cycling in the past and present water-agro-food system also allows us to predict the environmental effects of possible future changes in the design of human food provision. For example, two contrasting scenarios of the future of French agro-food systems have been constructed (Billen et al., 2018a; 2019a). One of these scenarios, called “Opening and Specialization” (O/S) is constructed by extending the historical trends observed in the French agro-food system during the past few decades: livestock and permanent grasslands disappear from the central regions of the watershed but livestock farming intensifies in the peripheral regions with an increased import of soybean; cereal production for export keeps growing; a human diet rich in animal protein persists; current environmental regulations, including those related to mineral and organic N fertilization, are maintained.

The second scenario, called “Autonomy, Reconnection and Demitarian Diet” (A/R/D), assumes the generalization of organic farming practices with long and diversified crop rotations and no industrial fertilizers, local livestock and crop farming reconnection, and a human diet of half the current content of meat and milk. At the scale of France, both scenarios were shown to be able to meet the needs of the projected French population for 2050, in both cases with ample exportation of cereals. In the O/S scenario France also exports animal products but imports massive amounts of feed; by contrast in the A/R/D scenario no significant net export of meat and milk occurs and no import of feed is required. At the scale of the Seine basin (which hosts 25% of the French population), the A/R/D and O/S scenarios require importing of, respectively, 33% and 86% of animal protein requirements (Fig. 8a, Table 2).

Table 1 : Main functional characteristics and production fluxes of the agro-food system of the Seine watershed (in bold) and the whole of France (in italic) for the present situation (2004-2014) and for the two prospective scenarios O/S and A/R/D (Billen et al., 2018a).

		2004–2014 Reference	2050 Opening Specialization	2050 Autonomy Reconnection Demitarian diet
Population	M hab	16 (62)	19 (75)	18 (75)
Vegetal protein consumption	ktN/yr	39 (145)	42 (169)	66 (273)
Animal protein consumption ¹	ktN/yr	58 (232)	82 (330)	33 (135)
Agricultural area used	M ha	4.2 (28)	4.1 (27)	4.2 (28)
% permanent grassland	%	16 (34)	4 (29)	19 (36)
Synthetic N fertilizer use	ktN/yr	521 (1955)	656 (1942)	0 (0)
Permanent grassland production	ktN/yr	96 (829)	35 (1093)	69 (633)
Cropland production	ktN/an	520 (2192)	541 (2508)	393 (1770)
Cereal Import (+) / export (–)	ktN/yr	-367 (–540)	-443 (–1089)	-213 (–222)
Livestock	M lu ²	1.3 (19)	0.9 (37)	1.8 (12)
Meat and milk production	ktN/yr	18 (261)	11 (383)	21 (138)
Meat and milk import (+)/ export (–)	ktN/yr	40 (–29)	+71 (–53)	+11 (–3)
Livestock ingestion	ktN/yr	144 (1955)	91 (3731)	183 (1224)
Grazing on permanent grassland	%	64 (42)	38 (29)	36 (45)
Ingestion of local crops	%	36 (35)	24 (26)	64 (55)
Ingestion of imported feed	%	0 (23)	38 (45)	0 (0)
Feed import (+) / export (–)	ktN/yr	0 (+438)	+ 34 (+1687)	0 (0)

¹ Excluding fish and seafood; ² lu : livestock unit, ruminants and monogastric animals

Simulated water quality in the Seine drainage network shows much lower nitrate contamination in the A/R/D than in the O/S scenario (Fig. 8b), and a much lower N loading to the Seine Bight (respectively 3200 and 2360 kN/km²/yr for A/R/D and O/S, vs. 4200 kN/km²/yr for 2010-2014). N₂O emission from cropland soils is also considerably lower in the A/R/D than in the O/S scenario (Fig. 8c).

Figure 8. a. GRAFS representation of the agro-food system of the Seine watershed in the O/S and A/R/D scenarios for the year 2050 (Billen et al., 2018a). **b.** Simulated nitrate concentration in the Seine drainage network in both scenarios compared with the present situation (calculated with the Senèque-Riverstrahler model, Garnier et al., 2019a). **c.** calculated N₂O emission by agricultural soils in both scenarios compared with the present situation (Garnier et al., 2019b)

These works underline that radical changes in the structure of the agro-food system are required to reach a good ecological status of the hydrosystem, rather than simple improvements in farming practices or policies to increase N use efficiency during the different transformation stages. Climate change is not taken into account in these scenarios which typically cover the next 30 years.

8. Conclusion

During the past 30 years, the field of biogeochemistry, which was still in its infancy at the time the eponymous journal was founded, has evolved toward a major discipline at the core of several issues of vital importance for human life on Earth. Numerous paradigms have been formulated during this period, which today serve as the backbone of environmental sciences. The river continuum concept was extended to a full land-to-sea continuum vision; combined with the synoptic approach of agro-food systems it resulted in the water-agro-food concept that we applied here to the study of the nitrogen cascade.

The case study of the Seine basin illustrates how the knowledge gained during the past 30 years of the long term PIREN-Seine program (since 1989), on the processes involved in the N cycle and its perturbations, has made it possible to quantitatively describe the associated fluxes at the scale of a whole watershed, over a timespan of more than one century. Changes in land use of the watershed, and particularly in the agricultural activities and in the management of urban wastewater resulting from human nutrition are by far the main driver of the observed trajectory of the functioning of the water-agro-food system. Several possible future scenarios for the agro-food system can be constructed and their consequences estimated in terms of water quality and ecological functioning of the whole continuum of aquatic systems from rivers to the sea; their impact on the climate system through greenhouse gas emission can also be calculated. What is more challenging is to incorporate the effect of global climate change into such prospective scenarios at the regional scale. If robust estimations of the future changes in temperature, rainfall, and runoff are available for the next 30-50 years, it is feasible to incorporate these changes and calculate how they affect the control on the kinetics of the processes described in the ecosystem models. Such explorations have already been initiated with changes in hydrology but not yet with temperature (Raimonet et al., 2018; Garnier et al., 2018). A still more challenging issue is however to take into account the indirect effects of climate change on agriculture. Current cropping systems may well be severely affected by these changes, and new crops and farming practices might be introduced with consequences that are difficult to predict using our current knowledge. This issue probably remains a research priority for the coming decades.

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