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## Curative vs. preventive management of nitrogen transfers in rural areas: Lessons from the case of the Orgeval watershed (Seine River basin, France)



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## ABSTRACT

The Orgeval watershed (104 km<sup>2</sup>) is a long-term experimental observatory and research site, representative of rural areas with intensive cereal farming of the temperate world. Since the past few years, we have been carrying out several studies on nitrate source, transformation and transfer of both surface and groundwaters in relation with land use and agriculture practices in order to assess nitrate (NO<sub>3</sub><sup>-</sup>) leaching, contamination of aquifers, denitrification processes and associated nitrous oxide (N<sub>2</sub>O) emissions. A synthesis of these studies is presented to establish a quantitative diagnosis of nitrate contamination and N<sub>2</sub>O emissions at the watershed scale. Taking this watershed as a practical example, we compare curative management measures, such as pond introduction, and preventive measures, namely conversion to organic farming practices, using model simulations. It is concluded that only preventive measures are able to reduce the NO<sub>3</sub><sup>-</sup> contamination level without further increasing N<sub>2</sub>O emissions, a result providing new insights for future management bringing together water-agro-ecosystems.

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### 1. Introduction

In the early 20th century, the invention of the Haber-Bosch process allowing industrial production of mineral nitrogen (N), mostly used as fertilizers after World War II, profoundly changed agricultural practices (Davidson et al., 2012). Although agricultural productivity increased, providing food to the growing human population, the nitrogen cycle was widely opened, leading to severe environmental degradation (Sutton et al., 2011). The control of nitrogen pollution is therefore a major challenge in agricultural river basins (Billen et al., 2007; Grizzetti et al., 2012). Continental water masses (from lentic to lotic and from surface- to groundwater) are often substantially contaminated by nitrate (NO<sub>3</sub><sup>-</sup>), causing major problems for drinking water supply (Ward et al., 2005) as well as for aquatic biodiversity (James et al., 2005). Moreover, nitrogen

fluxes mostly originating from diffuse sources are delivered to the coastal zones in excess with regard to other major nutrients such as silica and phosphorus, possibly participating in eutrophication problems caused by harmful algal blooms with damage to various economic activities (fisheries, tourism, etc.) (Cugier et al., 2005; Howarth et al., 2011; Lancelot et al., 2011; Romero et al., 2012).

In many intensive agricultural areas, such as the Paris Basin, inorganic nitrogen applied as fertilizers to arable soil exceeding the amount exported by crop harvesting, are leached to surface water and aquifers. NO<sub>3</sub><sup>-</sup> can also be denitrified in soils and riparian zones (Haycock and Pinay, 1993; Billen and Garnier, 1999; Burt et al., 2002; Rassam et al., 2008) as well as in river and pond sediments (Garnier et al., 2000; Tomaszek and Czerwieniec, 2000; David et al., 2006; Gruca-Rokosz and Tomaszek, 2007; Garnier et al., 2010; Passy et al., 2012) before ultimately reaching the coastal zone. The process of denitrification, at every stage of the nitrogen cascade, thus represents a natural mechanism of elimination of NO<sub>3</sub><sup>-</sup> contamination, re-injecting nitrogen into the pool of inert atmospheric di-nitrogen. However, during this process, nitrous oxide (N<sub>2</sub>O) is produced as an intermediate, which is emitted into the

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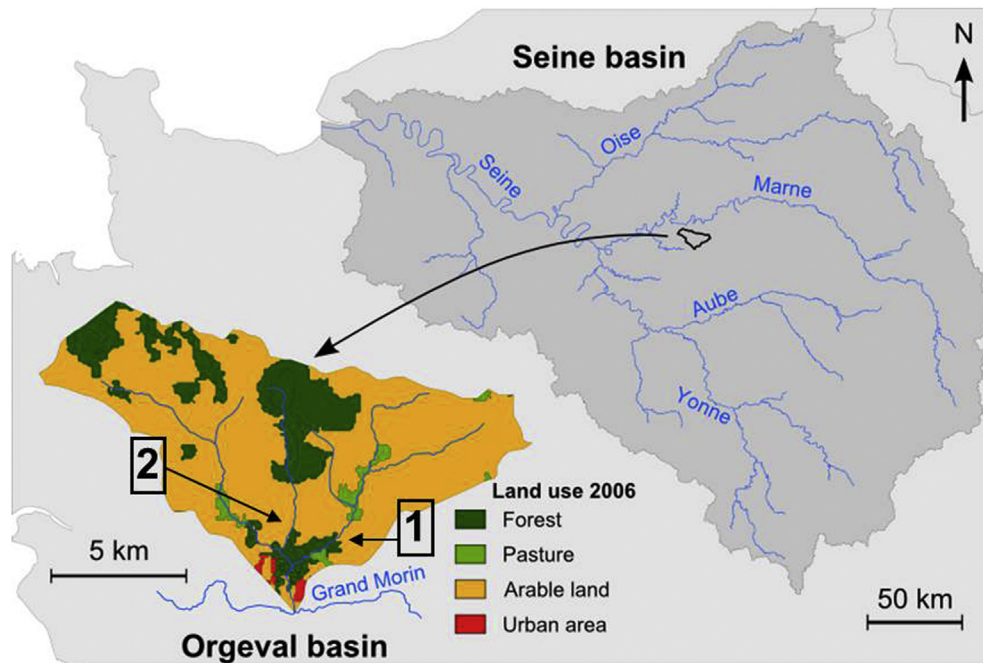


Fig. 1. Location of the Orgeval watershed in the Seine Basin and the two sites studied.

atmosphere, particularly under suboptimal conditions of carbon (C) and nitrogen substrate concentrations (Knowles, 1982; Tallec et al., 2006; Saggar et al., 2012). A budget made at the scale of the Seine Basin showed that agricultural soils are dominant contributors of the overall  $N_2O$  emission budget (Garnier et al., 2009).  $N_2O$  is a powerful greenhouse gas, also contributing to the destruction of the stratospheric ozone layer, and the increase of its emission, possibly related to increased  $NO_3^-$  use in agriculture or to remediation actions aimed at eliminating  $NO_3^-$  from water through denitrification, is a matter of serious concern.

Whereas the application of Urban Wastewater Directive (UWWTD, 1991) and Water Framework Directive (WFD, 2000) have already contributed to a quite significant reduction in phosphorus load, much is expected for nitrogen reduction from changes in the Common Agricultural Policy (CAP) encouraging “greening” practices (EU, 2013).

The small Orgeval watershed ( $\approx 100 \text{ km}^2$ ) is representative of the dominant landscape of the central Seine Basin ( $\approx 76,000 \text{ km}^2$  at the entrance of the estuary) characterized by an intensive cereal crop belt surrounding the large Paris conurbation, which has completely shaped its hinterland during historical periods (Billen et al., 2009a, 2013; Barles, 2010).

The Orgeval watershed is a long-term experimental observatory and research site initiated in the early 1960s by IRSTEA, the French National Research Institute of Science and Technology for the Environment and Agriculture. Whereas early research was mostly dedicated to the issues of hydrology and agricultural drainage, with the intensification of cereal cropping at the expense of cattle breeding, attention has been progressively paid to water quality issues, especially because the aquifers of the Orgeval watershed contribute to the production of drinking water for the city of Paris.

In this paper, we present a synthesis of the long-term field and modelling research carried out in this watershed, with the aim of making a diagnosis of the sources of nitrogen contamination, its transfer and transformation processes at the catchment scale. We then explore, using the GIS-based modelling approach developed for the Seine basin (Seneque-RiverStrahler, Ruelland et al., 2007;

Billen et al., 2009b), several management options for decreasing nitrogen contamination of surface and groundwater, with particular emphasis on the risk of pollution swapping between water  $NO_3^-$  contamination and increased  $N_2O$  emission.

Although we use the Orgeval watershed as a practical well documented case study in which a fully detailed modeling exercise can be carried out, the scope of the results obtained, largely encompasses this particular study site and the conclusions are of general relevance for all rural areas with intensive industrial crop farming.

## 2. Site studied and methods

### 2.1. Characteristics of the Orgeval watershed

The Orgeval watershed is located 70 km East of Paris (France) and is a small sub-catchment covering  $104 \text{ km}^2$  in the Marne sub-basin of the Seine River upstream from Paris (Fig. 1).

The climate is semi-oceanic, with annual rainfall about 700 mm and a mean annual air temperature around  $10^\circ \text{C}$  (varying from  $0.6$  to  $18^\circ$  seasonally).

The Orgeval watershed is highly homogenous in terms of pedology, climate and topography (mean altitude, 148 m, with few slopes except in the valleys). The Orgeval watershed is covered with a 10-m loess layer, under which two tertiary aquifer formations are separated by a discontinuous grey clay layer (Mégnién, 1979). The shallowest aquifer of the Brie Limestone Oligocene formation, with more interactions with surface waters, has a relatively shorter water residence than the deepest Champigny Limestone Eocene aquifer. The lower layer of the surface loess cover is enriched with clay, resulting in waterlogged soils in the winter. For this reason, up to 90% of the arable soils of the Orgeval watershed have been artificially tile-drained since the early 1960s. Land use is mostly agricultural land (82%), dominated by cereal crops (wheat, maize, barley and pea), with conventional practices, mainly based on mineral nitrogen fertilization. The remaining surface is covered by woods (17%) and urban zones or roads (1% of the surface) (Fig. 1).

## 2.2. Sampling and field studies, lab experiments and chemical analysis

Within the Orgeval watershed, series of nitrogen measurements (mainly nitrate as well as dissolved  $\text{N}_2\text{O}$ ) have been carried out at least since 2005 on surface waters. Two specific sites have been equipped (Site 1 since 2007, Site 2 since 2011) for water table  $\text{NO}_3^-$  and  $\text{N}_2\text{O}$  dissolved concentration and for  $\text{N}_2\text{O}$  emissions from agricultural soils. A farm drainage pond was also sampled.

### 2.2.1. Surface water

$\text{NO}_3^-$  concentrations were weekly measured since 1975 at the Mèlarchez station (order 1) and, since 2005 at the outlet of the Avenelles sub-watershed and the Orgeval one (Le Theil station) in the framework of IRSTEA routine programme. Dissolved  $\text{N}_2\text{O}$  in surface water have been measured from 2006 to 2008 at monthly intervals at the same three sampling stations (partly in Vilain et al., 2010, 2012c) (Fig. 1).

### 2.2.2. Water table

On site 1 (Fig. 1), three piezometers were installed along a slope from the plateau to the riparian zone in January 2007. This 6% inclination slope oriented northwestward reaches the Avenelles River. This site is typical of the whole Orgeval watershed both in terms of agricultural practices (grain crop with wheat, barley and maize as the main rotation) and fertilizer applications (from 120 to 160 kg N  $\text{ha}^{-1}$  for wheat/barley, to 180 kg N  $\text{ha}^{-1}$  for maize). Three piezometers were also installed in July 2011 in site 2. The piezometers were sampled for  $\text{NO}_3^-$  and  $\text{N}_2\text{O}$  determination in the Brie aquifer since their installation.

### 2.2.3. Agricultural soils

Suction ceramic cups were also installed on site 1 (Fig. 1) during two winter drainage periods (January to March 2010 and December 2012 to April 2013) to quantify the sub-root  $\text{NO}_3^-$  concentrations for a conventional agricultural system. Other data were obtained at site 2 (in the winters 2012 and 2013) for an organic agricultural system and are used for the characterisation of organic agriculture scenarios (see below).

On site 1 along the piezometric slope, hermetically closed chambers (open bases measuring 50 × 50 × 30 cm) allowed quantifying  $\text{N}_2\text{O}$  emissions (see Vilain et al., 2010) from cropping soil according to the methodology described by Hutchinson and Livingston (1993) and Livingston and Hutchinson (1995). Measurements were taken at different topographical landscape positions from the uphill to the riparian position from May 2008 to July 2009; a forested soil was investigated for comparison.  $\delta^{15}\text{N}$ -isotopic measurements in the soil organic matter were taken along two transects at six different locations on one occasion in March 2007 (Billy et al., 2011). For each transect, soil was sampled at 10-cm intervals from the surface to 90 cm deep. Air-dried and sieved (2 mm), the soil samples were homogenized prior to organic N isotopic composition analysis. These measurements were used as an integrated estimator of long-term soil denitrification processes.

To pursue the determination of the source of  $\text{N}_2\text{O}$  emissions in greater detail, soils sampled between 2009 and 2011 at several periods of the season, from the same site 1 cropped slope were incubated in batch experiments under optimal laboratory conditions (nutrients, temperature). Since  $\text{N}_2\text{O}$  is known to originate from nitrification and denitrification, both processes were investigated. As described in Garnier et al. (2010) and Vilain et al. (2012b), batch experiments were run and the  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$  concentrations followed during a short incubation time (4–6 h), to avoid any confinement in the flasks, in triplicate and in the dark. For nitrification assays, ammonium was added and the flasks were flushed

with ambient air to ensure aerobic conditions, while for denitrification assays,  $\text{NO}_3^-$  was added and the flask was flushed with  $\text{N}_2$  in order to produce anaerobic conditions. Production of  $\text{N}_2\text{O}$  associated with the processes was also measured.

### 2.2.4. Farm drainage pond

A drainage farm pond on site 2 (Fig. 1) was also investigated over 3 years for  $\text{NO}_3^-$  concentrations (2007–2010) in order to evaluate the pond's potential for eliminating nitrogen leached from agriculture (Passy et al., 2012).  $\text{N}_2\text{O}$  concentrations dissolved in the water column were determined seasonally in 2010, allowing to estimate emissions (Garnier et al., 2009).

### 2.2.5. Analytical methods

Analytical methods for  $\text{NO}_3^-$  and  $\text{N}_2\text{O}$  concentrations in water are described in Jones (1984) and Garnier et al. (2009), respectively.

$\text{N}_2\text{O}$  concentrations in gas sample were analysed by gas chromatography, as described by Vilain et al. (2010).

Measurement of organic N isotopic composition of the soil is described by Billy et al. (2010).

## 2.3. Simulating N reduction measures

The biogeochemical model (RiverStrahler) describing the ecological functioning of aquatic systems (Billen et al., 1994; Garnier et al., 2002, currently implemented at the scale of the Seine Basin embedded in the GIS-Seneque interface tool (Ruelland et al., 2007; Thieu et al., 2009; Passy et al., 2013) has been used here for exploring scenarios of mitigating measures at the scale of the Orgeval watershed. The principle of the model is illustrated in Fig. 2.

## 3. Quantifying the N cascade through the Orgeval watershed

### 3.1. N leaching from agricultural soils to sub-root water, tile-drains and aquifers

Wheat, maize, pea and barley cover around 44, 14, 6 and 4%, respectively, of the cultivated area in the Orgeval watershed (RGA-Recensement Général Agricole, 2000). The main crop rotations are wheat-pea-wheat (28%) and maize–winter wheat–spring barley (20%), with a mean crop yield of about 5500 kg cereal equivalent per ha, corresponding to about 100 kg N  $\text{ha}^{-1}$   $\text{yr}^{-1}$ . The fertilizer application rate ranges from 120 to 180 kgN  $\text{ha}^{-1}$   $\text{yr}^{-1}$ . Atmospheric deposition of N adds around 15 kg N  $\text{ha}^{-1}$   $\text{yr}^{-1}$  and atmospheric  $\text{N}_2$  fixation (through non-symbiotic fixation and by legume crops in some rotations) about 10 kg N  $\text{ha}^{-1}$   $\text{yr}^{-1}$  (Billy et al., 2010). The soil N balance thus reveals a long-term surplus of about 50 kg N  $\text{ha}^{-1}$   $\text{yr}^{-1}$ .

Sub-root concentrations measured from 2010 to 2013 with suction cups installed 1 m deep under representative arable plots average 22 mg  $\text{NO}_3^-$  N  $\text{L}^{-1}$  (SD = 15). This value is close to the average concentration observed in tile drains in the same area (26 mg  $\text{NO}_3^-$  N  $\text{L}^{-1}$ ) (Fig. 3). These sub-root concentrations are quite similar to those observed elsewhere in the Seine Basin in the 1990s. Indeed, in the chalky Champagne, East of Paris, the concentrations obtained were 27.2 mg  $\text{NO}_3^-$  N  $\text{L}^{-1}$  for a 10-year wheat/beet rotation but significantly less with the introduction of alfalfa in the rotation (20.8 mg  $\text{NO}_3^-$  N  $\text{L}^{-1}$ ) (Beaudoin et al., 1992). Similar figures were found in the Northern or Western sectors of the Seine Basin, i.e., respectively, 19 mg  $\text{NO}_3^-$  N  $\text{L}^{-1}$  (Machet and Mary, 1990) and 29 mg  $\text{NO}_3^-$  N  $\text{L}^{-1}$  (Arlot and Zimmer, 1990).

With an average discharge of 0.36  $\text{m}^3$   $\text{s}^{-1}$  at the outlet of the Orgeval watershed, a yearly N leached flux can be estimated to 2400 kg  $\text{km}^{-2}$   $\text{yr}^{-1}$  (50% variation).

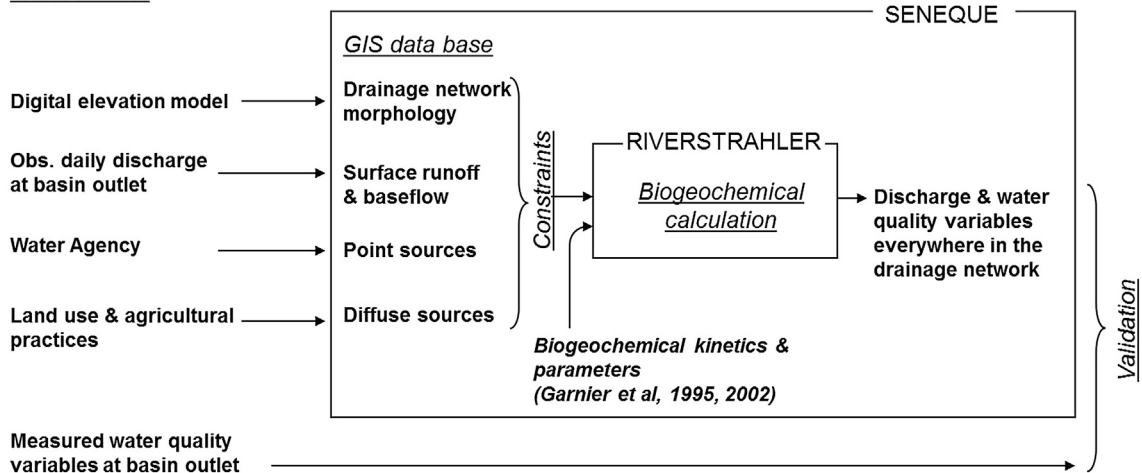
*Data sources*

Fig. 2. Representation of the Seneque/RiverStrahler model.

$\text{NO}_3^-$  concentrations in the Brie aquifer, measured from samples collected in the piezometers installed uphill, are around  $13.2 \text{ mg NO}_3\text{-N L}^{-1}$ . Samples collected midslope or below the riparian buffer strip show 35–40% lower concentration, down to  $8.6 \text{ mg NO}_3\text{-N L}^{-1}$  (Fig. 3), probably because of denitrification processes occurring when the water table reaches the biogeochemically active upper soil layers. In the pond studied, the average annual concentration was even lower ( $7 \text{ mg NO}_3\text{-N L}^{-1}$ ), compared to the average concentration entering the pond ( $13.5 \text{ mg NO}_3\text{-N L}^{-1}$ ). At the outlet of the Orgeval watershed, the average river water concentration is  $11 \text{ mg NO}_3\text{-N L}^{-1}$ .

### 3.2. Denitrification and $\text{N}_2\text{O}$ emissions in soils along a cropped slope

Both nitrification and denitrification in soil are able to produce the greenhouse gas  $\text{N}_2\text{O}$ , particularly under suboptimal conditions (limitation by substrates, oxygen tension, pH, temperature, etc.)

(Firestone and Davidson, 1989), although several other microbial processes are able to consume the  $\text{N}_2\text{O}$  emitted (e.g. nitrifier denitrification (Wrage et al., 2001), dissimilatory  $\text{NO}_3^-$  reduction to ammonia (Burgin and Halminton, 2007), anammox in specific conditions (Dalsgaard et al., 2005, 2013).

In the same line as the research on wastewater treatment plants (Tallec et al., 2006), the relative magnitude of nitrification or denitrification in the emission of  $\text{N}_2\text{O}$  was experimentally explored in Orgeval watershed soil samples (Vilain et al., 2012b, c, 2014). It appeared that potential rates of  $\text{NO}_3^-$  production (nitrification) and  $\text{NO}_3^-$  reduction (denitrification) were, on average, within the same range ( $0.8\text{--}0.9 \mu\text{g NO}_3\text{-N g}^{-1} \text{ dw h}^{-1}$ ), but the associated potential  $\text{N}_2\text{O}$  production was much lower (by a factor of 100) for nitrification than denitrification (Table 1), corroborating previous findings by Tallec et al. (2006). The ratio of  $\text{N}_2\text{O}$  production to  $\text{NO}_3^-$  reduction was up to 20% for the denitrification potential, while the ratio of  $\text{N}_2\text{O}$  emission to  $\text{NO}_3^-$  production by nitrification was only about 0.2%.

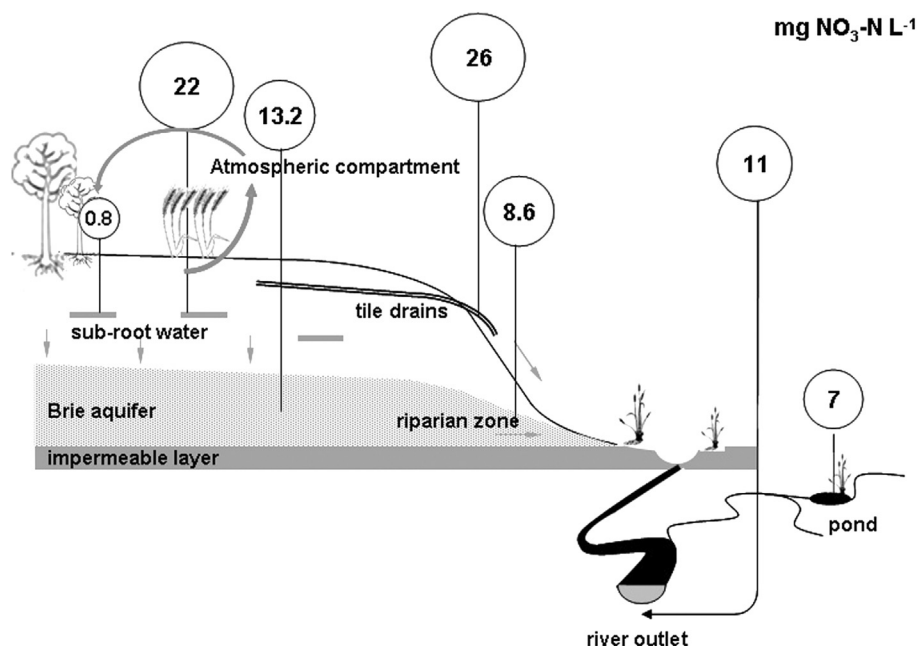


Fig. 3. Concentrations of nitrate cascading within the Orgeval watershed (see text for explanations, unit in  $\text{mg N L}^{-1}$ ).

**Table 1**

Average potential values for agricultural soils in denitrification and nitrification in experimental conditions (batch experiments at 20 °C), and associated N<sub>2</sub>O production (SD for Standard Deviation, 7 experiments). Percentages of N<sub>2</sub>O production are also given for comparison.

	Potential NO <sub>3</sub> <sup>-</sup> production/reduction rates	Potential N <sub>2</sub> O production rates	Ratios of potential N <sub>2</sub> O/NO <sub>3</sub> <sup>-</sup> rates
	μgNO <sub>3</sub> <sup>-</sup> -N g <sup>-1</sup> dw h <sup>-1</sup>	μgN <sub>2</sub> O-N g <sup>-1</sup> dw h <sup>-1</sup>	%
Denitrification	0.89 (SD = 0.47)	0.15 (SD = 0.08)	24.4 (SD = 20.7)
Nitrification	0.81 (SD = 0.271)	0.002 (SD = 0.001)	0.18 (SD = 0.16)

Direct in situ measurements of N<sub>2</sub>O emissions by agricultural and forest soil using closed chambers were taken on 21 dates from May 2008 to August 2009 (Vilain et al., 2010, 2012c). For uphill plateau sites, a value equalling 0.29 mg N<sub>2</sub>O-N m<sup>-2</sup> d<sup>-1</sup> was estimated for cropland, higher than the average one found for forested soils: 0.15 mg N<sub>2</sub>O-N m<sup>-2</sup> d<sup>-1</sup>.

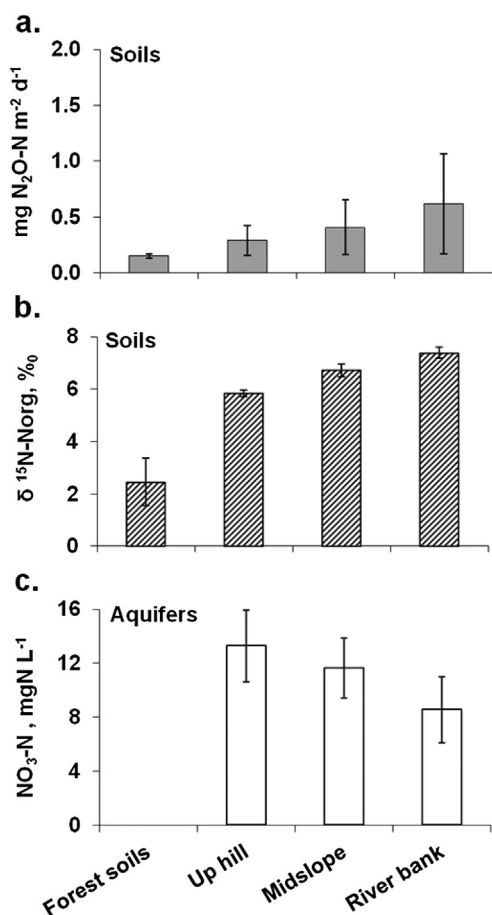
Higher values, close to 0.41 mg N<sub>2</sub>O-N m<sup>-2</sup> d<sup>-1</sup> were measured in downslope sites, with the level of the water table closer to the soil surface. N<sub>2</sub>O emissions, averaged for footslope and riparian zone was 0.61 mg N<sub>2</sub>O-N m<sup>-2</sup> d<sup>-1</sup> (Fig. 4a). These results show increasing transformation of nitrogen (denitrification mainly) along the slope, and concomitant increasing N<sub>2</sub>O emission.

δ<sup>15</sup>N fractionation values of soil organic nitrogen along a cropped slope and averaged over a 1-m soil profile, were higher than the primary nitrogen (N) sources from which they are derived, such as mineral nitrogen fertilizers, atmospheric deposition and

symbiotic N<sub>2</sub> (all characterized by δ<sup>15</sup>N values close to zero), indicate indeed the existence of a long-term denitrification process (Billy et al., 2010; Vitousek et al., 2013). Based on a modelling approach of the isotopic composition of the soil N compartment, Billy et al. (2010) estimated that a 1‰ δ<sup>15</sup>N-Norg increase above that of the primary N sources corresponds to a denitrification of ~10 kg N ha<sup>-1</sup> yr<sup>-1</sup> (i.e. 2.7 mg N m<sup>-2</sup> d<sup>-1</sup>) which confirm the prevalence of denitrification.

The distribution of δ<sup>15</sup>N of the bulk soil N pool from the uphill plateau down to the riparian zone of the river shows a regular increase from 2.4‰ in plateau forested soils and 5.8‰ in crop soil, to 7.4‰ in the downslope arable soil and in the buffer strip, results well in agreement with N<sub>2</sub>O emission from denitrification (Fig. 4b).

N<sub>2</sub>O concentration in the aquifer was also measured by sampling the piezometers. The values found were largely oversaturated (20 μg N<sub>2</sub>O-N L<sup>-1</sup> on average), taking into account that N<sub>2</sub>O saturation in water with respect to the atmospheric level of 330 ppb varies from 0.35 to 0.5 μg N<sub>2</sub>O-N L<sup>-1</sup> depending on the temperature (Fig. 4c). We interpreted these high N<sub>2</sub>O values in the aquifer as resulting from leaching from the root zone, although denitrification and N<sub>2</sub>O production in the aquifer itself is not fully excluded, critical oxygenation around 2–3 mg O<sub>2</sub> L<sup>-1</sup> being occasionally observed (Vilain et al., 2012a). The lower N<sub>2</sub>O concentrations in the downslope sites can be explained by microbial transformation into N<sub>2</sub>, i.e. again corroborating a complete denitrification along the slope. N<sub>2</sub>O degassing from the aquifer along the underground flow, i.e. indirect N<sub>2</sub>O emissions, is not excluded.



**Fig. 4.** a. Seasonal average of N<sub>2</sub>O emission from soils in a forested area and an agricultural slope, redrawn from Vilain et al. (2010). b. Variations of δ<sup>15</sup>N of nitrogen organic matter averaged over a 1-m soil profile, recalculated from Billy et al. (2010). c. Seasonal averages of NO<sub>3</sub>-N concentrations in the water of the Brie aquifer as sampled in the piezometers along the slope, modified from Vilain et al. (2012a).

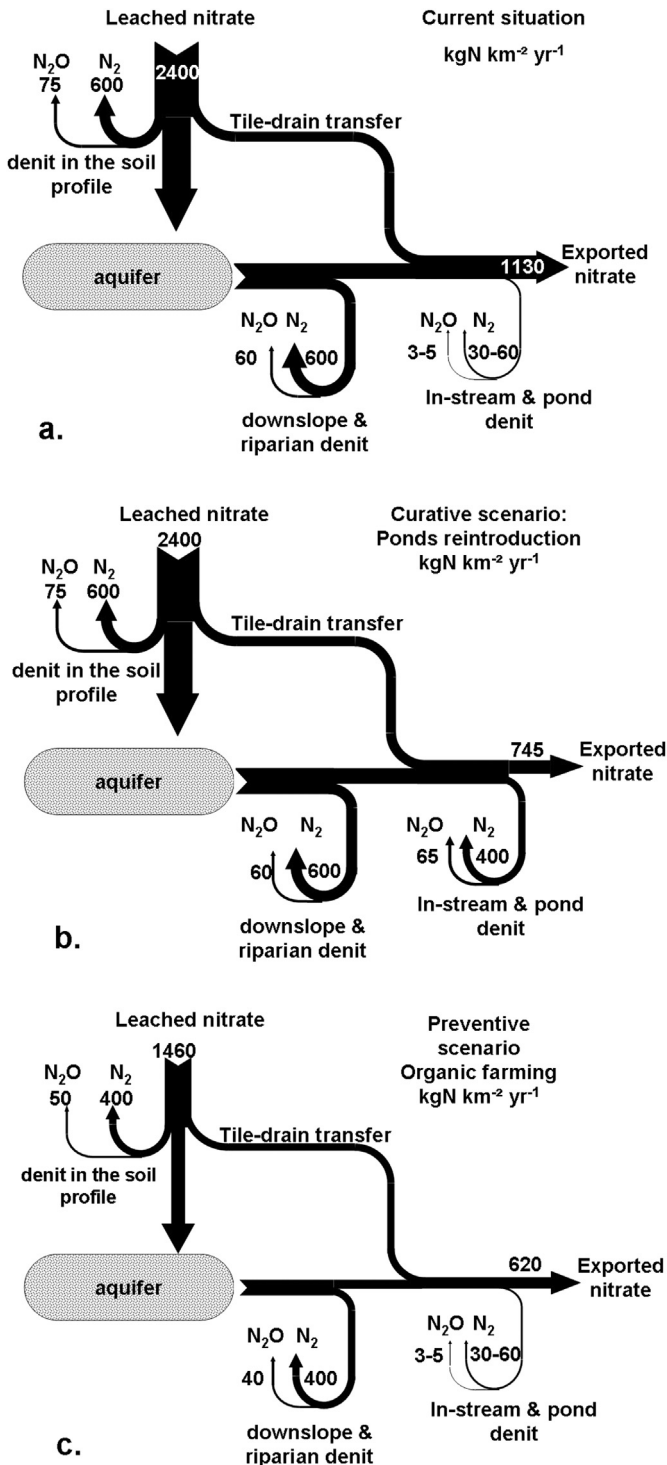
### 3.3. In-stream N elimination processes

Direct measurement with bell-jars allowed estimating the rate of benthic denitrification in river sediments. Consumption rates on the order of 3.1 (SD = 1.1) mg N m<sup>-2</sup> h<sup>-1</sup> were observed (Thouvenot-Korppoo et al., 2009; Billy et al., 2011). Considering a river bottom area of about 175,830 m<sup>2</sup> for the Orgeval watershed as a whole, this leads to a maximum estimate of 3000–6000 kg N yr<sup>-1</sup> for benthic denitrification (30–60 kg N km<sup>-2</sup> yr<sup>-1</sup> at the watershed scale), showing that in-stream processes represent a marginal value in the nitrogen elimination of the 2400 kg N km<sup>-2</sup> yr<sup>-1</sup> found at the base of the root zone.

Accordingly, N<sub>2</sub>O concentrations, above saturation, observed in small rivers of the Orgeval watershed, are inherited from the groundwater feeding them, instead of being produced through in-stream processes. Indeed, these concentrations rapidly decrease from the spring downwards until reaching saturation (Garnier et al., 2009).

### 3.4. A synthetic budget of N transfers in the Orgeval watershed

Based on the data summarized in the above paragraphs, a tentative budget of nitrogen transfer at the scale of the Orgeval watershed was established (Fig. 5), describing the fate of NO<sub>3</sub><sup>-</sup> mostly coming from the surplus nitrogen left by agricultural soils. Denitrification in the soil profile and in the downslope areas (where a temporarily or permanently shallow water table comes in contact



**Fig. 5.** Summarizing budget of nitrate transfer and transformation, and associated nitrous oxide emissions in the Orgeval watershed. Calculations are based on the average hydrology from 2006 to 2012. a) Current situation based on measurements; b) pond reintroduction scenario; c) organic farming scenario.

with the upper biogeochemically active layers of the soil) eliminates more than 40% of the nitrogen leaving the root zone.

The various denitrification figures in this budget are in good agreement with the values found (i) for soil denitrification (Pinay et al., 1993; Hefting et al., 2006), (ii) for the riparian zones (Billen and Garnier, 1999) and (iii) for in-stream benthic denitrification

at the scale of the whole Seine hydrographic network (Thouvenot-Korppoo et al., 2009).

On the basis of (i) the  $\text{N}_2\text{O}$  emissions from soils together with a fine resolution of the topography and land use in the watershed, (ii) the  $\text{N}_2\text{O}$  fluxes from rivers and groundwater deduced from concentration measurements (Garnier et al., 2009; Vilain et al., 2010, 2012a), the total  $\text{N}_2\text{O}$  emissions for the whole Orgeval watershed were estimated at  $142 \text{ kg N}_2\text{O-N km}^{-2} \text{ yr}^{-1}$  (Vilain et al., 2012c). This represents about 10% of the sum of the denitrification rates occurring in soils, footslopes and riparian zones and in-stream sediments (see Fig. 5a). This  $\text{N}_2\text{O}$  percentage emission is in agreement (within a factor of 2) with the potential values found experimentally for denitrification.

#### 4. Curative management measures to reduce $\text{NO}_3^-$ contamination

Drainage or irrigation water retention ponds are often seen as buffer interfaces where N elimination is effective. The creation of such systems is often considered within the framework of compensatory measures, possibly included in the wetland status (Dahl, 2011). In addition, these waterbodies can be viewed as anthropogenic refuge for biodiversity (Chester and Robson, 2013).

##### 4.1. $\text{NO}_3^-$ and $\text{N}_2\text{O}$ concentrations in an artificial pond

We investigated such a pond established at the outlet of a tile drain collector draining 35 ha of cultivated land. Its surface area is  $3700 \text{ m}^2$ , with a volume of  $8000 \text{ m}^3$  (i.e. a mean depth of about 2 m). The concentrations at the entrance of the pond averaged  $13.5 \text{ mg NO}_3\text{-N L}^{-1}$  (Fig. 6a) over the period studied, close to the value found for the concentration in the Brie aquifer (see Fig. 3).  $\text{NO}_3^-$  concentrations in the pond show a systematic summer decrease, down to  $1.5 \text{ mg NO}_3\text{-N L}^{-1}$  in late summer (annual mean,  $7 \text{ mg NO}_3\text{-N L}^{-1}$ ).

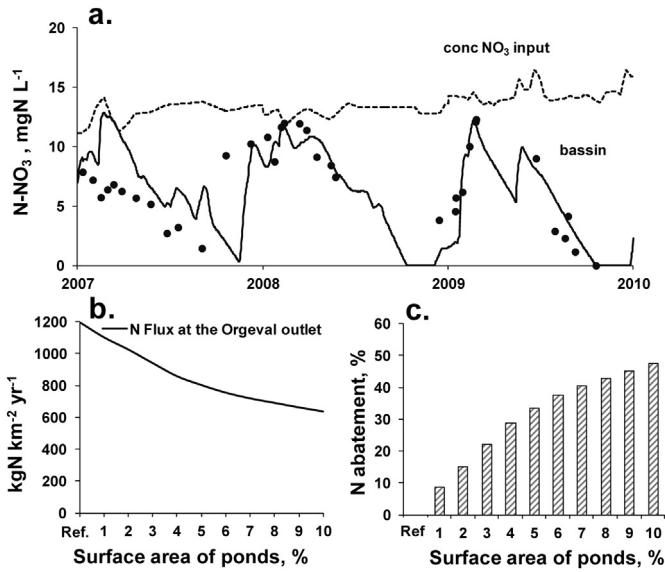
These values are accurately reproduced by a simplified model of stagnant water (Garnier and Billen, 1993; Garnier et al., 2000; see also Passy et al., 2012) (Fig. 6a).

Regarding  $\text{N}_2\text{O}$  concentrations, the values averaged  $3.8 \text{ } \mu\text{g N}_2\text{O-N L}^{-1}$ , i.e. a tenfold over-saturation (with extreme concentrations of 8.4 and  $1.1 \text{ } \mu\text{g N}_2\text{O-N L}^{-1}$  for a data series in 2010,  $n = 14$ ). Based on the saturation concentration (Weiss and Price, 1980) and the gas transfer coefficient of  $0.4 \text{ m h}^{-1}$  (Wanninkhof, 1992; Borges et al., 2004), the annual mean  $\text{N}_2\text{O}$  emissions at the pond surface can be estimated at  $3.4 \text{ mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$ , a value similar to the emission at the cropped downslope (see Fig. 4).

The observed decrease in  $\text{NO}_3^-$  concentrations in the pond during the period of high biological activity suggests that such ponds could effectively be used as curative management infrastructures for  $\text{NO}_3^-$  reduction in surface water. However, the concomitant outgassing of  $\text{N}_2\text{O}$  represents a serious limitation, as it can result in the simple swapping from one type of pollution to another.

##### 4.2. Simulation of the effect of pond creation at the scale of the Orgeval watershed

Interestingly, historical maps of the Orgeval area (e.g. the so-called Cassini map, dating back to the middle of the 18th century) reveal that the traditional landscape of the Brie region was characterized by a large number of ponds established on the headwaters, both for driving mills and for pisciculture. In the Orgeval watershed, the number of ponds was in the range of 60, and their surface area amounted to 1% of the total surface area of the



**Fig. 6.** a. Interannual  $\text{NO}_3\text{-N}$  concentrations in a drainage pond in the Orgeval watershed. Dotted line:  $\text{NO}_3\text{-N}$  concentration at the entrance; solid line: simulated  $\text{NO}_3\text{-N}$  concentrations in the pond; black dots are the measured  $\text{NO}_3\text{-N}$  concentrations. b. Simulated N fluxes at the outlet of the Orgeval watershed with a range of surface area of ponds (from the reference situation to 10% of the total surface area of the Orgeval watershed); c. Associated N abatement is shown in comparison (recalculated from Passy et al., 2012).

watershed (Passy et al., 2012). Most of these ponds were dried and converted to cropland during the first half of the 19th century.

In order to explore the role of pond implementation in the Orgeval watershed as a measure to reduce the nitric contamination of surface water, the Senéque/RiverStrahler model (Ruelland et al., 2007; Thieu et al., 2009; Passy et al., 2013) was run, and connected drainage ponds were virtually introduced at different surface areas (Passy et al., 2012). The results showed that a 34% and 47% reduction of the N flux at the outlet of the Orgeval watershed can be expected with a total surface area of ponds equalling 5% and 10% of the watershed, respectively, compared to 9% abatement with the 1% pond coverage of the Cassini map (Fig. 6b, c). Reintroducing ponds in the landscape necessarily increases the residence time of the water masses, increases the primary production providing more carbon for denitrification, for example. However, although possibly a refuge for biodiversity, e.g. for fish to feed and spawn, a shift from lotic to lentic species can be damageable.

Whereas the process of denitrification could be used for mitigation measures in combatting nitric contamination in the hydro-systems by creating or restoring wetlands, caution must be taken to

limit a shift from nitric to  $\text{N}_2\text{O}$  pollution. Considering the  $\text{N}_2\text{O}$  emitted in the experimental pond studied, an increase of the  $\text{N}_2\text{O}$  emission to about  $60 \text{ kg N}_2\text{O-N km}^{-2} \text{ yr}^{-1}$  by the Orgeval catchment could be expected in the case of 5% pond area, close to the emission by agricultural soils (see Fig. 5b). However due to contradictory results (cf. Welti et al., 2012), a comprehensive assessment of ecosystem services and disservices in agricultural landscapes remains a challenge (Burgin et al., 2013).

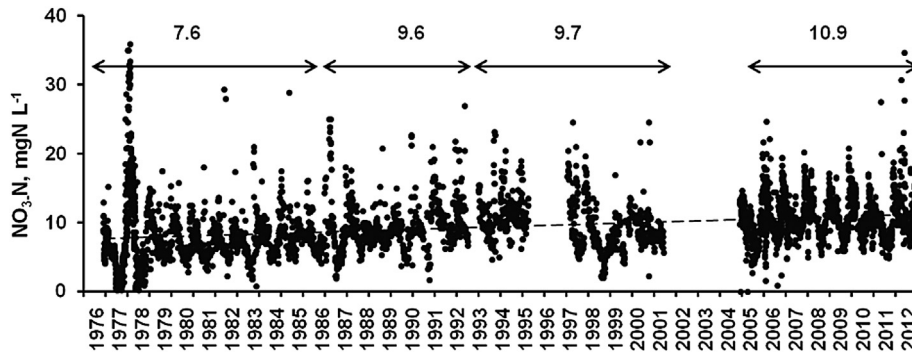
## 5. Preventive management measures to reduce nitrogen contamination

### 5.1. Good Agricultural Practices

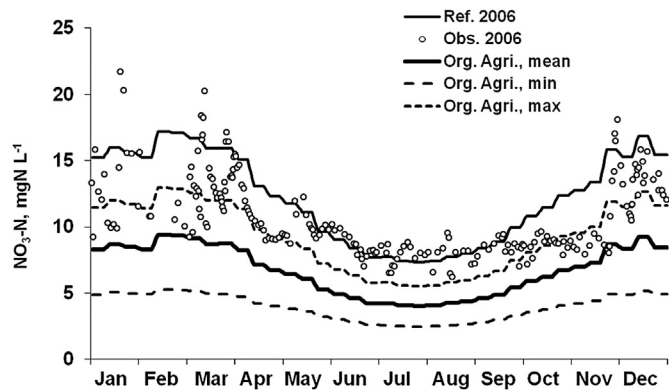
Good Agricultural Practices, consisting in lowering and fractionation of N fertilization, return of crop residues to the soil and introduction of catch crops, were promoted in the 1990s. When correctly applied, these measures are able to significantly reduce N leaching (Beaudoin et al., 2005). The long-term chronicle of  $\text{NO}_3^-$  concentrations in a headwater stream of the Orgeval watershed, available since 1976 from IRSTEA, however shows that  $\text{NO}_3^-$  concentration has only levelled off in the 1990s to  $9.7 \text{ mg NO}_3\text{-N L}^{-1}$  on average, and reached  $10.9 \text{ mg NO}_3\text{-N L}^{-1}$  in the 2000s (Fig. 7). No trend toward a reduction is in fact observed for the Orgeval catchment. It appears that the current agricultural practices, although they involve careful calculation of the nitrogen fertilization with respect to the requirement of crop growth during the vegetative period, are not able to further reduce the nitrogen surplus which is leached during the winter period. Alternative agricultural systems are therefore probably required for reducing  $\text{NO}_3^-$  leaching.

### 5.2. Organic farming

A few farms in the Orgeval watershed have been converted to organic farming practices. These farms use long crop rotations (8 yrs), established on small plots (<10 ha), starting with 2 or 3 years of alfalfa, then alternating cereals and legumes (peas or horse bean). External inputs of organic nitrogen, partly in the form of composted manure, are extremely limited. Although the cereal yield of these exploitations is about 15–20% lower than the conventional yield, their overall nitrogen surplus is much lower. Preliminary measurements (Benoit et al., unpublished) of sub-root  $\text{NO}_3^-$  concentrations measured with suction cups under the different plots of one such farm (site 2, Fig. 1) shows values of about  $13.4 \text{ mg NO}_3\text{-N L}^{-1}$  (SD = 4.8), i.e. about half the value found for conventional farming. Note that the value found is higher than the range of the values reported by Thieu et al. (2011) for organic farming based on literature data.



**Fig. 7.** Long-term chronicle of observed  $\text{NO}_3\text{-N}$  concentrations in the Melarchez River, a headwater stream in the Orgeval watershed.



**Fig. 8.** Seasonal variations of  $\text{NO}_3\text{-N}$  concentrations at the outlet of the Orgeval watershed, the year 2006 taken as an example. Rather good agreement is obtained between the observations and the simulation for 2006. Compared to the reference simulation, the organic agricultural scenario shows a 45% decrease in annual mean nitrate concentrations (Org. Agri., mean). The amplitude of the response is shown with the exploration of the SD range (Org. Agri., min and max).

### 5.3. Modelling $\text{NO}_3^-$ contamination resulting from GAP and generalized organic farming

The Seneque/RiverStrahler model has been run for exploring the effect of changes in agricultural practices at the scale of the Orgeval watershed. The current situation, modelled by considering a mean sub-root water concentration of  $22 \text{ mg NO}_3\text{-N L}^{-1}$  under arable land, was compared with that corresponding to a concentration of  $13.4 \text{ mg NO}_3\text{-N L}^{-1}$  (SD = 4.8) (organic farm, see above). An average decrease of 45% (25–68%) of the annual nitrogen concentrations at the outlet of the watershed is obtained (Fig. 8). Such a preventive measure would not increase  $\text{N}_2\text{O}$  emissions, a result corroborated by our own experimental measurements in the Orgeval watershed (Benoit et al., unpublished) and could even reduce them (Aguilera et al., 2013). Fig. 5c compares the implication of this preventive scenario to the curative one (Fig. 5b) and the current situation (Fig. 5a).

## 6. Discussion and Conclusions

The introduction of reactive nitrogen into the biosphere by modern agriculture has drastically increased, and the sequence of effects it causes in the atmosphere, in terrestrial ecosystems, in freshwater and marine systems, and on human health, is known as the nitrogen cascade (Galloway et al., 2003). In a river network with a continuous unidirectional transport of water and elements, the N cascade superimposed on the N spiraling, a concept defined as the travel distance of a water N atom before returning to the water downstream (Howard-Williams, 1985).

A front-line question for the near future is: Can we change agricultural practices to re-equilibrate the nutrient stoichiometry of surface water, preventing eutrophication, and still satisfy the needs of the population (in food and drinking water) with sustainable agriculture? Considering that more than 50% of terrestrial reactive nitrogen is now from Haber-Bosch mineral nitrogen ‘industrial production’ (mostly in the food system or a consequence of it), to overcome environmental problems of N pollution in the next 50 years, suggestions for future research should focus on new approaches for analysing water-agro-food systems (Billen et al., 2013), based on the concepts of socio-ecological trajectory (Fischer-Kowalski and Rotmans, 2009) and territorial ecology (Barles, 2013). The territorial watershed scale would be a suitable scale to initiate new directions in agricultural systems. Many discussions

are converging to request a tightening of the feedback loop between production and consumption so as to achieve sustainability (Sundkvist et al., 2001; Davis et al., 2012). A political consensus on this matter is very difficult to achieve (Leridon and De Marsily, 2011; Swinnen and Squicciarini, 2012), but the regional scale allows a good level of coherence for decision and management, i.e. a level at which implementation of measures appears relatively possible.

The Orgeval watershed is nowadays one of the long-surveyed watershed case study areas that has been subjected to biogeochemical investigations in addition to the 50 years of study in hydrology. The facilities offered for monitoring have made it possible to determine a comprehensive budget of nitrogen transfer and transformations at the scale of this territory. Specific nitrogen fluxes delivered at the outlet of the Orgeval watershed has been estimated at  $1130 \text{ kg N km}^{-2} \text{ yr}^{-1}$  and is on the order of that delivered at the outlet of the Seine Basin as a whole ( $1600 \text{ kg N km}^{-2} \text{ yr}^{-1}$  for the 2002–2007 period; see Passy et al., 2013). A similar observation can be made for the  $\text{N}_2\text{O}$  emission,  $\approx 140 \text{ kg N}_2\text{O-N km}^{-2} \text{ yr}^{-1}$  for the Orgeval watershed compared to the  $180 \text{ kg N}_2\text{O-N km}^{-2} \text{ yr}^{-1}$  obtained at the scale of the Seine watershed (Garnier et al., 2009).

The studies conducted in the Orgeval watershed, reveal that denitrification, mostly in waterlogged soils in slope shoulders and riparian zones, is a major process for nitrogen elimination along its cascade from agricultural soil to the river outlet, already reducing the fluxes of leached nitrogen between the base of the root zone and their discharge into the river system by 40–50% (see Fig. 3). Globally, at least 10% of the total denitrification flux ends as greenhouse gas  $\text{N}_2\text{O}$  emissions.

Among the measures which can be envisaged to further reduce nitrogen contamination of surface water, the creation of shallow ponds can be valuable, especially in many traditional landscapes, which were once characterized by numerous ponds. Historical land use situations are indeed recognised useful for planning measures to achieve environmental targets (Glavan et al., 2013). Many authors have stressed the value of such landscape management, especially when other ecological functions can be associated, such as conservation of the biodiversity, connectivity in the landscape, etc. (Ruggerio et al., 2008; Le Viol et al., 2012; Armitage et al., 2012). However, ponds, often promoted as compensation measures or even for wastewater management (Howard-Williams, 1985), should not be implemented excessively or inconsistently: the connectivity of pond networks should be considered at the territorial landscape scale so that they remain favorable to biodiversity. Bronner et al. (2013), for instance, report that in the US, the policy of environmental compensation measures has led to a strong decrease of high-quality forested wetlands at the expense of low-quality wetland area, such as many isolated freshwater ponds. Using the Seneque/RiverStrahler model, we have shown that a 30–40% reduction of  $\text{NO}_3^-$  at the outlet of the watershed could be obtained by introducing drainage ponds, up to 5% of the total surface area of the watershed. However, this would increase  $\text{N}_2\text{O}$  emissions by about 50%.

A more effective, preventive reduction measure would be the conversion of agriculture to organic farming practices with low fertilization, which has been shown to allow significant reduction of  $\text{NO}_3^-$  concentration at the base of the root zone with respect to current conventional practices. This type of measure not only reduces nitrogen contamination at the source, thus also acting on groundwater contamination, but is the only one which allows reducing instead of increasing overall  $\text{N}_2\text{O}$  emissions by the watershed. The generalization of organic farming which requires local supply in organic manure as well as an outlet for its fodder production would be facilitated by the reintroduction of livestock



farming in this specialized cereal cropping area. Clearly, meeting the objectives of the Water Framework Directive requires deep structural changes in the agriculture towards more sustainable and efficient systems (EU, 2013), rather than simple adjustments of farming practices (Volk et al., 2009; Glavan et al., 2012).

The combination of local studies together with an adapted modelling tool has proved here to be a relevant approach for quantifying nitrogen transformations and transfers at the watershed scale, even allowing the exploration of mitigation measures prior to field applications of ecological engineering investigations. Although several other process-based models might have been used (e.g. SWAT, Arnold et al., 1998, Neitsch et al., 2005; INCA, Whitehead et al., 1998; Wade et al., 2002), Seneque/RiverStrahler, was preferably used here, especially because it is currently used by the Seine Water Agency for WFD reporting. Other models based on regression approaches (e.g. GREEN, Grizzetti et al., 2005; MONERIS, Behrendt et al., 2002; NEWS-DIN, Dumont et al., 2005), would not have been able to explore scenarios like those tested here, because they would be too far from the calibrating data sets.

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