The role of climate on inter-annual variation in stream nitrate fluxes and concentrations

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In recent decades, temporal variations in nitrate fluxes and concentrations in temperate rivers have resulted from the interaction of anthropogenic and climatic factors. The effect of climatic drivers remains unclear, while the relative importance of the drivers seems to be highly site dependent. This paper focuses on 2–6 year variations called meso-scale variations, and analyses the climatic drivers of these variations in a study site characterized by high N inputs from intensive animal farming systems and shallow aquifers with impervious bedrock in a temperate climate. Three approaches are developed: 1) an analysis of long-term records of nitrate fluxes and nitrate concentrations in 30 coastal rivers of Western France, which were well-marked by meso-scale cycles in the fluxes and concentrations with a slight hysteresis; 2) a test of the climatic control using a lumped two-box model, which demonstrates that hydrological assumptions are sufficient to explain these meso-scale cycles; and 3) a model of nitrate fluxes and concentrations in two contrasted catchments subjected to recent mitigation measures, which analyses nitrate fluxes and concentrations in relation to N stored in groundwater. In coastal rivers, hydrological drivers (i.e., effective rainfall), and particularly the dynamics of the water table and rather stable nitrate concentration, explain the meso-scale cyclic patterns. In the headwater catchment, agricultural and hydrological drivers can interact according to their settings. The requirements to better distinguish the effect of climate and human changes in integrated water management are addressed: long-term monitoring, coupling the analysis and the modelling of large sets of catchments incorporating different sizes, land uses and environmental factors.

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1. Introduction

High nitrate concentrations in streams and aquifers are a major concern for drinkable water supplies and for the health of aquatic ecosystems. In many regions of intensive agriculture, quantifying the efficiency of implemented mitigation measures is crucial. The first difficulty in accomplishing this is the variable, and usually long, residence times for solutes that have been observed in groundwater systems, even when these systems are shallow (Bouraoui et al., 1999; Burns et al., 1998; Martin et al., 2006; Molenat et al., 2000, 2002; Molenat and Gascuel-Odoux, 2002; Worrall and Burt, 1999). The second issue is the large temporal variation of the nitrate fluxes and concentrations in rivers, which can be observed at seasonal, inter-annual called here meso-scale (i.e., over 2–6 years) and decadal time scales. Thirdly, the interaction of anthropogenic and climate drivers, which can act at each of these temporal scales and can hide the effect of changing management, presents additional difficulties. In a broader perspective, it is important to assess how climate variability and trends can affect the overall nitrogen efficiency of these systems.

The effect of climate on the cycling, concentration and fluxes of nitrate is still in debate. Climate is a major driver for biological, chemical and physical processes which determine N cycling and losses (Howden and Burt, 2008, 2009; Jones and Smart, 2005; Monteith et al., 2000; Zhang and Schilling, 2005). The storage of nitrogen in soil and groundwater can play a major role in N losses because it can be quite large as compared to the fluxes into and out of the system. Thus, climate can govern two kinds of processes: i) soil processes related to the mineralisation of organic soil nitrogen, for which soil temperature and wetness are the main climatic drivers. These processes play an important role in leaching rates because small imbalances between inorganic nitrogen availability in the soil and biological uptake may lead to marked changes; and ii) hydrological processes, mainly driven by effective rainfall (gross input minus evaporation), that can couple or uncouple the nitrate supply and its leaching in time and space. Soil processes can be assessed at both local and catchment scales, and have been studied extensively (see Gruber and Galloway, 2008; Borken and Matzner, 2009 for recent reviews). Hydrological processes can be adequately assessed at the catchment scale. Experimental research on processes is generally carried out in small headwater catchments,
mainly because they are easier to monitor, while available long-term records and the implementation of water management strategies often pertain to large basins. Basins are made up of many elementary headwater catchments that can be heterogeneous, both in terms of landuse and in terms of physiographic features; some processes, such as denitrification of wetlands and streams (Montreuil and Merot, 2006) or organic nitrogen production due to the suspended matter (Brunet and Astin, 1999), can be enhanced in the presence of a large river. Thus, it is difficult to assess whether the processes and drivers identified in small experimental catchments are relevant in large basins. It is therefore important to assess the effect of climate on hydrological processes, and on the cycling, concentration and fluxes of nitrate in a large range of catchment sizes and features using different methodologies.

In agricultural areas, long-term records generally show a clear upward trend in the nitrate concentrations of rivers since the 1960s (Burt et al., 1988; Betton et al., 1991; Johnes and Burt, 1993; Herpe and Troch, 2000). Large-scale ploughing of grasslands, unbalanced N budgets in farming areas and the increase in the use of mineral fertiliser are the main causes identified (Jones and Smart, 2005; Howden and Burt, 2008). However, other temporal variations often occur alongside this trend and may be explained by climatic drivers. Four situations regarding the climatic drivers of inter-annual variations of nitrate concentrations have been reported: i) a first set of papers underlines that cold, dry winters are correlated to nitrate maxima; they mostly concern northern or continental environments where freezing in the upper soil horizons has a biocidal effect on microbial biomass and damages plant roots. These events induce inter-annual cycling which can be explained by the North Atlantic Oscillation (NAO; Mitchell et al., 1996; Monteith et al., 2000). This first explanation will not be considered here, because the present study is located in an oceanic temperate area; ii) conversely, a second set of papers underlines the effects of droughts and summer temperatures, showing that high winter peaks are often driven by droughts during the previous summer (Burns et al., 1998; Reynolds et al., 1992, 1997; Reynolds and Edwards, 1995). The effect of the drastic 1976 drought in Northwestern Europe is often mentioned (Jones and Smart, 2005); iii) some papers, i.e., Howden and Burt (2008), specifically test the effect of rainfall variables and highlight the lack of correlation between these factors and nitrate concentrations in most of the catchments studied; and iv) lastly, some papers show the combined effect of several climatic variables such as winter drainage, summer rainfall and temperature, which can act successively (Jones and Smart, 2005). In short, these studies show that at some periods and in specific sites, climate variations can affect nitrate concentrations. The studies mainly focus on decadal trends rather than inter-annual variations, and seldom consider the interplay of climatic and agricultural drivers, although the temporal scale and the interaction are crucial to identifying the effects of mitigation measures.

This paper aims to identify and explain the effects of climate variables on nitrate concentrations and fluxes in an intensive farming region where N organic and mineral inputs have been high for the last four decades. The analysis focuses on meso-scale variations, intermediate between seasonal variations (less than a year) and long-term trends (decades), because the effects of mitigation measures need to be evaluated at this temporal scale. The objective of this study is to determine to what extent these variations are related to anthropogenic or climatic drivers using different approaches, i.e., analysing data from a large range of catchments, testing simple hypotheses using conceptual modelling, and more detailed modelling of the nitrogen dynamics in two contrasted catchments.

2. Study area

The region of Brittany is located in Western France and covers an area of 27,000 km² (Fig. 1). Low hills with gentle slopes (usually less than 5%) and a high drainage density (about 1 km/km²) dominate the landscape due to the crystalline bedrock and the humid climate. Headwater catchments represent 30% of the total area (Crave and Davy, 1997). The mean annual precipitation varies from 1200 mm in the west to 700 mm in the east, while the mean annual evapotranspiration varies between 600 mm and 500 mm. Three main formations are identified from the soil surface to the bedrock: the soil, the unconsolidated weathered bedrock, and the fissured and fracture-weathered bedrock. The soils are silty loams, with depths ranging from 0.5 to 1.5 m. The organic matter content varies from less than 2% in the east and northeast, to 7–8% in the southwest. The bedrock is granite or Brioverian schist. A shallow and permanent groundwater develops in the unconsolidated weathered bedrock and also in bottom land soils along the stream channel. Due to the heterogeneity of the thickness and the hydrodynamic properties of the unconsolidated weathered bedrock layer (Martin et al., 2006), the hydrology and the mean residence times of water vary greatly among headwater catchments (Ruiu et al., 2002b; Martin et al., 2006; Ayraud et al., 2008).

The landuse in this region is dominated by intensive farming. Since the 1950s, agricultural landscapes have been progressively but deeply

Fig. 1. Location of the 30 catchments studied on a regional map (Brittany, France).
modified: grassland areas have been ploughed, hedgerows removed (60% were suppressed from 1960 to 1980), fields enlarged and wetlands drained. The animal density has increased progressively; currently, approximately 2 cows, 9 pigs and 22 chickens are found per hectare of agricultural area, and 55%, 40% and 25% of the national production of pigs, chickens and milk, respectively, are located in this region. Consequently, the specific nitrate fluxes are high at approximately 25–30 kg N ha$^{-1}$ year$^{-1}$, with a high variability in space and time; values can exceed 100 kg N ha$^{-1}$ year$^{-1}$ in some catchments, and 160 kg N ha$^{-1}$ year$^{-1}$ in an exceptionally rainy year, such as 2001 (Arousseau, 2001).

Nitrate concentrations often display seasonal variation in streams and are generally higher in winter than in summer, though the reverse can also be observed. These seasonal variations have been intensively studied in headwater catchments (Molenat et al., 2002; Martin et al., 2004) belonging to the ORE AgrHyS (long-term environmental observatory of agro-hydrosystems: http://www.caren.univ-rennes1.fr/ORE-AgrHyS/), which is the French equivalent of the US Long Term Ecological Research network (LTER). These studies have demonstrated that shallow groundwater acts as an unlimited nitrate store at the annual scale, i.e., the mean annual concentration in the groundwater does not depend on the annual discharge (Ruiz et al., 2002a) and the annual nitrate flux is linearly related to the annual water flux with no asymptotical pattern (Molenat et al., 2008). The shallow groundwater controls the seasonal variation of the nitrate concentration in stream: generally, higher nitrate concentrations are observed in shallow rather than deep groundwater (Pauwels et al., 2000; Grimaldi et al., 2004) or in riparian wetlands due to denitrification (Molenat et al., 2002; Clement et al., 2003; Hefting et al., 2004). This pattern can be more complicated when the history of agricultural management and/or the distribution of the physical properties of the weathered layers induce complex vertical stratification in nitrate concentrations (Martin et al., 2004).

### 3. Methods

Three approaches were used in this study: 1) an analysis of long-term records, from the 1960s to present, on 30 coastal rivers of Western France, to describe the pattern of the temporal variations of the climatic variables and their effects on the fluxes and concentrations of nitrate; 2) a test of the climatic control of these fluxes and concentrations using a conservative mixing process and a lumped two-box model; and 3) detailed modelling of the nitrate fluxes and concentrations and the nitrate stored within the groundwater. This modelling was conducted on two contrasted, medium-size catchments (20 and 40 km$^2$) subjected to a programme of mitigation measures (a non-equilibrium situation). The effects of the climatic variables on the relative importance of hydrological versus geochemical processes on the observed patterns, and on the response time of the catchment, were assessed.

#### 3.1. Analysis of long-term records on 30 coastal rivers

The monitoring network maintained by the national or regional authorities comprises 122 sampling points for nitrate concentration, each comprising between 1 and 32 measures per year for 11–40 years. The discharge data are lacking a few points or were not measured at exactly the same location. From these 122 data points, 33 data points corresponding to 30 coastal catchment outlets and 3 subcatchment outlets have been selected based on three criteria (Arousseau and Vinson, 2006): i) at least one measurement per month; ii) no more than three missing data points per year and no missing data in the winter or for two consecutive dates; and iii) a minimal series duration of 16 years.

The areas of the 30 catchments range from 20 to 1000 km$^2$ (Fig. 1) and encompass a diversity of land uses, farming systems and physiographic contexts. Most of the records have two values per month. Nitrate was analysed using colorimetric methods. Despite variations in the methods, we did not detect any obvious effect of changes in analytical methods (Fig. 2). In particular, the relationship between discharge and concentration did not change through time.

Daily discharge data are available. If lacking, daily data of concentrations were estimated by linear interpolation between measured values. These daily data have been used to calculate the annual fluxes. For annual data, the use of the hydrological year (beginning the 1st of October) was used preferentially over the calendar year. The fluxes were estimated at the sample point where the concentrations were measured. When the discharge was not measured at the same point, it was estimated using the ratio of specific effective rainfall between the catchments defined by the two points. The low frequency of measurements and the different locations of sampling and discharge measurement points resulted in significant uncertainties in the estimation of annual fluxes in some catchments. However, a quick analysis of the data where more precise information is available showed that these uncertainties are not high enough to affect the patterns discussed in this paper. As an example, the measured and daily interpolated nitrate concentrations on the Aulne River present the same range of variation and the similar patterns (Fig. 2).

#### 3.2. Testing climatic controls, using a lumped two-box model, simulating a conservative mixing process

To test the hypothesis that the observed meso-scale cycles of nitrate concentrations in streams could only be caused by the climate pattern, we used the lumped model ETNA, which has been shown to simulate contrasted seasonal patterns of nitrate concentration in headwater catchments (Ruiz et al., 2002b). Daily groundwater recharge, calculated with a simple bucket model from daily rainfall and potential evapotranspiration, was used as the forcing variable of the model. Daily stream flow and nitrate concentration were computed as the

![Fig. 2. Measured and interpolated nitrate concentrations from the Aulne River, from 1973 to 2007.](image-url)
mixing of water draining from two linear reservoirs with different time constants, representing respectively the shallow and deep groundwater characterized by contrasting coefficients of discharge, as observed in headwater catchments (Molenat et al., 2002; Martin et al., 2004). The shallow groundwater reacts quickly to recharges and is the main contributor of stream flow during winter high flows, while the deep groundwater dominates during summer and fall low flows. Each reservoir comprises two water stores, one mobile, contributing to discharge, the other immobile, where nitrate moves only by diffusion. The storm flow, which accounts for less than 10% of the annual flux, is not considered here. Six parameters were adjusted for each catchment to fit the observed data: the proportion of deep losses of water, if necessary; the proportion of the two reservoirs; and the size and initial concentration of the two immobile stores.

In the present work, we kept the nitrate concentrations constant within each groundwater reservoir to eliminate the effects of long-term trends. We used a larger value in the shallow groundwater (13.56 mg N−NO₃⁻/L−¹) than in the deep groundwater reservoir (4.52 mg N−NO₃⁻/L−¹), thus considering a chemical equilibrium status of the catchment. This is justified by the observed nitrate concentrations in groundwater, which were little affected by annual recharge (Molenat et al., 2008). This leads to simulated seasonal patterns characterised by larger nitrate concentrations in the stream during the winter than during the summer, which is the most commonly observed pattern (Molenat et al., 2002; Martin et al., 2004). The values of coefficient of discharge were taken from Ruiz et al. (2002b). The model was run with a 30 year climate record (1977–2007) obtained from the Quimper weather station, located approximately 20 km south of the Aulne river outlet.

3.3. Modelling of the nitrate dynamics on two contrasted catchments

The agro-hydrological model TNT2 (topographic-based nitrogen transfer and transformations; Beaujouan et al., 2002; Oehler et al., 2009) was used to model nitrogen dynamics in two catchments. The model integrates three existing models: a distributed hydrological model, TNT, based largely on the assumptions of TOPMODEL (Beven, 1997; Beven and Kirkby, 1979), which explicitly simulates the soil–aquifer interactions; a crop model STICS (Brisson et al., 2003) simulating N soil processes and plant responses to water and nitrogen stresses; and, a denitrification model, NEMIS (Henault et Germon, 2000), modified to take into account the role of water circulation in riparian zones. TNT2 was specifically developed to study nitrogen dynamics in agricultural catchments. The model was fully distributed: agricultural practices were described for each field, and computations were performed at a daily time step for each 20×20 m grid cell of the DTM of the catchment. The flow routing between grid cells was multidirectional and was driven by topography.

The model was applied to the Horn and Haut Gouessant catchments, 44 and 21 km² in area, respectively (Table 1). These catchments are fairly contrasted, although they are both dominated by agricultural areas (80% of the surface area). N input, comprising mineral and organic fertilizers (195 kg N ha⁻¹ year⁻¹ in Horn versus 159 kg N ha⁻¹ year⁻¹ in Haut Gouessant), as well as value of N agriculture excess (22.1 kg N ha⁻¹ year⁻¹ in Horn vs. 0.4 kg N ha⁻¹ year⁻¹ in Haut Gouessant) are higher in the Horn catchment than in the Haut Gouessant catchment (Table 1). These catchments also differ in their storage capacities of groundwater. In the Horn catchment, the water table is deeper and the storage capacity of the groundwater higher than in the Haut Gouessant catchment. Consequently, the estimated mean residence time is longer in the Horn (7 years) than in the Haut Gouessant catchment (2 years). Mean annual N concentrations in the streams are also different, being equal to 16 mg N−NO₃⁻/L−¹ for the Horn and 7 mg N−NO₃⁻/L−¹ for the Haut Gouessant in 2007.

Simulations were run from 1992 to 2007. Surveys of the agricultural practices in 2000–2001, 2003–2004 and 2006–2007 allowed us to reconstruct agricultural practices each year. These catchments were both part of the “Bretagne Eau Pure” regional programme, aimed at reducing nitrate pollution in streams used for drinkable water supplies, and the inputs of nitrogen were reduced by 30% from 2000 to 2007. As a result, during the simulation period, the catchments were in a transient state as far as both management practices and water quality are concerned.

4. Results

4.1. Long-term observations of nitrate concentration in 30 catchments

Most of the 30 studied rivers presented three features. Firstly, nitrate concentrations were much less variable than nitrate fluxes (Figs. 3

![Fig. 3. Nitrate fluxes at 33 data points (30 catchment outlets and 3 subcatchment outlets) from 1973 to 2007.](image-url)
and 4). For example, for the Aulne river, the standard deviation of the fluxes was approximately 40% of the mean (mean nitrate specific flux of 40 kg N ha\(^{-1}\) year\(^{-1}\), standard deviation of 16 kg N ha\(^{-1}\) year\(^{-1}\)), while the standard deviation of the concentrations was only approximately 20% of the mean (mean nitrate concentration of 4.97 mg N l\(^{-1}\), standard deviation of 0.90 mg N l\(^{-1}\)).

Secondly, variations in the fluxes and concentrations followed very similar temporal patterns. The fluxes and the concentrations showed an upward trend beginning in about 1976 (Figs. 3 and 5). This trend, computed for the 30 points for fluxes from 1976 to 2006, shows a low but significant increase of 0.36 N kg year\(^{-1}\), despite a high variability in time and space. This increase of the fluxes implies an increase in concentrations, which is not clearly visible. The trend was approximately 0.038 mg N–NO\(_3\) l\(^{-1}\)/year and 0.10 mg N–NO\(_3\) l\(^{-1}\)/year, computed for the Aulne River from 1981 to 2006 (Fig. 3), and for the seven rivers from 1983 to 2006 (Fig. 5), respectively. Meso-scale variations were superimposed on this trend and showed a cyclic pattern (Fig. 3). This cyclic pattern is clearly shown on the Aulne River for the fluxes as well as the concentrations (Fig. 4). For the nitrate fluxes, this cycling pattern was relevant to all the rivers. The correlation coefficients between the annual nitrate fluxes of the 16 rivers for which the data set is complete from 1990 to 2005, showed that these rivers present the same pattern governed by the hydrological regime (Table 2). However, the range of variation of the cycles varies depending on the river. The cycle of nitrate concentrations is particularly evident in only the seven rivers highlighted in Fig. 5. For the other rivers, this cyclic pattern is less obvious or absent. These cycles typically start with a dry year, with low fluxes and concentrations, followed by increasingly wetter years. The first cycle is often difficult to identify and then four cycles can be clearly identified: 1988–89 to 1991–1992; 1991–1992 to 1996–1997; 1996–1997 to 2001–2002; 2001–2002 to 2004–2005; a fifth one begins in 2004–2005 and is still ongoing. These cycles last between 4 and 6 years.

A third feature can be observed by analysing the data of each individual river. Fig. 4 shows a detailed analysis of the Aulne River, which presents a cyclic pattern of fluxes and concentrations. The cyclic patterns of the concentrations of this river are asymmetric compared to those of the fluxes. The concentrations increase more abruptly at the beginning of the cycle than the fluxes, and decrease more slowly after the peak, thus showing hysteretic patterns in annual concentration cycles (Fig. 6). The link between concentrations and fluxes in time clearly indicates that catchment hydrology is the main driver of the fluxes due to the variation in the discharge, and secondarily in the nitrate concentrations. Due to the trend and the hysteresis, the correlation between fluxes and concentrations is not significant.

4.2. Test of the climatic control using a lumped two-box model simulating a conservative mixing process

The simulated relative variation of annual nitrate concentration in the stream (Fig. 7) displays cyclic variations that follow a pattern
very similar to those observed in rivers in the Brittany region and described above. In particular, the four meso-scale cycles identified in Fig. 5 are clearly identified in the simulation. During dry years, the most reactive reservoir quickly dries up and the average concentration decreases to the low value of the less reactive reservoir. Conversely, when a wet year follows a dry year, the most reactive reservoir quickly fills up and the stream concentration increases rather abruptly. When there are several successive humid years, the less reactive reservoir fills up and its contribution becomes increasingly important, inducing a slow decrease in the average stream concentration. This simple hydrological mechanism, conceptualized by a superficial and a deep one reservoir with both have a constant concentration, can reproduce the cyclic as well the hysteretic pattern identified in the observed data set. The properties of these reservoirs can also represent the variability between the catchments. Thus, a simple conceptualisation is able to explain the meso-scale variation in nitrate fluxes and concentrations in space and time for a stationary state of the chemical concentrations in the shallow groundwater.

4.3. Models of nitrate dynamics on two contrasted catchments

Discharge was simulated for the calibration, with a Nash criterion of 0.63 and 0.62 for the Horn and Haut Gouessant catchments, respectively. The relative errors were 13% and 26% for the nitrate concentration of the Horn and Haut Gouessant catchments, respectively. These results are satisfactory. The observed data are not shown in Fig. 8 for the sake of clarity.

The results of the simulation (Fig. 8) show that N fluxes in both catchments follow the same cyclic pattern as the other catchments in the area. However, these cycles do not completely hide the clear decreasing trend, beginning during the particularly wet years of cycle 3. This trend is even more visible in the variations of the concentrations: variation was stable (Horn catchment) or increased steadily (Haut Gouessant) during the first 6 years and then slowly (Horn) or rapidly (Haut Gouessant) decreased over the 8 subsequent years. The dynamics of the two catchments differ substantially. In the Horn catchment, the fluxes are very large and the concentrations respond progressively to the decrease in agricultural inputs, but a succession of very wet and very dry years (e.g. 2000–2001 and 2001–2002) can result in a transient increase of the concentrations. In the Haut Gouessant catchment, the fluxes are much lower and the concentrations are highly variable and are strongly affected by management changes which mask any potential hysteretic response to climatic variations, similar to that described above.

Table 2: Coefficients of correlation between the annual specific loads in N–NO₃ from 1990 to 2005 in 16 rivers.

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Fig. 7. Relative variations in the annual nitrate fluxes and concentrations from 1977 to 2007, computed by the two-box lumped model ETNA.
5. Discussion

5.1. Meso-scale variation in nitrate concentrations in the context of long-term anthropogenetically-induced change

Although this paper does not aim at explaining long-term trends, some general information is useful to contextualize the meso-scale variation. The increasing trend of the fluxes and the concentrations can be explained on one hand by decreases in the grassland areas, the suppression of hedgerows and agricultural drainage, all of which imply a strong decrease in the N pool of the soil. This trend can also be explained by the intensification of farming practices and increases in livestock, i.e., nitrogen input. Therefore, this trend can be explained by higher N fluxes in input and in fluxes within the catchment, as frequently mentioned. Events during the year 1976, characterized by very dry spring and summer in Northern Europe, provoked a sudden increase in nitrate concentrations and fluxes that triggered awareness of this problem (Fig. 2). This is explained by the low crop yields in the summer, the consequent high N residues after harvesting, the high mineralization rate in the subsequent rainy autumn, and thus, the high N losses in winter (Hong et al., 2005; Jones and Smart, 2005). However, the increasing trend would still have been observed without the above mentioned events in this particular year, and landuse and land management changes were clearly the dominant drivers of the trend up to the mid 1990s. In the last decade, these changes have slowed and a progressive and limited decrease in the inputs has begun (although not of the livestock density) due to the enforcement of the European policy (Nitrate Directive). It is thus likely that anthropogenic factors have gradually become less dominant as drivers of the meso-scale variations.

5.2. Meso-scale cycling at the regional scale

Anthropogenic trends have caused clear cycles in patterns of nitrate concentrations and fluxes, which are linked to the cyclic behaviour of rainfall. This climatic pattern remains unexplained, and is not correlated with variation of the NAO.

This cycling pattern affects the entire region, as indicated by the high correlation coefficients between the annual nitrate fluxes of the different rivers (Table 2). This relative homogeneity is due to the similar hydrological functioning of the catchments. All of the catchments have a shallow groundwater, where the water table really varies in time according to the topographic position, in the granite as well in the Brioverian schist, and has in time relatively stable nitrate concentrations in the shallow groundwater (Molenat et al., 2002; Martin et al., 2004). The relative contribution of the shallow groundwater is related to the water table, and thus to the annual water recharge and the effective rainfall. The degree of variation of the cycles depends on the river and is mainly attributed to the mean water residence time of the corresponding catchment, and is probably related to the bedrock and to the intensity of the weathered processes. Thus, this set of catchments could constitute an original data set for exploring such a relationship.

Fig. 8. Variations in nitrate fluxes and nitrate storage in the groundwater and nitrate concentration at the outlet, for the Horn and Haut Gouessant catchments from 1992 to 2006, computed using the fully distributed coupling crop, transfer and transformation nitrogen models TNT.
5.3. The hydrological control of meso-scale cycles of nitrate fluxes and concentrations

Simulations of the conceptual ETNA model show that the climatic pattern can account for the observed mid-term cyclic pattern in stream nitrate fluxes and concentrations, and for the hysteretic behaviour of nitrate concentrations in river. This pattern and the amplitude of the simulated cycles depend on the parameterisation of the two reservoirs in the model, i.e., their respective coefficients of discharge and nitrate concentrations. Obviously, the amplitude of the cycles is linked to the difference between the two fixed concentrations. It also directly depends on the contrast between the two coefficients of discharge. Thus, the occurrence of meso-scale cycles in rivers depends both on the hydrological properties of the catchment, which is linked to geological and geomorphological features described by the parameters of the model, and on the long-term history of agricultural practices. This history determines the contrast of nitrate concentrations between the two groundwater reservoirs. The model confirms that a simple mechanism accounts for the diversity in the meso-scale variation of nitrate concentrations in rivers that have been reported in the literature (Lucey and Goolsby, 1993; Mitchell, 2001; Moog and Whiting, 2002).

These features can also be analysed in terms of the contrasts between transport-limited and supply-limited catchments (Burt, 1988; Creed and Band, 1998). In transport-limited catchments, the nitrate fluxes are controlled by the hydrology, as opposed to the supply-limited catchments where the nitrate fluxes are controlled by annual input or soil pools of nitrate. The main difference between these two kinds of catchments can be attributed to differences in their hydrological processes. When transport-limited cases, subsurface flow is dominant and the water table fluctuations control the N fluxes, whatever the average concentration is (Molenat et al., 2008); conversely, in supply-limited cases, factors such as agricultural drainage and ditches (i.e., all situations where the annual mineralization interacts directly with the annual surface and subsurface flow) are dominant. Almost all of the catchments studied here were controlled by hydrological conditions, as tested by the ETNA model, and therefore can be considered to be transport-limited. In a recent paper, Burt and Worrall (2007) report a “curious reversal in the ‘memory’ effect” in a 35-year record of the Slapton Wood catchment, and propose an explanation based on a shift from a supply-limited to transport-limited situation. In our opinion, transport-limited situations occur when annual effective rainfall is lower than the internal water storage capacity of the catchment, which can be considered to be an intrinsic property, in the absence of drastic climate or water management (intensive drainage or pumping) changes. This memory effect can therefore be explained by groundwater concentrations changes in the long-term, leading to an inversion of the relative concentrations between the shallow and deep groundwater reservoir. Previous simulations of the ETNA model have shown that the model can produce inverted seasonal variations (with maximum concentration during low flow period) in these situations. These kinds of “inverted” seasonal variations, although uncommon, have been reported in the literature (Betton et al., 1991; Ruiz et al., 2002b; Martin et al., 2004). Future studies could explore how such changes might affect mid-term cycles, mixing climatic and agricultural scenarios.

Although all of these catchments could be considered to be transport-limited and nitrate fluxes could be considered to be controlled by the hydrological conditions, the cyclic patterns of fluxes or concentrations were not always observed or simulated in our study cases. Determining where, when and why the catchments do not present these features could be the aim of future investigations. The two main cases are discussed below.

The first case demonstrated an absence of cyclic patterns in observed nitrate concentrations of some of the 30 coastal rivers. Only 7 of the 30 coastal rivers analysed in our study showed a clear cyclic pattern of nitrate concentrations. This is probably due to the heterogeneity of the hydrological properties and the history of agricultural management of the catchments. Indeed, the absence of the cyclic pattern could simply be explained by low vertical or lateral stratification of the chemical concentrations in space, which was observed in some of the headwater catchments. Another possible explanation for the absence of this pattern is the high heterogeneity of the elementary headwater catchments of the rivers, or by the increased extension of the bottom lands which buffered the different signals coming from the headwater catchments in large catchments (Montreuil and Merot, 2006).

The second case in which the cyclic pattern in nitrate concentrations was not clearly observed was in a catchment modelled by the TNT. The representation of the processes in the TNT model could be involved; the model may include a poor representation of the chemical stratification inside the groundwater unlike in the ETNA model. However, because of a good agreement between the observations and the simulations by TNT, explanations other than the processes included in the model have to be considered. The poor cycling pattern observed in the simulation could be attributed to the non-equilibrium situation which acts on the catchments studied. In such a situation, we shift from hydrological control strictly determined by the fluxes of water, to control by the chemical concentration in the groundwater which can vary more quickly or less quickly according to the characteristics of the groundwater. In the Horn catchment, where the variations of the store are slow, this shift to a chemical control is slow. The Horn catchment is typically dominated by the groundwater, where the stores of nitrogen in the groundwater are so high that high concentrations and fluxes are maintained in the stream long after N inputs decrease. The mean annual concentrations are fairly damped and are almost insensitive to rainfall. In contrast, in the Haut Gouessant catchment where the fluctuations of the store occur over a short time scale probably due to the large extent of the agricultural drained areas, the perturbation of the cyclic pattern might be more important. This is particularly true in 2000–2001, when two important characteristics were observed concurrently: three successive rainy years diluted the upper part of the groundwater; a high decrease in the input of N had a similar effect on the groundwater. Thus, the Haut Gouessant catchment, a supply-limited catchment, could be considered to be at its limit. In this catchment, the effects of rainfall and of agricultural cycling (under the control of N input and complex climatic patterns) interact to produce a quicker and more irregular response to changes in both drivers.

5.4. Consequences for integrated water management

The observations and simulations from this study suggest complex meso-scale variations in nitrate fluxes and concentrations. This complexity is caused by three factors which have implications for water management.

The first explanation is the variability in the hydrological setting of the catchment, which is summarized well by the concept of mean residence time. The higher the mean residence times, the lower are the meso-scale variations in fluxes and concentrations. Consequently, the analysis of the variability in discharge, fluxes and concentrations is a good indicator of the mean residence time in transport-limited catchments, i.e., where the amount of nitrate in the groundwater reservoir is large in comparison to the annual leaching.

The second explanation is the heterogeneity in size or order of the monitored catchments. Small headwater catchments are dominated by hillside lateral flow and are usually relatively homogenous in terms of landuse and geology. In larger coastal catchments, stream chemistry results from the mixing of water coming from different hillslopes with different land uses and bedrocks, and is also affected by processes occurring during the longitudinal transport in the stream, riparian and hyporheic zones. The meso-scale variations in elementary headwater catchments caused by this heterogeneity can be dampered in larger catchments. Therefore, it is much easier to assess the effect of mitigation measures in headwater catchments than in larger basins. This is contradictory to most information from
operational monitoring of the water resources implemented in large river basins. Large scales may be relevant for observing long-term trends, but is inefficient for analysing the effect of recent changes. The third kind of explanation is the variability and complexity of agricultural management history, which can affect both the amount of N stored in groundwater and the distribution of concentrations within this store. The meso-scale climatic variations will modify the way this stored N is transferred in the stream. Thus, there is a high uncertainty in the response of the stream chemistry to agricultural changes during the few years following these changes (Souslby et al., 2008).

These observations highlight the necessity of long-term studies, not only for examining nitrate concentrations and fluxes in the stream, but also for evaluating management practices and groundwater chemistry. The results also show the usefulness of combined observation and modelling approaches for interpreting the data more in depth. The next step is to use the models, once properly tested, to perform scenario analyses and to assess current or alternative mitigation measures.

6. Conclusion

Although meso-scale variations of nitrate fluxes and concentrations are conspicuous in the data series, they have scarcely been discussed in the literature. In this study, we highlighted the complex interplay of climate, hydrology and management practices in determining the chemical signature of streams in farming areas, particularly for the meso-scale temporal variations. Simplistic interpretations created by applying local observations to the catchment scale are not scientifically sound. The timing and amount of nitrate leached at the scale of soil profiles is strongly controlled by the balance of the fertilization and by the rate of the biological processes; inter-annual variations can therefore be easily related to climate variables (temperature, rainfall) and to management practices. At the catchment scale, even in a shallow groundwater context, these relationships are no longer valid because of the buffering effect of the groundwater which delays the delivery to the streams and dampens out the variations of the concentrations of soil drainage waters.

In intensive agricultural regions, mitigation measures have been implemented and in terms of the effects of agriculture in future years, the implementation is crucial both in terms of social acceptability and in terms of policy assessments. The data record presented here shows meso-scale cyclic patterns as being very important to fluxes, less visible but with some hysteresis in the concentrations, and weakly visible in medium-sized catchments where mitigation measures take place and can affect nitrogen storage. These measures depend directly on the annual effective rainfall; i.e., the water and nitrate recharge the shallow groundwater. These results suggest that in all the catchments analysed here, nitrate delivery to streams is transport-limited. Nevertheless, this functioning varies between the catchments, and the cycles can be widely different from site to site, depending on the physical and chemical characteristics of the aquifer and of the importance of management changes. Although the meso-scale climatic variations can accelerate or slow down the response of the catchments to agricultural changes, these changes are clearly the main drivers of the long-term trends. However, the hydrological setting of each catchment can induce large variations in the dynamics of the response to climatic and anthropogenic drivers. This variability is an additional difficulty in assessing the effects of pollution mitigation measures, which highlight the interest of long monitoring records and detailed modelling at different scales.

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