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Continuous measurement of nitrate concentration in a highly event-responsive agricultural catchment in south-west of France: is the gain of information useful?

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Abstract:

A nitrate sensor has been set up to measure every 10 min the nitrate signal in a stream draining a small agricultural catchment dominated by fertilized crops during a 2-year study period (2006–2008) in the south-west of France. An *in situ* sampling protocol using automatic sampler to monitor flood events have been used to assume a point-to-point calibration of the sensor values. The nitrate concentration exhibits nonsystematic concentration and dilution effects during flood events. We demonstrate that the calibrated nitrate sensor signal gathered from the outlet is considered to be a continuous signal using the Nyquist–Shannon sampling theorem. The objectives of this study are to quantify the errors generated by a typical infrequent sampling protocol and to design appropriate sampling strategy according to the sampling objectives. Nitrate concentration signal and flow data are numerically sampled to simulate common sampling frequencies. The total fluxes calculated from the simulated samples are compared with the reference value computed on the continuous signal. Uncertainties are increasing as sampling intervals increase; the method that is not using continuous discharge to compute nitrate fluxes bring larger uncertainty. The dispersion and bias computed for each sampling interval are used to evaluate the uncertainty during each hydrological period. High underestimation is made during flood periods when high-concentration period is overlooked. On the contrary, high sampling frequencies (from 3 h to 1 day) lead to a systematic overestimation (bias around 3%): highest concentrations are overweighted by the interpolation of the concentration in such case. The *in situ* sampling protocol generates less than 1% of load estimation error and sample highest concentration peaks. We consider useful such newly emerging field technologies to assess short-term variations of water quality parameters, to minimize the number of samples to be analysed and to assess the quality state of the stream at any time.

KEY WORDS agricultural nitrate; storm chasing protocol; nitrate flushing

INTRODUCTION

Excessive fertilization of agricultural fields is the largest source of nitrogen emissions in European fresh water. The determination of stream concentrations, nitrogen fluxes and water quality is an integral component of many monitoring programs. River loads often have to be estimated from continuous discharge data but relatively infrequent sampling of sediment, solute or pollutant concentrations. Two standard ways of doing this are to multiply mean concentration by mean discharge and to use a rating curve to predict unmeasured concentrations. The uncertainty of such estimates has been explored for a lot of context, solute or particle. Previous numerous studies have combined turbidity sensors with sampling protocol to monitor suspended matters in streams and rivers (Walling & Webb, 1981; Fergusson, 1987; Webb *et al*., 1997; Moatar *et al*., 2006; Phillips *et al*., 1999). Other studies focus on the influence of various water quality sampling strategy on phosphorus and suspended load estimates for small streams (Robertson & Roerish, 1999) or estimation methods for a large panel of gauged (Johnes, 2007; Birgand *et al*., 2010; Cohn *et al*., 1989) or ungauged catchments (Shrestha *et al*., 2008). (Preston *et al*., 1989) have evaluated load estimation methods for nutrients, heavy metals and polychlorinated biphenyls for sampling intervals ranging from 1 week to 3 months. More recently, Jordan *et al*. (2007) and Rasmussen *et al*. (2008) have used new technologies to measure continuously phosphorus transfers to identify the origin of fluxes in the scope of assessment of mitigation measure performance. The focus of our study is the nitrate fluxes in a small agricultural, high event responsive catchment. Some previous studies focus on nitrate exportation estimates from forested catchment (Arheimer *et al*., 1996; Rusjan *et al*., 2008). Rusjan *et al*. (2008) have

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focused on the flushing of nitrate from a forested watershed. They have demonstrated using 15-min recording sensor that the concentration (mean of about 1.5 mg $N - NO_3^-$ during base flow) is highly variable during flood events (from 1 to 5 mg $N - NO_3^-$), and the role of specific flood events proved to be important for predicting the rates of nitrate flushing. These techniques based on sensor and *in situ* measurements are promising to approach the 'true' load estimate. Previous approach of 'true load' was based on Monte Carlo simulations. They were used on weekly nitrate sampling to allow exact dates on which samples were taken to vary randomly within the corresponding workweek (Guo *et al*., 2002). Recently, Bowes *et al*. (2009) estimate that newly emerging field-based automated sampler/analyser technologies have to be deployed for routine high-resolution monitoring of water quality to assess complex catchment nutrient processes and transfers. However, the question of making efforts in recording high-resolution time series of nitrate concentrations has to be legitimate regarding the gain of information. (Alewell *et al*., 2004) have assessed how much of the heterogeneity of solution concentrations is lost because of temporal integration of measurements, using high-resolution measurements (daily interval) of ion concentrations in runoff and soil solution. They have concluded that high-resolution measurements are considered to be too expensive compared with the gain of information. However, the authors explain that these conclusions apply neither to agriculturally used systems nor to extreme hydrological conditions. Birgand *et al*. (2010) have made an evaluation of the uncertainty in annual nitrate loads and concentrations as induced by infrequent sampling and by the algorithms used to compute fluxes, using hourly to daily flow and concentration data in nine watersheds in Brittany (West of France). The main nitrate concentration dynamic in this context is a typical systematic dilution during flow peaks with a high concentration during base flow (between 8 and 10 mg $N - NO_3^-.l^{-1}$).

In this high density of references dealing with the uncertainty of constituent concentration and load estimate, we find very few studies that report very high sampling frequency (≤1 h) of nitrate concentration in agricultural catchment where spikes of nitrate concentration are following the usual dilution associated with runoff fluxes. In that scope, we have measured nitrogen concentration during two years by monitoring a 10-min signal using a nitrogen sensor at the outlet of an intensive agricultural catchment in south-west of France. This research catchment was already sampled since 1985 to measure the impact of the implementation of agricultural mitigation practices on the water quality (Ferrant *et al*., 2011). The water quality was supposed to be sampled and analysed often enough such that a basic interpolation between consecutive samples likely represented actual concentration. This previous monitoring program has highlighted that dilution periods are sometimes followed by high concentration peak (between 5 and 30 mg $N - NO_3^-.l^{-1}$) during major flood events occurring in the end of winter, the beginning of spring and the end of summer (citepferrant2011).

The aim of this study is to assess how much of the heterogeneity of nitrate concentrations is lost by infrequent sampling strategy and how high is the error in estimating nitrate fluxes by reconstructing the concentration signal for this specific high event responsive agricultural catchment. Optimal sampling interval is proposed *a posteriori* in function of each hydrological condition and study objectives. A fast Fourier transform (FFT) algorithm was used to decompose the sequence of nitrate concentration into components of different frequencies. We have then used the Nyquist–Shannon sampling theorem to verify that the 10-min concentration signal could be considered as a continuous signal. It provides a sufficient condition for perfect reconstruction of the original signal, here the real nitrate concentration. The signal is then considered as continuous. A Monte Carlo approach [such as in (Guo *et al*., 2002)] is useless as we do not have to deal with the randomness of sampling dates. Then, we have systematically subsampled the continuous nitrate concentration signal using sampling interval from 20 min to 25 days to compute all differences between reconstructed load and reference load. The reliability of any estimation method is usually assessed in terms of both the bias and the variance of a particular sampling strategy. Bias measures drift of the estimated load distribution centre from the reference value, whereas variance reflects how tightly the distribution of the estimate is clustered about its centre (Walling and Webb, 1981). Our specific objectives are to evaluate the accuracy (bias and precision) of the different load computation approaches and to test their sensitivity to the sampling frequency. The data set is also used to determine both errors in load estimation and loss of high-resolution signal information associated with different sampling intervals, two different interpolation methods and hydrological or seasonal conditions. As the study is focusing on a highly event responsive stream, which is draining an intensive agricultural area, the conclusion of Alewell *et al*. (2004) is completed by our study.

MATERIALS AND METHODS

Study site

The Montoussé catchment at Auradé (Gers, France) is an experimental research site monitored since 1985 by GPN-Agriculture (TOTAL group) and by EcoLab in collaboration with GPN since 2004. It is a tributary of the Save River, which is a left tributary of the Garonne River, located in the Gascony, an intensively cultivated region in south-western France (Figure 1). The catchment drainage area is 3.5 km^2, and the stream is 1 m wide at the outlet. Nitrate measurements were started in 1985 by AZF Toulouse (now GPN) to measure the impact of best agricultural practices and landscape management on decreasing nitrate concentrations in streams. The Montoussé stream was selected for intensive monitoring because of the

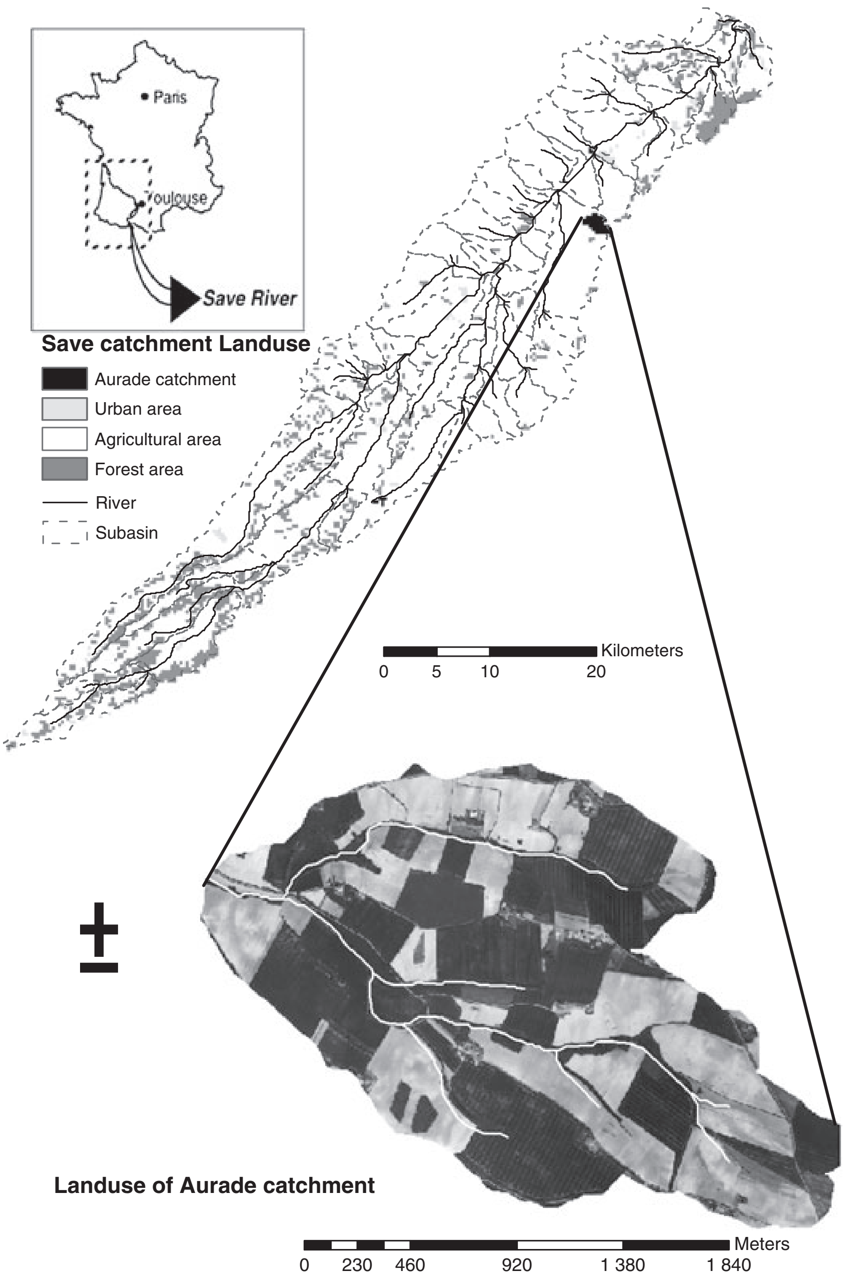

Figure 1. Study site location within the Save river basin. Stream network and landuse of the study site of Auradé (aerial photo, cartoexplorer; IGN)

'flashy' nature of its flood, the dominant lateral flow and the intensive agricultural context. The substratum of the catchment consists of impervious Miocene molassic deposits. No significant aquifer has been found except some sand lenses contributing to sustain local spring at mid-slope. The depth of the calcareous soils depends on elevation, with a maximum of 2 m downslope and less than 50–70 cm upslope, with many bedrock outcrops. Average annual rainfall calculated for the last 20 years is 656 mm, with a maximum in spring. An average of 86% of the rainfall is evaporated, mainly during summer and during some warm autumns. In this intensive farming area, about 87% of the total catchment area is used for crop production, consisting of a sunflower and winter wheat rotation with two or three applications of mineral fertilizer between February and end of April depending on crop growth. During the last decade, best management practices have been examined with the aim of decreasing nitrogen leaching from soil and river nitrate loads at the outlet. The more significant actions were raising farmers' awareness about the best use of mineral fertilizers, the implementation of rye-grass and poplar stripes along the stream and ditches, and a delay in the burying of straws after harvest.

Sampling strategy and data collection

A sampling strategy to evaluate the water quality and nitrogen loads is required to measure nitrate concentrations depending on flood events. However, owing to the variability of nitrate concentrations during these periods, a new sampling strategy was devised. An *in situ* ion-specific electrode (ISE; YSI Company) was set up at the gauging station and had been operating for 2 years from May 2006 to July 2008. Nitrate concentration was measured every 10 min in the mid-depth of the water column using a YSI 6920 EDS multiparameter sensor monitoring $N - NO_3^-$ (only available for freshwater), pH (Standard Probe YSI 6561), pressure of the water column (corrected with atmospheric pressure), conductivity and temperature (YSI 6560 Sensor), turbidity (YSI 6136) and dissolved oxygen (ROX optical sensor, lifetime luminescence detection). The multiparameter sensor has been connected to an Ecotech sampler AWS2002 (Bohn, Germany) to sample the nitrate concentration during the flood events. The pressure probe of the multiparameter sensor is recording the water level: if the water level is rising or decreasing more than a threshold fixed by the user (3 cm in this study), a sample of water is taken by the Ecotech sampler. An additional and more classical ISCO 3700 sampler (Lincoln, USA) has been programmed for basic daily sampling (at 7 pm).

We have used three complementary sampling strategy to catch the extreme variability of the concentrations:

- the raw nitrate concentration given for each 10 min by the ISE sensor that need a point-to-point calibration;
- the ECOTECH sampler that is sampling the rise and fall of the hydrograph;
- the ISCO sampler that gives available daily samples.

The operator (weekly visits) watch the sensor signal for both concentration and flood to determine which samples have to be analysed in the laboratory. In the case of recorded flood event, ISCO samples are giving the previous and the following state of water concentration before and after the flood, and the ECOTECH samples give punctual samples that are corresponding to the rise and fall of the hydrograph that should be a punctual reference for the sensor value calibration during the potential high variation of nitrate measurements during these period. The possible drift observed in point-to-point calibration (increase in the differences between sample concentration and the corresponding nitrate value provided by the probe) could be high during flood events and remain stable during base flow. This drift is not shown in this study as it depends on each sensor that has been replaced every 3–6 months (life span).

Weekly visits were carried out to check experimental material, download sensor data, empty the ISCO automatic sampler and take a manual sample of water that is analysed in 24 h. This was used to calibrate the sensor value during base flow periods with a weekly sampling interval. In the case of flood events, a SIM card phone connection allowed the operators to monitor remotely the water level or Ecotech number of samples taken and to check if a field visit is required.

Water samples were filtered in the laboratory through a 0.45 μm Millipore filter, then kept in the dark and refrigerated at 4 °C, before being measured for $N - NO_3^-$ concentrations with a high performance liquid–ion chromatography (Dionex Chromatograph ICS 2000). In all cases, the standard ranges were checked using international standard NWRI-ION-915, and the error was minor to 5%. The detection limit for nitrate is $0.02\ mg{\cdot}l^{-1}$.

No significant NH_4^+ concentration have been found in the stream water as well as in the samples kept cold; a pool of samples have been analysed during 2007, and the half of the measurement made were below the detection limit ($0.1\ mg{\cdot}l^{-1}$). The weak proportion of the NH_4^+ is neglected compared with the dominance of the $N - NO_3^-$ nitrogen form. The so called '*in situ*' sampling protocol stands for the weekly water samples taken by hand and ISCO and/or AWS2002 samples that have been selected by operators in case of nitrate concentration fluctuation during a flood event recorded by YSI sensor; 286 water samples were analysed during the study period, corresponding to a mean of 1 sample every 3 days but chosen according to nitrate concentration and water level variation. The collected data set recorded by the sensor consisted of a total of $n = 99, 703$ water level and nitrogen concentration measurements at 10-min time steps (144 samplings per day) corrected for each period by *in situ* protocol samples.

The discharge has been measured in continuous, with three types of sensors: a mechanical limnigraph with counterweight and float that is recording the water level signal on a millimetric paper, a digital ultrasonic sensor, and the pressure sensor used in the multiparameter probe. We have verified the coherence between the three signals during the study period. The water level recorded by the pressure sensor has been used to compute the corresponding water discharge, using the tare equation of the concrete gauge. The discharge estimation error is small using such method, so we are only focusing on the nitrate concentration estimation.

Data preprocessing

The first step was to calibrate the $N - NO_3^-$ probe values with the field data. A calibration coefficient is computed for each laboratory value: the sensor value is corrected by this coefficient to obtain the same value than obtained in the laboratory. We assume that this coefficient is varying linearly between two consecutive laboratory measures. This assumption has been verified for small interval between two HPLC measurements (few days). The drift amplitude (difference between the sensor value and field data) depends on the hydrological regime but also and more often on the sensor itself that we have to change each 3–6 months. The high-frequency sampling of the concentration gives an accurate correction of the sensor value that change markedly during flood events. The sensor value remains stable during low flow period so that a weekly sampling protocol is far enough to verify or correct the sensor value. We are thus obtaining a 10-min time step nitrate concentration signal that has been verified and corrected with 286 water samples.

A time-series analysis was performed using the OCTAVE software (GPL http://www.gnu.org/software/octave/about.html) to estimate the signal variability in terms of frequencies. A FFT algorithm was used to compute the $N - NO_3^-$ concentration spectrum. The power spectrum of the nitrogen signal collected from 4 May 2006 to 31 July 2008 at the outlet was computed. For this calculation, gaps in the data because of maintenance operations were not taken into account. We have used the Nyquist–Shannon sampling theorem to estimate the lowest sampling frequency that allows us to obtain a continuous signal. In essence, the theorem states that a continuous signal that has been sampled can be perfectly reconstructed from discrete samples if the sampling rate exceeds twice the highest frequency in the continuous signal. This gives us a first estimation of the minimum sampling frequency where errors are made by sub-sampling the $N - NO_3^-$ concentration signal. This is complemented by a second approach based on load error evaluation as described below. The concentration signal variability could lead to increase the load estimation error by subsampling this signal; we have also considered the signal during flood events and the signal during base flow separately. Signal analysis was thus carried out for all combined end-to-end flood events on one hand and combined end-to-end base flow periods on the other hand.

Load calculation method

'Exact' load estimation. The 10-min sampling interval gives an accurate estimation of all frequencies of concentration signal (see section 1). We consider the nitrate concentration signal as a continuous one. Exact nitrate loads are also computed as follows:

$$F_{ref} = \sum_{i=1}^{n} F(i) \tag{1}$$

where *C(i)*, *Q(i)*, and $F(i) = C(i)Q(i)$ are the reference $N - NO_3^-$ concentration ($mg \cdot l^{-1}$), discharge ($l \cdot s^{-1}$), and $N - NO_3^-$ load ($mg \cdot s^{-1}$) at time $i \in \{1, \ldots, n\}$.

This load is considered as the 'exact' nitrogen load for the whole record period.

Sampling strategy and load estimation. We have tested two sampling strategy and two interpolation method to compute the total nitrogen loads during the study period. One is using discharge and concentration sample to compute punctual loads that are interpolated in the time. It is equivalent to periodic visits to measure water discharge and nitrogen concentration, assuming that discharge is not monitored continuously. Concentration, discharge and load are downsampled at the sampling interval p from the time $j \in \{0, \ldots, p-1\}$ before being interpolated and resample. Such downsampled-interpolated concentration, discharge and load are labeled $C_{j,p}(i)$, $Q_{j,p}(i)$ and $F_{j,p}(i) = C_{j,p}(i)Q_{j,p}(i)$, respectively. The total load for the whole study period using downsampled-interpolated concentration and discharge with the sampling interval p from the beginning time j is (M1):

$$F_{j,p} = \sum_{i=1}^{n} F_{j,p}(i) = \sum_{i=1}^{n} C_{j,p}(i)Q_{j,p}(i) \tag{2}$$

This evaluation of nitrogen fluxes is using discrete discharge measurements, which is similar to other evaluations presented in Birgand *et al.* (2010) for the method M1 and M2 of their study.

The second strategy is using infrequent samples of the concentration signal to interpolate concentration. Loads are computed using the interpolated concentration and the continuous discharge. It is described in Equation (3) (sampling protocol 2). This is the typical strategy used in the studied gauged catchment. The flux F is computed for each sampling interval p with the offset j and the reference discharge during p is (M2):

$$F_{j,p} = \sum_{i=1}^{n} C_{j,p}(i)Q(i) \tag{3}$$

We have tested sampling intervals p as follows: all p values from $p = 20min$ to $p = 25days$ with an increment of 90 min. Two interpolation techniques, nearest neighbor (a) and linear (b), were considered. Four methods were therefore tested, M1(a), M1(b), M2(a) and M2(b). We have also used the 286 sampling points used for the *in situ* sampling protocol to evaluate load error computation using the method M2 as well as the loss of heterogeneity in the resulting concentration signal.

Evaluation criteria

We have calculated the error estimation $E_{j,p}$ for the downsampling period p with the offset j as follows:

$$E_{j,p} = \left(F_{j,p} - F_{ref}\right)/F_{ref} * 100 \tag{4}$$

We have computed the median ($e50_p$) and an index of dispersion (difference between the upper and lower deciles, $e90_p$ and $e10_p$) of all load error estimations for each sampling period p tested. Median or *e50* represents the bias. The analysis was performed for the whole signal, base flow signal and flood event signal. We have summarized the minimum sampling interval p (in hours) necessary to reach an error threshold ε. Two estimators were tested: $|e_{90} - e_{10}|$ ε and $|e_{50}| < \varepsilon$, which are the variance or index of dispersion and the bias or systematic error, respectively. Two thresholds ε are presented, 5% and 10%.

RESULTS

Is the signal continuous?

The power spectra analysis performed by FFT as proposed by Kirchner *et al.* (2001) and Feng *et al.* (2004) gives the minimum threshold of sampling frequency to explain 99% of the energy of the centered signal. This frequency is about 6 h for the data set and in accordance with Nyquist–Shannon sampling theorem, the reconstruction of the original signal is considered as perfect with a sampling interval of less than 3 h. Therefore, the 10-min recorded signal could be considered as a continuous signal. The error in sub-sampling signal arose with sampling intervals longer than 3 h. This result provides a first evaluation of the heterogeneity of the concentration signal that is subsample.

Discharge–concentration relations

Figure 2 shows the chemograph recorded at the outlet of the catchment with the nitrate sensor corrected or validated by samples taken with the *in situ* sampling protocol. The four major flood events are sorted by order of $N-NO_3^-$ load magnitude (no. 1 to no. 4). The mean discharge during base flow periods was $4.8\,L{\cdot}s^{-1}$. During flood event periods, the maximum discharge recorded was $1891\,l{\cdot}s^{-1}$ as a short peak of flow, and the mean discharge was $20.7\,L{\cdot}s^{-1}$ for the flood event signal recorded during the study period. The Montoussé river discharge is highly event responsive; flows are changing markedly during rainstorms. A mean of 9.15 mg $N-NO_3^-\,l^{-l}$ was observed during low flow, with a maximum of 15.4 mg $N-NO_3^-.l^{-l}$.

Sub-figures on the top of Figure 2 show variations in $N-NO_3^-$ concentration during major flood events 1–4. The black circles correspond to the position of the water samples analysed using ionic chromatography in laboratory. We ensure that the concentration peaks presented in this study are not a result of some glitch because the sampling strategy has been designed to avoid such situation and because the coherence of sensor value variations between each *in situ* samples over the study period is verified.

Weak dilution during the first runoff (2–6 h) was followed by a large concentration peak. Different types of concentration peaks were observed, for example, large and long lasting (3 days for flood event 1), long lasting only (1.5 days for flood event 3) or moderate (flood event 4). The maximum of instantaneous concentration was observed during the major load event (1), when $N-NO_3^-$ concentration increased from 5 to 35 and decreased to 20 mg $N-NO_3^-.l^{-l}$ in 11 h during flood event 1. The highest concentration peak (not sampled) corresponds to 29% of the total nitrogen flux during the flood event.

$N-NO_3^-$ concentration variations during the four major flood events are shown in Figure 3. $N-NO_3^-$ concentration is plotted as a function of discharge intensity. Arrows show the direction of time and exhibit anticlockwise hysteresis between rising and falling limbs of the hydrograph, except for flood event 2. As shown by Probst (1985) and Kattan *et al.* (1986), higher $N-NO_3^-$ concentrations during the rain fall period can be attributed to higher contribution of subsurface flow during this period. These contributions are observed for each flood events recorded in the study period but not in the same proportions and amplitudes. We have verified that there is no relevant statistical relationship between concentration and discharge, for the whole signal as well as for the base flow signal.

High temporal discharge and $N-NO_3^-$ load variations

We have plotted $N-NO_3^-$ loads at 10-min time steps in function of the discharge in Figure 4. Each point represents nitrate load in function of the corresponding discharge. The four major flood events are noticed with four different symbols. The heterogeneity of the nitrogen load for a same discharge is high, depending on each flood event: for instance, a discharge equal to $250\,l{\cdot}s^{-1}$ corresponds to a load from 0.25 to $4.44\,g{\cdot}s^{-1}$. On the other hand, the figure fcumulN.jpg shows three different trends between these correlated variables. First, loads during low flow are linearly correlated to discharge so that nitrogen loads are easily predictable during this

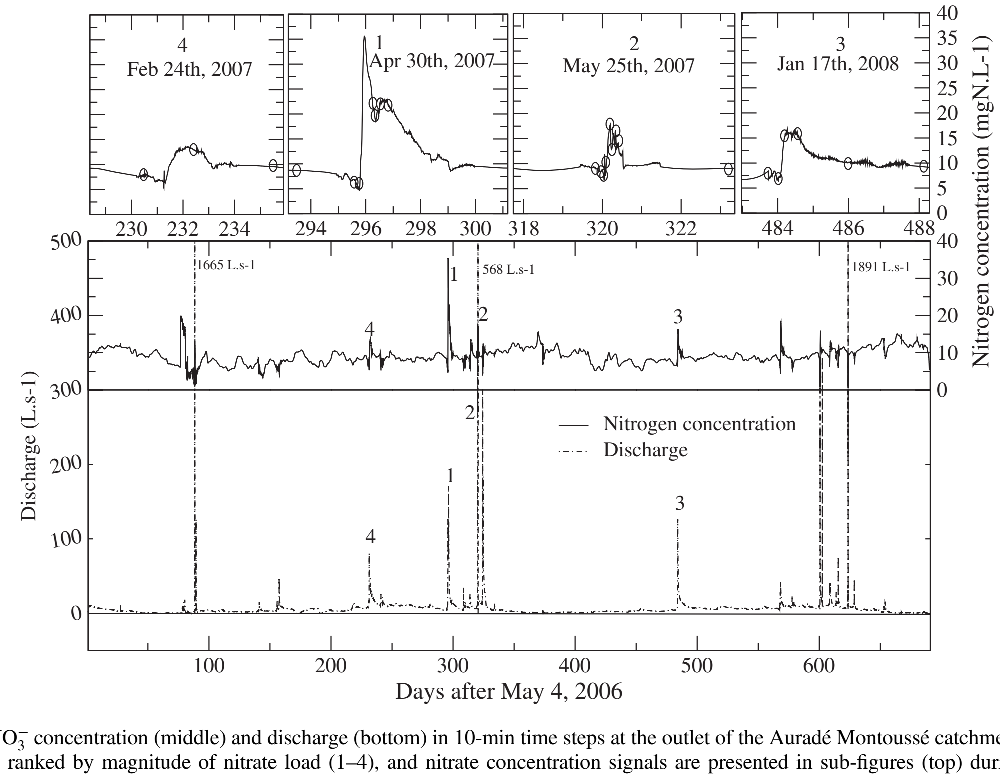

Figure 2. $N-NO_3^-$ concentration (middle) and discharge (bottom) in 10-min time steps at the outlet of the Auradé Montoussé catchment. The four main flood events are ranked by magnitude of nitrate load (1–4), and nitrate concentration signals are presented in sub-figures (top) during the four flood events. Black circles corresponds to the *in situ* samples

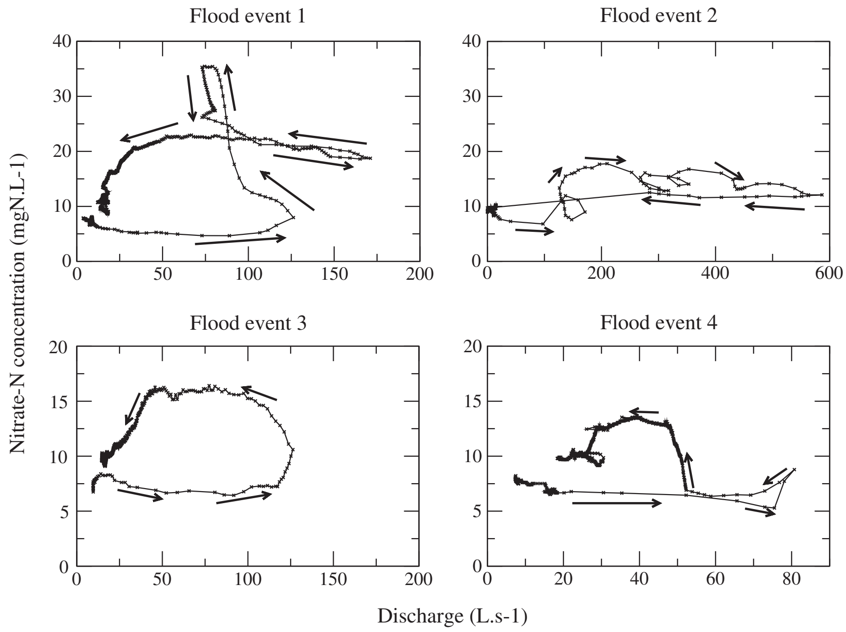

Figure 3. Relationship between 10-min $N - NO_3^-$ concentration and discharge measurement during the four major loads events of the study period. Flood event 1 on 30 April 2007, 5 days. Flood event 2 on 25 May 2007, 1 day. Flood event 3 on 17 January 2008, 4 days. Flood event 4 on 24 February 2007, 4 days. Scale is not the same between graphs. Arrows show the direction of change over time, and each cross corresponds to a 10-min measurement

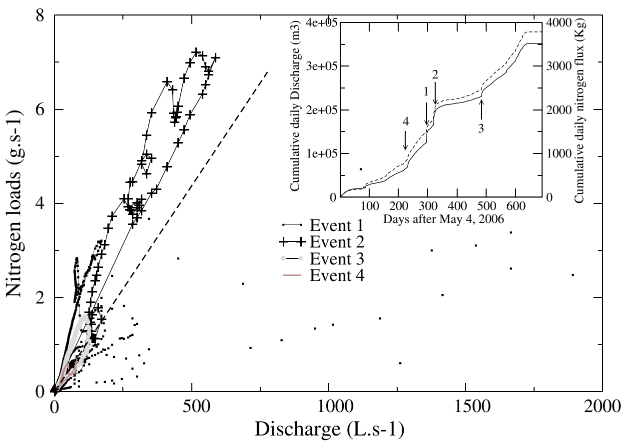

Figure 4. Ten-minute $N - NO_3^-$ loads as a function of discharge are presented in black points. The whole data set recorded is presented. The dotted line represents the highly significant linear relation for low flow period (below 40 $l{\cdot}s^{-1}$, Equation 5). Sub-figure in the top corner shows cumulative discharge and $N - NO_3^-$ loads during the study period. Loads are shown as solid lines, discharge as dotted lines. Events 1–4 are reported in both figures

period using regression methods. The linear relationship established between loads and discharge for small discharge (below 40 $l{\cdot}s^{-1}$) is

$$F(i) = 8.9438e^{-3} * Q(i) - 2.242e^{-5} \quad (5)$$

where *Q(i)* and *F(i)* are the 10-min discharge ($l{\cdot}s^{-1}$) and $N - NO_3^-$ load ($g{\cdot}s^{-1}$), respectively, at time $i \in \{1, \ldots, n10mn\}$. The regression between both dependent variables is highly significant ($R^2 = 0.95$, $n10mn = 90{,}417$).

The dotted line in the Figure 4 represents the previous relation for low flow period. The points, which correspond to the four major flood events, are situated up to this relation: for a same discharge, the nitrogen load is higher. In contrast, other flood events are situated below this line: for the same discharge, the nitrogen load is less important than during other periods. Several points for highest discharge recorded are corresponding to three flash flood events that have been recorded in 26 September 2006, in 13 May 2008 and in 10 June 2008. These major flood events (in term of discharge) are associated with high dilution effect. The resulting nitrate loads during these floods have not been prevailing compared with the four major loads identified. The instantaneous fluxes (between 1 and 2 $g{\cdot}s^{-1}$) is consequent, but the duration is really short (around 40 min).

Figure 4 also shows the cumulative daily discharge and nitrogen loads. The $N - NO_3^-$ loads during base flow are predominant, accounting for 66% (i.e. 2.3 t) of the total $N - NO_3^-$ load over the study period. 23% of the total discharge and 34% of the total $N - NO_3^-$ load (3.5 t of $N - NO_3^-$ loads) have been drained away during flood events, and half of this nitrate load (18.8% of the total $N - NO_3^-$ loads) has been drained away during the four major flood events (numbered 1 to 4 in Figure 2); 43% of the total $N - NO_3^-$ loads is measured between February and May, during fertilizer application period.

Loads are influenced first by discharge (as discharge is used to compute loads), but concentration becomes a non negligible factor during significant flood events so that loads are not any more predictable with discharge. Previous hydro-climatic conditions are leading nitrate concentration dilution or concentration in stream.

Load error computation by infrequent sampling strategy

Figure 5 represents the dispersion of all $N - NO_3^-$ load estimation errors as a function of the sampling interval p from 20 min to 25 days, using the M2 method and the

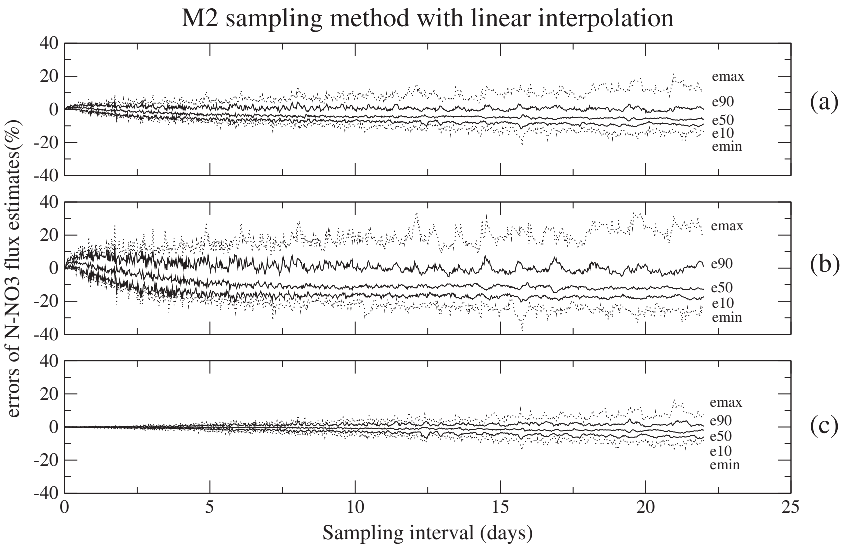

Figure 5. Quantiles (e10, e50 and e90) and extreme error (emin, emax) as a function of sampling interval (p) with the M2 protocol and linear interpolation: (a) total signal, (b) flood events signal, (c) base flow signal

linear interpolation for nitrate concentration. We have also separated signals during flood events and base flow. The concentration signal is noisy, and as a result, the dispersion of error in $N - NO_3^-$ load calculations is also noisy. The maximum dispersion (*e90-e10*) during the base flow period is around 8% (25 days of sampling interval) and is around 23% during flood events (Figure 6 (a) and (b)). The bias slope is negative, corresponding to a slight systematic underestimation increasing when p increases. On the other hand, the bias reaches a maximum for the small sampling interval ($e50 > 0$ in Figure 6) up to 1.5% (4.6% for the flood events signal) for the bias, for$p$ =6 h. We notice that the dispersion and bias are equal to 0 (not shown in figures) for $p < 3$h,, coherent with the result obtained using the Nyquist–Shannon sampling theorem.

Table I presents the minimum sampling interval needed to minimize error estimation below a threshold. Two estimators are presented, the index of dispersion (*e90-e10*) and the bias (*e50*). The M1 protocol imposes to sample every 5 h to minimize the bias or dispersion under 10%. The M2 protocol imposes to sample every 46 and 39 h the nitrate concentration in the stream to minimize the dispersion and the bias, respectively, under 10%. A sampling interval around 5 and 7 h, respectively, will be required to limit the dispersion and the bias, respectively, under 5% with the M2 method. The linear interpolation method with M2 gives the best load estimations, compare with the nearest neighbor interpolation method. For both estimators, an accurate estimation is always reached with smaller sampling interval during flood events than during base flow.

We have then computed the error estimation dispersion (*e90-e10*) using M2 method and linear interpolation for each 27 major flood events that have been recorded during the study period. We have then computed the minimum sampling interval needed to limit the error dispersion under

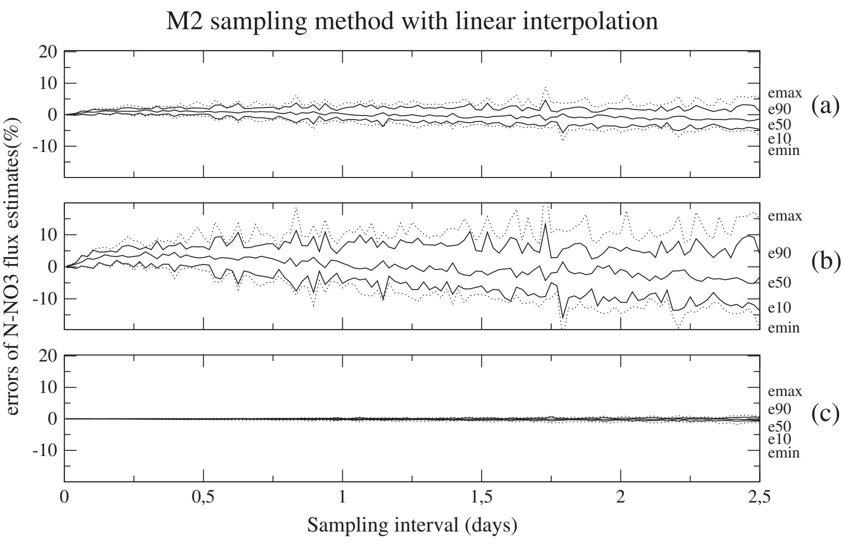

Figure 6. Change in scale with a focus on small sampling intervals of the quantiles (e10, e50 and e90) and extreme error (emin, emax) as a function of sampling interval (p) with the M2 protocol and linear interpolation: (a) total signal, (b) flood events signal, (c) base flow signal

Table I. Sampling method evaluation with dispersion and precision

(1) Index of dispersion less than 5%				
Minimum sampling period (hour)	M2(b)	M2(a)	M1(b)	M1(a)
Total $N - NO_3^-$ load signal	5.3	4.8	3.1	3.1
$N - NO_3^-$ load signal during flood events	1.1	1.1	1.3	1.3
$N - NO_3^-$ load signal during low flow	63	63	5.3	5.5
(2) Index of dispersion less than 10%				
Minimum sampling period (hour)	M2(b)	M2(a)	M1(b)	M1(a)
Total $N - NO_3^-$ load signal	46	21.5	4.1	5.3
$N - NO_3^-$ load signal during flood events	4.6	4.6	2.1	2.1
$N - NO_3^-$ load signal during low flow	100	100	8.8	9.8
(3) Bias (systematic error) less than 5%				
Minimum sampling period (hour)	M2(b)	M2(a)	M1(b)	M1(a)
Total $N - NO_3^-$ load signal	7	4.6	2.3	2.3
$N - NO_3^-$ load signal during flood events	1.1	1.3	1.6	1.6
$N - NO_3^-$ load signal during low flow	64.5	64.5	3.1	3.1
(4) Bias (systematic error) less than 10%				
Minimum sampling period (hour)	M2(b)	M2(a)	M1(b)	M1(a)
Total $N - NO_3^-$ load signal	39.3	14.1	4.3	4.3
$N - NO_3^-$ load signal during flood events	3.6	2.1	2.3	2.3
$N - NO_3^-$ load signal during low flow	125.8	125.8	4.8	5.6

a threshold of $\varepsilon = 10\%$. The results are presented in Figure 7. The minimal sampling interval computed for each flood is plotted in function of the flood duration. Black lines represent the theoretical limits when the minimal sampling interval is as long as the duration (e.g. one sample per event), half less long than the duration (e.g. two samples per event), and so on. The three more important flood events in term of loads (numbered 1–3) that occurred in the end of winter and during spring should have been sampled more than ten times to reach the objective (*e90-e10* < 10%). The flood event 1 especially should have been sampled every 4 h during the 120 h of flood to reach the objective. The floods recorded during summer does not require specific sampling strategy to obtain a good precision in the load evaluation (one sample per event), even for the longest flood. During the autumn, as well as winter and spring, an appropriate sampling strategy is required. For the higher durations (more than 80 h), at least more than five samples per event (except the flood event 4) are required. The variety of flood event imposes a variety of optimal sampling strategy, from a routine sampling protocol to a high sampling frequency. The nitrate concentration signal heterogeneity during specific flood events is the key factor that has to be controlled carefully with an appropriate sampling strategy for an accurate nitrate load evaluation.

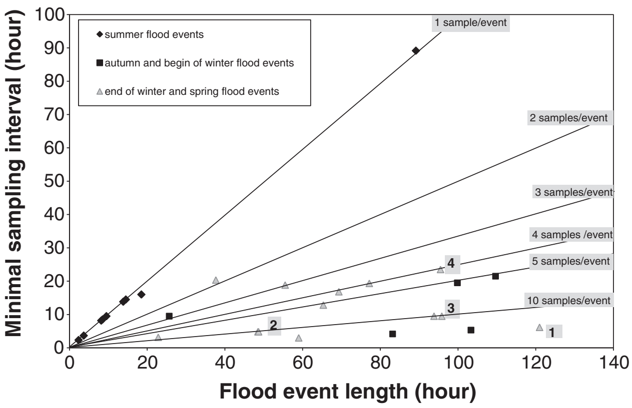

Figure 7. Minimum sampling interval for each flood event depending on flood event length and season. The minimum number of samples is calculated based on a threshold of 10% precision errors in sub-sampling $N - NO_3^-$ concentration signal with the M2 protocol and linear interpolation. The four major flood events identified in Figure 2 are numbered from 1 to 4

Load error computation induced by the in situ sampling protocol

Previous results evaluate the probable accuracy of fixed sampling interval during flood events. The gain in load estimation accuracy using a varying sampling interval in function of the chemograph is evaluated: the *in situ* sampling protocol, used to calibrate the nitrate sensor, gives an estimation of the total load less than 1% (Table II). To compare this error, we have computed the error of two typical methods:

- a widely used random fortnightly sampling frequency $p = 14$ days for small catchment (interpolated concentration is presented as a dotted line in Figure 8)
- the regression method between daily discharge and daily $N - NO_3^-$ load Equation (5).

The load estimation error for the 2-year period is −7.8% and −6.2% for the fortnightly sampling protocol and the regression method, respectively.

These two errors remain low (less than 10%) because more than the half of the loads are drained during base flow, when the regression is accurate, and the fortnightly sampling interval gives an estimation error that comprise between −3% (te10) and 1.5% (*e90*), the bias is around −1.7% (*e10*) (Figure 5(b)).

Reconstruction of the signal heterogeneity

The loss of heterogeneity by infrequent sampling of the concentration signal is illustrated in Figure 8. Both linear interpolation between each concentrations sampled with *in situ* sampling protocol and each sample taken with a basic fortnightly sampling interval are presented. The grey solid line corresponds to the reference concentration signal obtained from the calibrated sensor values. Extreme peaks and concentration values were not systematically sampled with the *in situ* protocol (solid line) and never sampled with the fortnightly sampling frequency (dotted line). Both

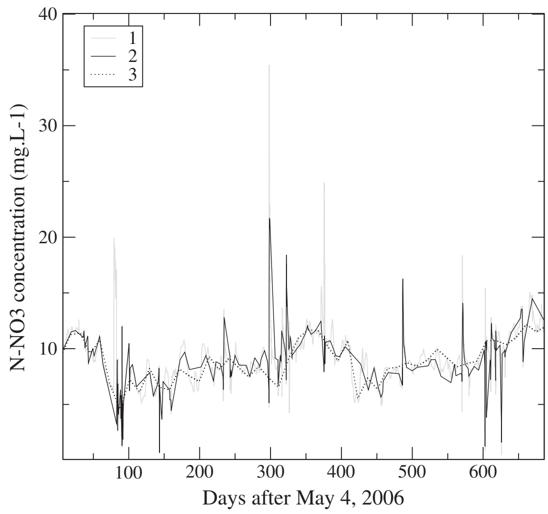

Figure 8. Comparison between $N-NO_3^-$ concentration signal measured by sensor (grey line, 1), linearly interpolated concentration sampled *in situ* (solid line, 2) and linearly interpolated fortnightly sampled concentration (dotted line, 3)

Table II. Error of *in situ* sampling protocol

Calculation error E for *in situ* protocol (%)	M2(b)	M2(a)
Total $N-NO_3^-$ load signal	0.8	1
$N-NO_3^-$ load signal during flood events	3	4.1
$N-NO_3^-$ load signal during low flow	0.03	−0.2

sampling protocols give an error in base-flow concentration dynamics because the frequencies of variations during these periods are smaller than the sampling period.

DISCUSSION

Interest of continuous nitrate recording

The numerous previous studies that have been reported in the literature have evaluated the uncertainty in loads estimate with monthly and even weekly sampling interval. Johnes (2007) have used daily phosphorus dataset to compute load estimate uncertainty and conclude that a limitation of their study was that daily records may fail to capture the full range of P export behavior in smaller catchments with flashy hydrographs. The implementing of aquatic sensor to measure continuously nitrate concentration has been recognized useful in some study to highlight the concentration heterogeneity in the time. Chapin *et al.* (2004) have shown the increase of nitrate concentration in a seasonal estuary during some winter precipitation event (from 0–1 to 28 mg $NO_3.l^{-1}$) and tidal cycling changing nitrate concentration by fivefold in few hours. Pellerin *et al.* (2009) have used optical nitrate sensor during a 5-day summer period to characterize the diurnal concentration variability in the San Joaquin River to have a better understanding of nitrate sources and cycling. We have set up this type of protocol to obtain a continuous nitrate concentration signal. Indeed, the heterogeneity of the concentration was already highlighted by previous monitoring programs in the study site during a long period (Ferrant *et al.*, 2011). As in most studies in the world, nitrate concentration exhibits concentration processes (peak of concentration following flood peaks) as well as dilution effects during winter (Webb and Walling, 1985; Birgand, 2000; Billy *et al.*, 2007). We have recorded all along the study period a quasi systematic dilution effect (for few hours) for each flood event (runoff is a dominant transfer during heavy rainfall) nonsystematically followed by concentration peak (few hours also).

What was the imprecision of previous sampling strategy and what is the gain of such continuous measurements in such context? Previous studies tried to estimate such uncertainties in annual loads and concentration estimation. Birgand *et al.* (2010) have worked with data set gathered from nine catchments in Brittany (France). Two of the 9 catchments only presented such concentration effects, whereas dilution effect was dominant for the seven other catchments. The authors indicate that both catchments are drained, explaining concentration peaks observed during flood events. They also conclude that the probability of sampling during these concentration events is small and leads to underestimate loads and concentration indicators. This results is coherent with our result: the systematic underestimation (as the bias is negative) of the nitrogen losses during flood events leads to a small underestimation considering the whole signal. During base flow, we have observed that the bias remain null. We presume that the more flood there is, the more important the total load underestimation is. However, our study highlights the slight overestimation made with small sampling interval (few hours). Such sampling interval is used for storm sampling protocol (Figure 2). Even the use of storm chasing sampling protocol does not characterize the concentration signal, maximal value or length of high concentration period (e.g. flood event 1). This overestimation is observed only with the flood event signal. The more frequent the sampling is, the more important the probability to sample high concentration. The linear or neighborhood interpolation methods overweight the short term high values the signal exhibits during these hydrological periods, leading to the slight systematic overestimation for small sampling interval. This nonintuitive result for high sampling frequency (small sampling interval) is highlighted, as the acquired signal is considered as continuous.

Optimal sampling strategy and errors associate

The present study gives optimal sampling interval to limit dispersion or precision errors below 5% or 10%. Indeed, the error dispersion and bias are not increasing highly with the sampling interval. Possible errors are included in the interval −9% and +1% (for $p=20$ days) with a slight systematic underestimation about −5%. This result should be compared with the result of the method M6 (linear interpolation of concentrations × continuous flow rates) presented by Birgand *et al.* (2010), showing a systematic overestimation of the nitrogen fluxes (bias is around 6%) but a dispersion that is less important (between −5 and +10% for a monthly sampling). The dilution effect is mentioned in this study to be the main source of uncertainty that leads to a systematic overestimation using the method M6. Littlewood (1995) are presenting the dispersion of load estimations generated by the infrequent sampling of a time series of synthetic nitrate concentration (reconstruction of a theoretical concentration signal based on the covariance of flow and concentration of a study site). The theoretical concentration signal is marked by concentration peak for each flood event, the heterogeneity is less high. They evaluate the bias about 5% for a 20-day sampling interval and a dispersion about 15%. The low concentration during flood events is not likely to be sampled with high sampling interval; the higher concentration during base flow will be interpolated during this period, leading to this overestimation. The effect is opposite in our study site where concentration effect are observed during some flood events. However, the underestimation for high sampling interval is slight (bias close to zero) because dilution effect is balancing concentration effect on the load estimation.

A slight difference between linear and neighborhood interpolation of the concentrations is presented in Table I: best accuracies in load estimation are made with linear interpolation, for any sampling interval. This result is confirmed by previous studies, (Kronvang and Bruhn, 1996) for annual transport of total nitrogen and total phosphorus, (Moatar and Meybeck, 2005) for a monthly interval of nitrate and orthophosphate loads in a large river.

Method M1 in the present paper is equivalent to the M2 method presented in Birgand *et al.* (2010). Such method leads to high dispersion of the error and systematic error. The error made is attributed to the error in reconstruction of the discharge. The use of continuous discharge recording is necessary to compute nitrate loads with reasonable certainty. However, Table I gives sampling interval that should be used in case of nongauged catchment to minimize the bias and dispersion of the nitrate flux estimation during the study period. This small interval (few hours) could be used for nongauged streams during short-term monitoring program.

Previous results indicate that an optimal sampling interval of 39 and 46 h will limit the precision and the dispersion below 10%, respectively. Indeed, this objective is rational in major monitoring program considering other nitrate post in the nitrogen loop within a catchment (agricultural fertilizer, soil mineralization for instance). In fact, the average nitrate exportation by the stream is evaluated to 12.5 $\mathrm{kgN \cdot ha^{-1}.y^{-1}}$ from 1987 to 2001 (Ferrant *et al.*, 2011) against around 100 $\mathrm{kgN.ha^{-1}.y^{-1}}$ of fertilization. The stream nitrate fluxes during the study period of the present study are corresponding to 5 $\mathrm{kgN.ha^{-1}.y^{-1}}$. This weak value is in the range of the driest year fluxes recorded during the last20 years. The study period has been marked by a severe drought. The discharge deficits (computed for a 20-year discharge data base) amount 51% and 45% for 2007 and 2008, respectively. In comparison, the Save River had deficits of about 32% and 17% for 2007 and 2008, respectively. In 2007, the Garonne River had a deficit of about 41%, which is the driest year since 1830 (Probst and Tardy, 1987; Probst, 1989). The major part of the nitrate loads is measured during the base flow period during which the precision and bias are really small. The dispersion could have been more important in a case of more humid years, during which the proportion of the nitrate transfer during rainfall events would have been more significant.

Another point of interest is that we have evaluated the estimation error of the *in situ* sampling protocol. The analytical effort is high (286 samples for the whole period), but it has led to minimize the error to 0.8% for the total loads, whereas the dispersion error for a fixed sampling interval for $p = 3$ days is between −6 and 2% with a bias around −2%. Adapting the sampling interval to hydrological condition is improving the accuracy of the estimation to a quasi 0% of estimation error. The bias and precision obtained for the *in situ* sampling strategy seem to be similar to the alkalinity fluxes presented by Aulenbach and Hooper (2006) always found to be ≤2% on an annual basis. However, the precision of the subsampling experiment was always ≤2% for quarterly and monthly sampling intervals as well. This is not the case of our study, where the bias and precision are increasing much more than that.

The accuracy of such protocol gives us a good indication of the possibility to monitor such small stream, draining agricultural catchment where the agricultural practices, fertilization input, nitrogen transfer and transformations processes could have been accurately known (by field work and modeling). There is indeed a need to estimate accurately the gain in water quality and pollutant transfer evolution to evaluate the efficiency of best agricultural practices as well as newly cropping technology designed for precision farming to reduce agricultural input and minimize agricultural contamination.

Figure 8 illustrates the reconstruction of the heterogeneity of the concentration signal by infrequent sampling strategy. The accuracy of the *in situ* protocol to sample the signal heterogeneity is high and exhibits the high concentration peaks following the peak of discharge. The highest concentration so far has not been sampled but deduced from the sensor. Such prospective insight of the main transfer processes as well as measurement and frequency of the maximum concentration the ecosystem is exposed to is relevant if the study is focusing of the flash impact of a pollutant such as pesticides or other pollutant known to be removed exclusively during rainfall events.

Key factors involved in concentration peaks

The present study does not highlight a direct relationship between soil nitrate content and nitrate concentrations in stream at the seasonal scale. Maximum nitrate concentration is observed during January, April and May (with the exceptional value of 35 $\mathrm{mg \cdot l^{-1}}$ recorded) and then in August and September. These results are confirmed by the previous high sampling frequency obtained in the study site during 16 years (Ferrant, 2009). The modeling work of the nitrogen cycle using the agro-hydrological model TNT2 (Ferrant *et al.*, 2011) has estimated mineralization rates in soils: a maximum is simulated during high temperatures in the end of summer; the minimum is found during winter (December, January and February). Furthermore, the contribution of lateral flow (sub-surface flow) to the total annual discharge (130 mm) is estimated to represent 46%. These fluxes are dominant during the hydrograph recession and their contribution to the nitrogen exportation is high (Probst, 1985; Kattan *et al.*, 1986). Another contribution could be nitrate-rich hill slope shallow groundwater (Altman and Parizek, 1995; Hill, 1996) during these events, when there is nitrate excess in soil.

Key factors controlling nitrate exportations during flood events should be the bare ground proportion of soil during winter, that will be sawn with sunflower the next spring, as well as the winter wheat mineral fertilization between January and April. During these periods, a combination of rainfall events generating subsurface flows should transfer a part of the soil nitrate remainder into the stream. These transfers during the winter are so unpredictable as they are more correlated to agricultural activities than to a seasonal cycle. The flood event 1 described in the results (Figure 2) is a succession of two rainfall events in 3 days. The discharge is less important during the first episode, during which the maximum concentration of the study period is recording. The maximum instantaneous flux also corresponds to the concentration peak. The second rainfall event generates more discharge than the previous one, the corresponding maximum of nitrogen fluxes is reached during the maximum of discharge, whereas the corresponding peak of concentration is lower (only 23 $mgN.l^{-1}$) than during the first event. Both maximum of instantaneous nitrogen fluxes are in the same range (2.9 and 3.2 $gN.s^{-1}$ for the first and the second event, respectively), but the first maximum is controlled by the concentration spike, whereas the second is controlled by the discharge spike. This example clearly shows a decrease of the soil reservoir contribution intensity after the first event.

The work of (Ferrant, 2009) has evaluated that this catchment is representative of a larger agricultural region that is mainly composed by cereal crops cultivated in hilly clayey landscapes. This region is the main source of nitrate pollution of the Save river, which is itself comparable to five other catchments of Gascony region.

CONCLUSION

The monitoring program at the Montoussé catchment aims to assess the heterogeneity of nitrate concentrations, the determination of all estimation errors that could be performed by infrequent sampling strategy, the role of hydrological conditions and seasonal variations on adapting the sampling strategy. The coupling of nitrate sensor and automatic samplers has provided a reliable continuous nitrate concentration signal that we used to answer previous questions. The real heterogeneity of concentrations requires to sample at an hourly time step some flood events when variations of nitrate concentrations follow discharge fluctuations with a time lag. During low flow, nitrate concentration signal is less variable, but small variations could be recorded using a sampling interval of 4 days. This study presents appropriate sampling frequency in order:

- to achieve acceptable error of nitrate load estimation;
- to record accurately the potential nitrate concentration peaks during flood events; and
- to sample each flood event to achieve a realistic nitrate load evaluation.

This study shows that estimation error on nitrate loads is leading to a systematic underestimation. However, this error is still acceptable because estimation errors associated to concentration and dilution subsampling effect offset themselves. On the other hand, usual storm chasing sampling protocol (generally controlled by the elevation or recession of the water level) fails to assess the heterogeneity of nitrate concentration during major flood. The *in situ* sampling protocol induces a cumulative error of around 3% for flood events. This average value for the 2-year study period does not reflect higher uncertainties during flood events. The concentration peak, which drives 29% of the nitrogen flux of the major flood event, has not been sampled by the *in situ* sampling protocol. There is a need for monitoring systems to describe the quality status of the water body, whereas European policies take stream water concentrations as an indicator of pollution; a good estimation of nitrate load does not mean that the extreme of stream water chemistry has been accurately determined.

This context of nitrate flushing from cultivated landscape is representative of a whole agricultural region and needs to be carefully sampled to assess nitrate concentration variations during within-day flood events. The *in situ* sampling protocol combined with *in situ* sensor measurements has provided an accurate calibration of the nitrate sensor values. The sensor information is very helpful in limiting the number of water samples to analyse. It is important to emphasize that this study illustrates the real nitrate variation in a stream water of an intensively agricultural catchment and that load estimation errors represents all possible errors made by subsampling this recorded signal. A 4-day sampling strategy is proposed to monitor seasonal and inter annual nitrate variations in streams, whereas a hourly sampling strategy is advocated to minimize load error estimation during flood events. The aim of monitoring such high event responsive catchment with newly monitoring technology is to have a better estimation of the increase in water quality in function of the change in agricultural practices in mitigation programs.

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