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Temporal variability of nitrate transport through hydrological response during flood events within a large agricultural catchment in south-west France

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ABSTRACT

The temporal variability of nitrate transport was monitored continuously in a large agricultural catchment, the 1110 km^2 Save catchment in south-west France, from January 2007 to June 2009. The overall aim was to analyse the temporal transport of nitrate through hydrological response during flood events in the catchment. Nitrate loads and hysteresis were also analysed and the relationships between nitrate and hydro-climatological variables within flood events were determined. During the study period, 19 flood events were analysed using extensive datasets obtained by manual and automatic sampling. The maximum NO_3^- concentration during flood varied from 8.2 mg l^{-1} to 41.1 mg l^{-1} with flood discharge from 6.75 $m^3\ s^{-1}$ to 112.60 $m^3\ s^{-1}$. The annual NO_3^- loads in 2007 and 2008 amounted to 2514 t and 3047 t, respectively, with average specific yield of 2.5 t $km^{-12}\ yr^{-1}$. The temporal transport of nitrate loads during different seasonal flood events varied from 12 t to 909 t. Nitrate transport during flood events amounted to 1600 t (64% of annual load; 16% of annual duration) in 2007 and 1872 t (62% of annual load; 20% of annual duration) in 2008. The level of peak discharge during flood events did not control peak nitrate concentrations, since similar nitrate peaks were produced by different peak discharges. Statistically strong correlations were found between nitrate transport and total precipitation, flood duration, peak discharge and total water yield. These four variables may be the main factors controlling nitrate export from the Save catchment. The relationship between nitrate and discharge (hysteresis patterns) investigated through flood events in this study was mainly dominated by anticlockwise behaviour.

1. Introduction

High nutrient levels in streams draining intensively cultivated catchments have become a widespread problem throughout Europe in recent decades (Heathwaite et al., 1996). Excessive application of nutrient fertilisers to agricultural fields is considered to be the largest source of nitrogen input to European freshwater systems, and intensive crop production in recent decades has resulted in a major threat to surface water quality due to the transfer of sediment and nutrients with associated contaminants. Excessive nitrate concentrations in surface waters contribute to eutrophication and algae development (Garnier et al., 1995; Jarvie et al., 2005). In general, nitrate concentrations in groundwater and stream water are a matter of concern for Western countries and environmental management policies. Long-term nutrient concentration datasets are a key resource for environmental scientists, catchment managers and policy-makers because they permit analyses of nutrient trends, loads, nutrient behaviour and the effectiveness of past nutrient migration and supporting data for future management decisions regarding issues of eutrophication and nutrient control (Burt, 2003). Therefore, monitoring programmes have been put in place to measure nutrient concentrations in water bodies such as in France (Probst, 1985), in north-eastern England (Bateman et al., 2006), in Central Europe (Haag and Kaupenjohann, 2001), in the Nordic and Baltic regions (Vagstad et al., 2004), and in Australia (DECC, 2007).

Hydrologically active periods, particularly flood events, are important because the addition of new water sources during such events mobilises distinctly new and different sources of nutrients from the catchment (Buda and DeWalle, 2009). However, the transfer of nutrients is also highly dependent on landscape characteristics and their influences on hydrological processes (Cirmo and McDonnell, 1997; Haag and Kaupenjohann, 2001). Knowledge of how hydrological response triggers nitrate transport at catchment level on the timescale of a single hydrological flood event is still lacking (Rusjan et al., 2008). The high frequency of data collection (nitrate and hydroclimatic data) during flood event is important to understand the nitrate dynamics and can help to identify factors influencing dynamic processes and transport. Moreover, accurate quantification of nitrate loadings at annual scale is hard to achieve over long time scale due to

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lacking high data frequency. Observations of event-scale hydro-biogeochemical transport of nitrate can be highly complex and can vary from one catchment to another. During flood events, hysteresis is often observed in nutrient concentration and discharge relationships. The study of nitrate concentrations and discharge relationships during flood events could be a useful approach to identifying the nitrate sources (McDiffett et al., 1989). Clockwise nutrient hysteresis patterns are produced when a particular nutrient has a higher concentration during the rising stage of a flood hydrograph, compared with the falling stage. This means that the nutrient is rapidly transported to the sampling point during the flood event, implying that the nutrient load is coming from either within the river channel itself, of from a catchment source that is rapidly transported to the river and it could also indicate a depletion of nutrient supply through the flood event (Bowes et al., 2009). An anticlockwise hysteresis pattern is produced when the nutrient concentration is highest on the falling limb of the flood hydrograph, and these patterns can be produced by either a dominance of nutrient supply that is mobilised slowly during a flood event, or could indicate a rapid input of nutrient from a source with a nutrient concentration lower than that in the river (Bowes et al., 2009). Hysteresis patterns have been used in previous studies to indicate changing sources of nutrient supply to rivers and changes in nutrient form through storm events (House and Warwick, 1998; Bowes et al., 2005; Stutter et al., 2008).

So far, little investigation with high frequency of data collection has been carried out within large agricultural catchments, where there are many difficulties such as spatiotemporal variability in climatic conditions, land use, agricultural practices and soil texture. Field measurements and data collection are generally difficult tasks, rarely achieved over long time scales in large catchments. A water quality programme has been continuously running since January 2007 within the Save catchment in south-west France, with the aim of establishing comprehensive water, sediment and nitrate budgets. The present study examined the temporal transport of nitrate through hydrological response during flood events within this large agricultural catchment. Analyses were also carried out to quantify the nitrate loads in stream water, to assess the relationships between nitrate and hydro-climatological variables during flood events and to study hysteresis.

2. Materials and methods

2.1. Study area

The Save catchment, located in the area of Coteaux Gascogne, France, is an agricultural catchment consisting of 1110 km^2 and has its source in the piedmont zone of the Pyrenees Mountains (south-west France) at an altitude of 600 m, joining the Garonne River after a 140 km course with a linear shape and an average slope of 3.6‰ (Fig. 1). This catchment lies on detrital sediments from the Pyrenees Mountains. It is bordered on the east by the Garonne River, on the south by the Pyrenees and on the west by the Atlantic Ocean. Throughout the Oligocene and Miocene, this catchment served as an emergent zone of subsidence that received sandy, clay and calcareous sediments derived from the erosion of the Pyrenees Mountains, which were in an orogenic phase at that time. The heterogeneous materials were of low energetic value and produced a thick detrital formation of molasse type in the Miocene. From the Pleistocene onwards, the river became channelized, cutting broad valleys in the molassic deposits and leaving terraces of coarse alluvium (Revel and Guiresse 1995). The substratum of the catchment, known as the underlying geology, consists of impervious Miocene molassic deposits. Calcic luvisols (UN FAO soil units) have developed on the tertiary substratum and local rendosols on the hard calcareous sandstone beds. The calcic cambisols that developed on hillsides with very gentle slopes have been subjected to moderate erosion. Calcic soils represent dominantly more than 90% in the whole catchment with a clay content ranging from 40% to 50%. Non-calcic silty soils, locally named *boulbènes*, represent less than 10% of the soil in this area (50–60% silt). The upstream part of the catchment is a hilly agricultural area mainly covered with pastures (5-year rotation including one year of corn and 4 of grazed fescue) and little forest, while the lower part is flat and devoted to intensive agriculture, dominantly a 2-year rotation of sunflower and winter wheat and little cornfields (90% of the area used for agriculture) (Fig. 1) (Macary et al., 2006). Fertilisers are generally applied from late winter to spring, with 20–100 kg N ha^{-1} in pasture areas (upstream) and 30–52 kg N ha^{-1} in sunflower and winter wheat area (downstream). Forest areas are not fertilised, but corn fields also receive fertiliser quantity (20–100 kg N ha^{-1}).

The climatic conditions are oceanic, with annual precipitation of 700–900 mm and annual evaporation of 500–600 mm. The dry period runs from June to August (the month with maximum deficit) and the wet period from October to May. The hydrological regime of the catchment is mainly pluvial, i.e. regulated by rainfall, with maximum discharge in May and low flows during summer (July to September). The catchment substratum is relatively impermeable due to its high clay content. Consequently, the river discharge is mainly supplied by surface and subsurface runoff, and groundwater is limited to alluvial and colluvial phreatic aquifers. The maximum instantaneous discharge for the long-term period (1965–2006) is 620 m^3 s^{-1} (1 July 1977) and mean annual discharge (1965–2006) is 6.29 m^3 s^{-1} (data from CACG: Compagnie d'Aménagement des Coteaux de Gascogne). During low flow periods, the Save River is sustained by approximately 1 m^3 s^{-1} from the Neste canal at the upstream area.

2.2. Instrumentation and sampling strategy

A Sonde YSI 6920 (YSI Incorporated, Ohio, USA) measuring probe and Automatic Water Sampler (ecoTech Umwelt-Meßsysteme GmbH. Bonn, Germany) with 24 one-litre bottles were installed at the Save catchment outlet (Larra bridge) in January 2007 to continuously monitor water quality (Fig. 2). The Sonde probe was placed near the bank of the river under the bridge, where homogeneity of water movement was considered for all hydrological conditions. The pump inlet was placed next to the Sonde pipe. The Automatic Water Sampler ecoTech connecting with the Sonde which was placed in the river, was programmed to activate pumping water on the basis of water level variations (Δx(cm)) ranging from 10 cm to 30 cm, depending on seasonal hydrological conditions for the rising and falling stages. This sampling method provided high sampling frequency during flood events. Manual sampling was also undertaken using a 2-litre bottle lowered from the Larra bridge, near the Sonde position, at weekly intervals when water levels were not very changeable.

2.3. Water sample analysis

During the study period (low and high flow periods), about 300 water samples were collected from automatic and manual sampling. These water samples were filtered in the laboratory using a pre-weighed nitrocellulose filter (GF 0.45 μm) to separate out the suspended sediment fraction. After filtration, each water sample was stored at 4 °C until analysis as soon as possible. Nitrate (NO_3^-) was determined with a Dionex (DX-120) instrument by the High Performance Ionic Chromatography (HPIC) method. Analyses were carried out in triplicate on 10% of all samples and on a standard control for every 10 samples to assess the reproductivity of the measurement, with the errors of less than 2%. Quality control standards were analysed alongside each batch. Temperature, pH and electric conductivity were measured by WTW instrument (pH/Cond 340i/SET) on weekly water samples in the field.

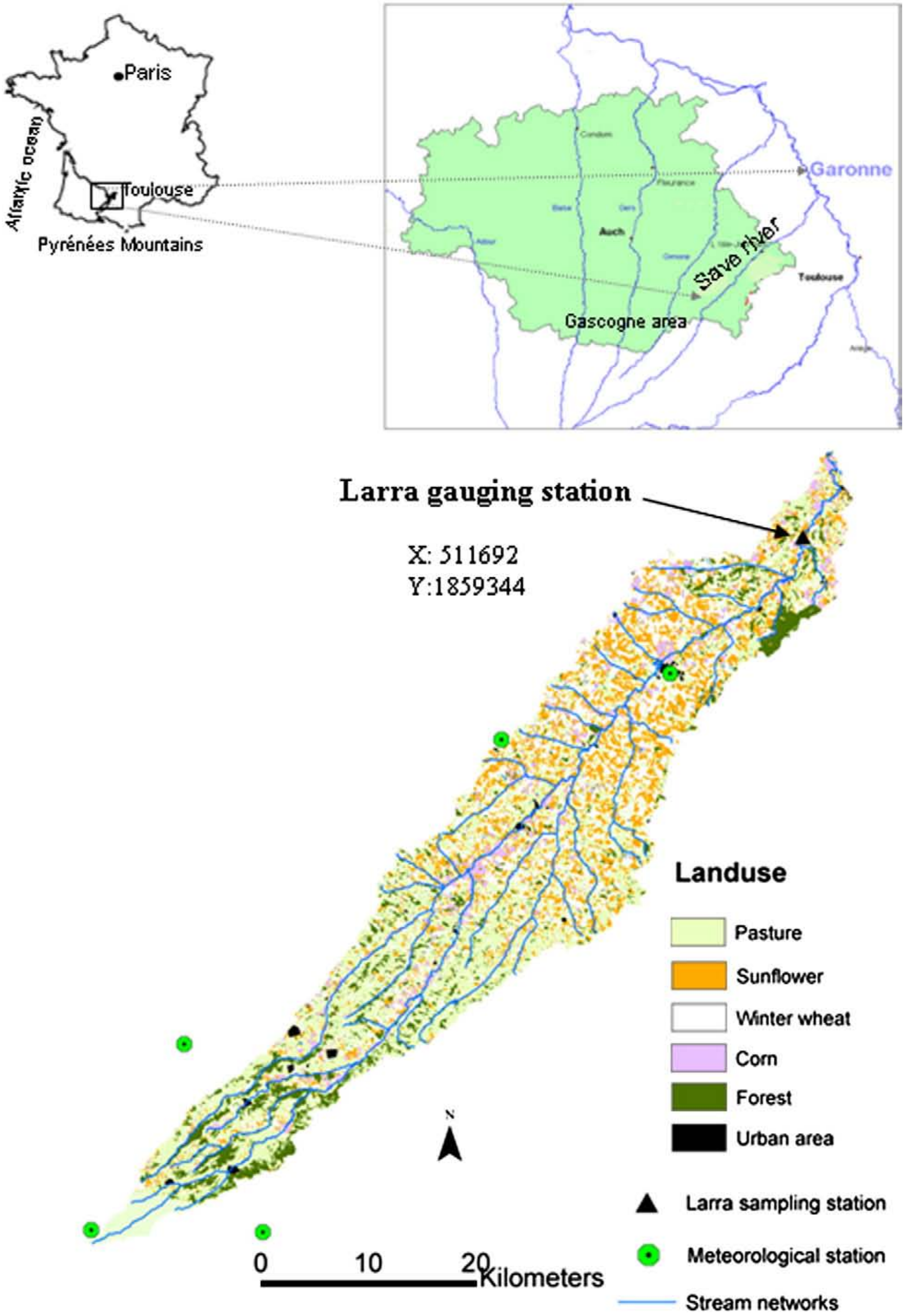

Fig. 1. Location, land use maps of the Save catchment.

2.4. Statistical analysis

Statistical analyses were performed using statistical techniques (Pearson correlation matrix) and Principal Component Analysis (PCA) in the STATISTICA package in order to determine the relationships between precipitation, discharge and nitrate variables (concentration and load). The results of these statistical analyses allowed factors influencing hydrological and nitrate responses during flood events to be identified. A database was generated for each flood event and contained two main groups of variables: antecedent variables to the flood conditions and flood variables (precipitation, discharge and nitrate concentrations during the flood). Variables used in the characterisation of floods are summarised in Table 1. Antecedent variables comprised accumulated precipitation one day before the flood (P1d, mm), five days before (P5d), and ten days before (P10d), beginning baseflow (Qb) before the flood starts and the antecedent flood corresponding to the current flood (Qa). Flood variables comprised the precipitation that caused the flood as characterised by total precipitation (Pt) and hourly maximum intensity of the precipitation (Imax). Total water yield (Wt) during the flood was expressed by the total water depth of the event, total duration of the event (Fd), and mean (Qm) and maximum discharge (Qmax) corresponding to the time of rise to reach the peak discharge (Tr). The discharge speed to reach the peak flow during flood events was defined by flood intensity If ($If = (Q_{max} - Q_b) / Tr$). Nitrate variables comprised mean discharge-weighted nitrate concentration (Nm), maximum flood nitrate concentration (Nmax) and nitrate transport (load) during flood events (Nt).

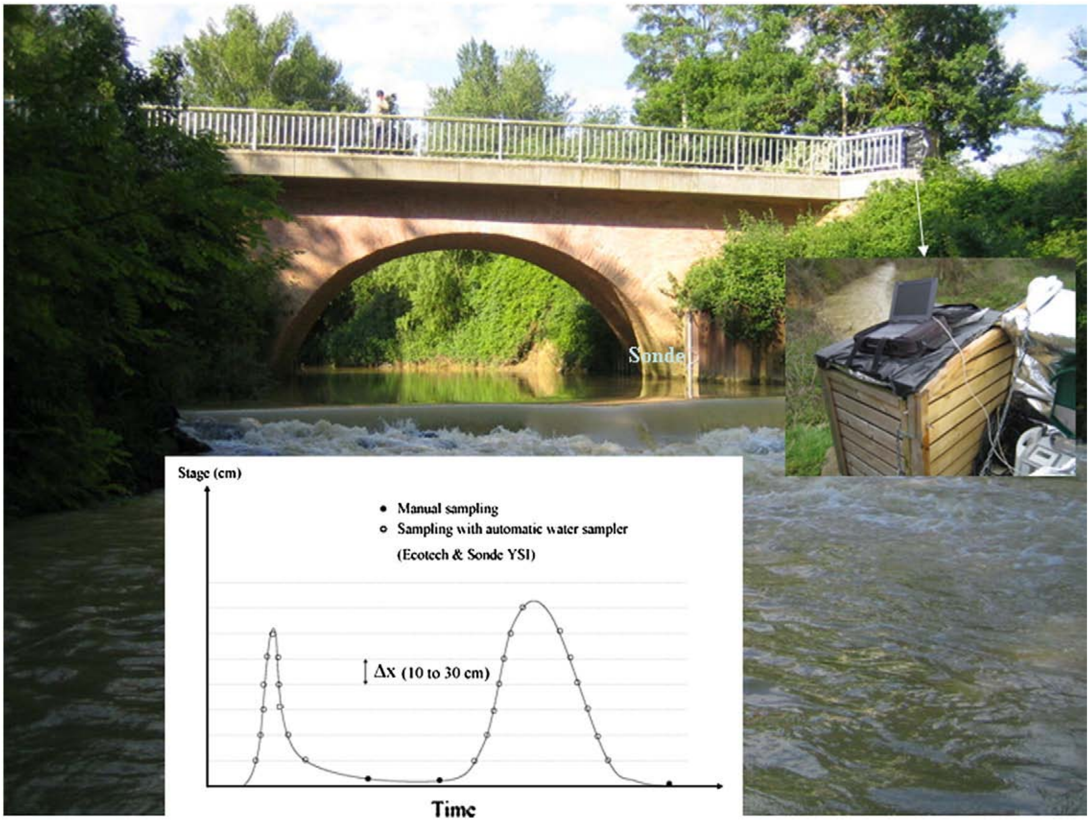

Fig. 2. Instrumentation and sampling method based on manual and automatic sampling using Ecotech and Sonde YSI.

2.5. Data sources and load calculation

Mean total precipitation and intensity in the entire catchment were derived using the Thiessen Polygon method on data obtained from five meteorological stations (Meteo France) in the catchment (Fig. 1). Data on hourly discharge at the Larra hydrometric station were obtained from CACG (Compagnie d'Aménagement des Coteaux de Gascogne), which is responsible for hydrological monitoring in the Gascogne region. Discharge was plotted by the rating curve in which water level was measured hourly by pressure at a rectangular weir (length 12 m) and then transferred by teletransmission. The nitrate load for each flood event was calculated using the method recommended by the Paris Commission for estimating river loads (Walling and Webb, 1985):

$$\text{Load} = V \times \frac{\sum_{i=1}^{n}(Ci \times Qi)}{\sum_{i=1}^{n} Qi}$$

where Ci is the instantaneous concentration for each sample point (mg l^{-1}), Qi is the hourly discharge at each sample point ($m^3\ s^{-1}$), V is the water volume over the flood period (m^3) and n is the number of samples. This is the preferred method for flux estimates given the available data (Littlewood, 1992) and is common in the literature for estimates of dissolved loads (e.g. Hope et al., 1997; Dawson et al., 2002; Worrall et al., 2003; Worrall and Burt, 2005).

Based on the high frequency of data collection (3 min to 24 h per sample during flood) and weekly sampling during stable flow, a linear interpolation method was applied between two neighbouring instantaneous sampling points to construct a continuously nitrate concentration series, then we are able to calculate continuous daily load through the product of concentration and water volume.

Table 1
Names, abbreviations and units for the variables used to characterise flood events and to perform Pearson correlation matrix and factorial analysis.

	Abbreviation	Unit
Antecedent event conditions		
Accumulated precipitation 1 day before the flood	P1d	mm
Accumulated precipitation 5 days before the flood	P5d	mm
Accumulated precipitation 10 days before the flood	P10d	mm
Baseflow before the flood	Qb	$m^3\ s^{-1}$
Antecedent maximum discharge	Qa	$m^3\ s^{-1}$
Flood event conditions		
Flood duration	Fd	h
Time of rise (time to reach maximum discharge)	Tr	h
Total precipitation during the flood	Pt	mm
Maximum rainfall intensity of the flood	Imax	mm h^{-1}
Flood intensity	If	$m^3\ min^{-2}$
Total water yield	Wt	hm^3
Mean discharge	Qm	$m^3\ s^{-1}$
Maximum discharge	Qmax	$m^3\ s^{-1}$
Mean nitrate concentration	Nm	mg l^{-1}
Maximum nitrate concentration	Nmax	mg l^{-1}
Nitrate transport during flood	Nt	t

3. Results

3.1. Hydro-meteorological context of observed flood events

The term ‘flood’ is used here to refer to a complete hydrological event with rising and recession limbs. During the observation period, 19 flood events were studied. There is not a particularly strong seasonal distribution in terms of event (5 in winter, 9 in spring and 5 in autumn) (Fig. 3). Table 2 summarises all flood characteristics for all flood events studied. Total annual rainfall during the study period from January 2007 to June 2009 amounted to 1755 mm (603 mm in 2007, 787 mm in 2008 and 365 mm in first 6 months of 2009). Major rainfall events generally occurred in autumn (October to December) and spring (March to June), with minor rainfall in summer (July to October). Total precipitation

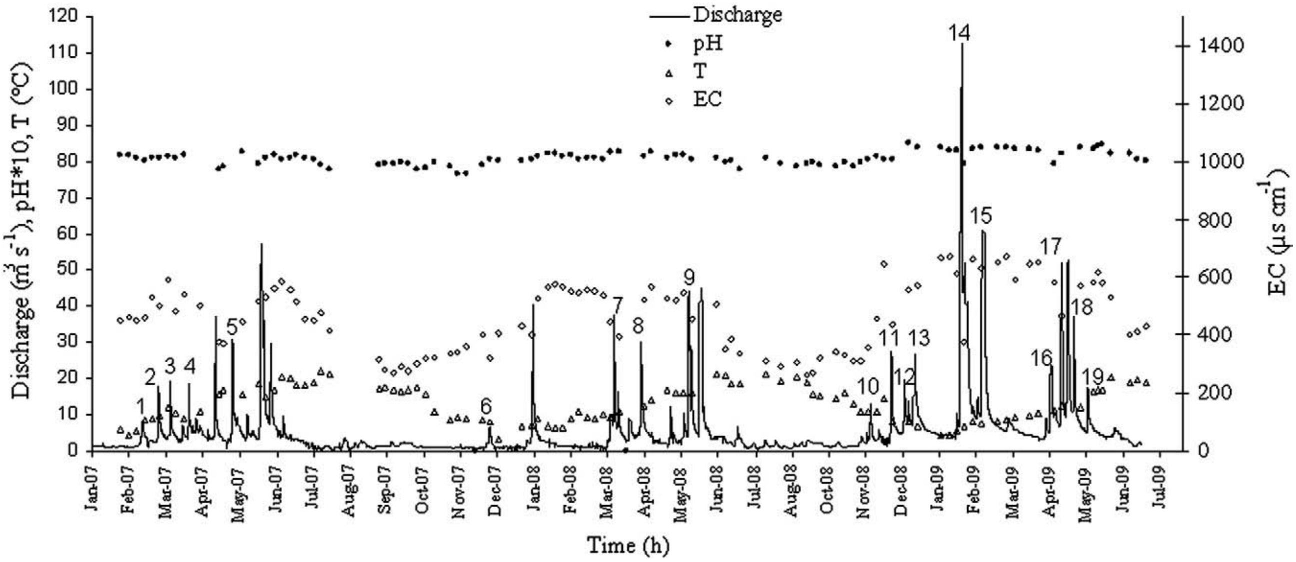

Fig. 3. Hourly discharge with 19 studied flood events and weekly measurement of pH, water temperature (T) electrical conductivity (EC) during study period.

during flood events varied from 1.1 mm to 74.5 mm (mean = 23.9 mm; st. dev. = 17.2 mm). The low total precipitation in event 18 (2 May 2009) was explained by high accumulated precipitation one day before the food event. The largest rainfall event was observed in winter 2009, with total precipitation of 74.5 mm on 27 Jan 2009. Maximum rainfall intensity in the whole catchment ranged from 0.7 to 17.2 mm h^{-1} (mean = 3.9 mm h^{-1}; st. dev. = 3.5 mm h^{-1}). The duration of flood events ranged from 95 h to 351 h, with a mean value of 172 h. Seven events were longer than average duration, while 12 events were shorter. Longer events with high magnitude mostly occurred in spring. However, the longest flood of 351 h occurred in winter, on 27 Jan 2009. This event was a 10-year return period flood. Maximum hourly discharge during observed flood events varied from 6.75 m^3 s^{-1} (on 11 Dec 2007) to 112.60 m^3 s^{-1} (on 27 Jan 2009) (mean = 31.79 m^3 s^{-1}; st. dev = 24.19 m^3 s^{-1}). The highest flood intensity (2.48 m^3 min^{-2}) was recorded on 1 June 2008 with the shortest time of 16 h to reach the peak, while the mean rising time to reach peak flood was 39 h (st. dev. = 18 h). The total water yield of the two full study years, 2007 and 2008, was 98 mm and 120 mm, respectively. These values are below the long-term mean value of 136 mm for the period 1985–2008. A year was considered dry when the annual water yield was below the long-term value. Within this context, both years can be classified as dry but the first year (2007) was very dry, since no major floods occurred in autumn.

3.2. Temporal variability of nitrate concentrations and loads

The temporal variability during all hydrological conditions (January 2007–June 2009) is shown in Fig. 4. Generally, nitrate concentrations were at a minimum (5–10 mg l^{-1}) from summer to early autumn and at a maximum (15–42 mg l^{-1}) from late winter to spring (all hydrological conditions: discharge-weighted mean concentration = 22.1 mg l^{-1}; st. dev. = 7.7 mg l^{-1}). During flood periods, the maximum nitrate concentration ranged from 8.2 mg l^{-1} on 11 Dec 2007 to 41.1 mg l^{-1} on 2 May 2007 (Table 2) (mean = 29.5 mg l^{-1}; st. dev. = 7.6 mg l^{-1}). It is observed that the increase of nitrate concentration in the river following a small flood event on 11 Dec 2007 reached the similar level of nitrate concentrations during the autumn floods (November to December

Table 2
General characteristics of all flood events observed in the Save catchment during the study period (January 2007 to June 2009).

No.	Event date	Season	Number of samples	Fd (h)	Tr (h)	If (m^{3}min^{-2})	Pt (mm)	Imax (mm h^{-1})	Qb (m^3 s^{-1})	Qm (m^3 s^{-1})	Qmax (m^3 s^{-1})	Wt (Hm^3)	Nm (mg l^{-1})	Nmax (mg l^{-1})	Nt (t)
1	13/02/07	Winter	7	132	55	0.11	15.6	4.8	***1.89***	4.20	7.97	2.13	15.9	17.7	34
2	27/02/07	Winter	8	140	30	0.47	9.6	1.4	3.61	6.67	17.62	3.82	30.2	41.0	115
3	09/03/07	Winter	8	164	41	0.37	7.5	1.3	3.83	6.05	19.11	4.12	28.2	34.2	116
4	25/03/07	Spring	8	139	21	0.72	12.6	2.6	3.83	7.74	18.94	3.68	***6.6***	29.0	24
5	02/05/07	Spring	7	200	21	1.27	20.2	2.5	3.61	10.30	30.36	5.79	**35.3**	**41.1**	204
6	11/12/07	Autumn	5	128	46	***0.08***	9.2	2.8	3.16	***3.46***	***6.75***	***1.71***	7.1	***8.2***	***12***
7	28/03/08	Spring	11	228	**84**	0.42	39.3	2.8	2.56	10.39	37.60	8.56	23.7	29.0	203
8	21/04/08	Spring	6	189	22	1.19	19.4	4.0	4.06	9.60	30.20	7.10	24.2	30.4	172
9	01/06/08	Spring	11	228	***16***	**2.48**	50.0	**17.2**	4.28	15.70	44.02	12.75	24.1	40.0	307
10	08/11/08	Autumn	***4***	105	46	0.22	23.8	4.6	2.96	6.18	12.97	2.40	16.4	24.8	39
11	26/11/08	Autumn	8	191	43	0.53	35.9	4.4	4.90	9.08	27.57	3.42	23.2	28.2	79
12	06/12/08	Autumn	5	126	54	0.28	27.7	5.3	4.90	10.12	19.77	3.21	25.2	27.7	81
13	14/12/08	Autumn	5	256	27	0.73	13.3	1.6	6.95	11.63	26.74	6.01	26.2	28.0	157
14	27/01/09	Winter	21	**351**	69	1.57	**74.5**	4.1	4.06	**34.50**	**112.60**	**43.71**	20.8	30.7	**909**
15	11/02/09	Winter	**26**	233	54	0.94	32.9	4.2	9.99	25.94	60.66	19.71	21.4	27.9	422
16	14/04/09	Spring	10	141	29	0.64	29.5	4.5	5.10	14.08	23.80	7.15	28.5	32.2	204
17	22/04/09	Spring	15	112	36	1.26	19.3	4.2	6.75	24.31	52.24	9.80	25.9	30.5	254
18	02/05/09	Spring	18	116	22	1.20	***1.1***	***0.7***	**11.00**	15.90	37.47	7.18	23.7	31.0	170
19	15/05/09	Spring	7	***95***	26	0.48	13.0	1.9	5.10	9.68	17.62	3.31	26.5	28.7	88

Maximum values in bold type, minimum values in bold italics.

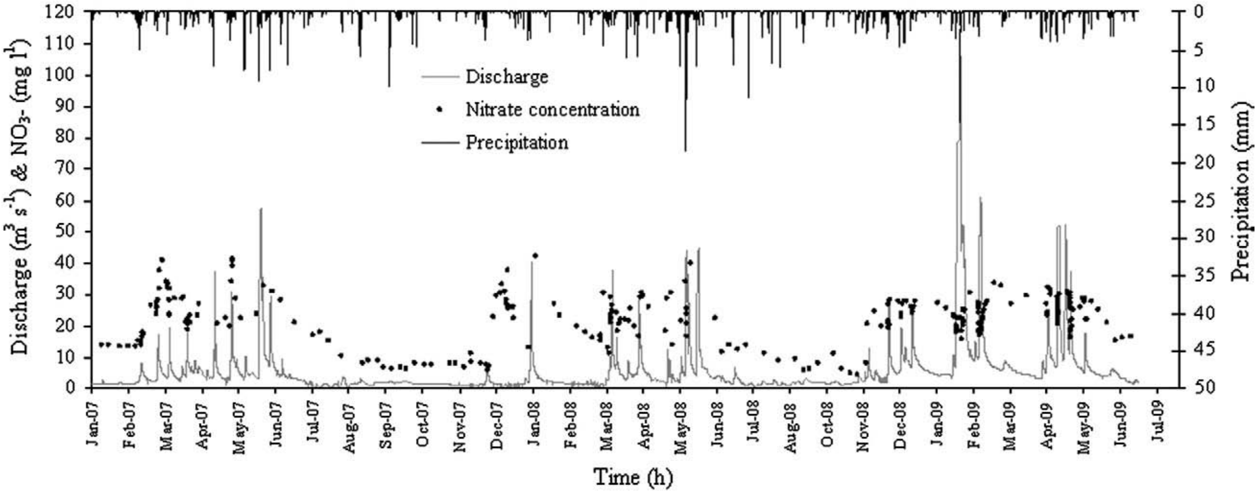

Fig. 4. Temporal variability of nitrate concentrations recorded between January 2007 and June 2009 at Larra station.

2008) (Fig. 4). In both cases, the nitrate level is comparatively high to that during winter and spring floods.

The results from the study period demonstrate the temporal transport of nitrate load during different seasonal flood events. Less nitrate load was transported in autumn than in winter and spring due to lower flood magnitude and the absence of crop fertilisation. The nitrate load transported during observed floods varied from 12 t to 909 t (mean = 189 t; st. dev. = 203 t). The highest nitrate load (909 t) was transported during the flood with the highest magnitude and longest duration on 27 Jan 2009, while the lowest transport (12 t) was observed during the flood with the lowest magnitude on 11 Dec 2007. The variation in loads occurred from late winter to late spring due to high flood magnitude combined with long flood duration and high nitrate availability after crop fertilisation (Fig. 5). Annual nitrate transport of 2007 and 2008 accounted for 2514 t (2.2 t km^{-12}) and 3047 t (2.74 t km^{-12}), with an average value of 2.5 t km^{-12} y^{-1}. Annual nitrate transport during floods was 1600 t (64% of annual load; 16% of annual duration) in 2007 and 1872 t (62% of annual load; 20% of annual duration) in 2008.

3.3. Relationships between nitrate and hydro-climatological variables

Relationships between antecedent and flood event variables were assessed to find the controlling factors influencing hydrological and nitrate response during flood events in the Save catchment. A Pearson correlation matrix and factorial analysis that included all the above-

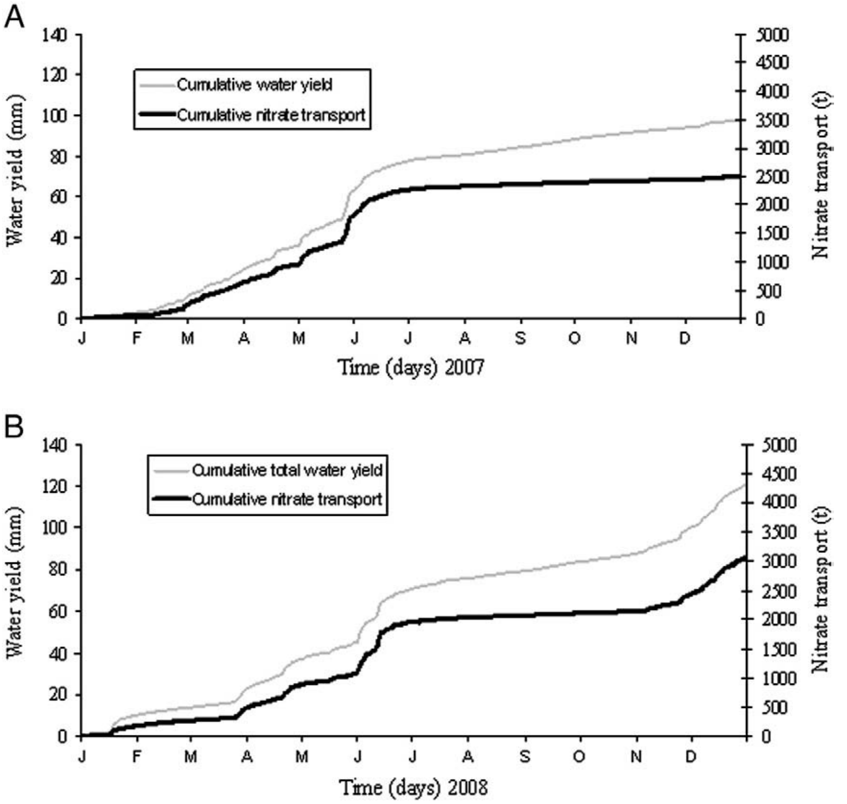

Fig. 5. Cumulative water yield (in millimetres) and nitrate transport (t) during (A) 2007 and (B) 2008.

mentioned variables (Table 1) were generated for the 19 flood events. Table 3 shows the relationships between precipitation, discharge and nitrate variables in the Save catchment. Total precipitation (Pt) showed a good correlation with mean discharge (Qm) (R = 0.64), maximum discharge (Qmax) (R = 0.76), and total water yield (Wt) (R = 0.79). Flood duration (Fd) was well correlated with Qmax, Wt and Pt. Mean and maximum nitrate concentrations had weak relationship with Pt (R = 0.04 and R = 0.18, respectively). Nmax was fairly correlated with flood intensity (If) (R = 0.58), but lowly correlated with flood duration (Fd) and discharge variables (Qb, Qm and Qmax). Nitrate transport (Nt) showed a strong relationship with Pt (R = 0.78) and Fd (R = 0.79) and very strongly significant correlations with peak discharge and total water yield during flood events (R = 0.97 and R = 0.99, respectively). However, weaker relationships were found between nitrate variables and antecedent conditions of the catchment (baseflow, antecedent flood discharge and antecedent precipitation P1d, P5d and P10d).

In the Principal Component Analysis (PCA) taking samples and variables into account, two factors explained 60% of the total variance. Factor 1, which explained 38% of the total variance, was characterised by a high negative Eigen-value (>0.80) for total rainfall (Pt), mean and maximum discharge (Qm; Qmax), flood duration (Fd), total water yield (Wt) and nitrate transport (Nt), which suggests a response of nitrate load transport through hydrological responses during flood events. Four factors were retained for rotational analysis. A summary of varimax rotated factor of all variables is given in Table 4. The first four axes absorbed 82% of the total variance.

Table 4
Summary of varimax rotated factor for all variables presented in Table 1 (Eigen-values <0.50 were excluded).

Variables	Factor 1	Factor 2	Factor 3	Factor 4
Fd	**−0.81**	–	–	–
Tr	–	0.74	–	–
If	−0.73	−0.59	–	–
Pt	**−0.82**	–	–	–
Imax	–	−0.55	–	–
P1d	–	−0.78	–	–
P5d	–	−0.82	–	–
P10d	–	−0.70	–	–
Qa	–	–	0.52	–
Qb	–	–	0.81	–
Qm	**−0.91**	–	–	–
Qmax	**−0.96**	–	–	–
Wt	**−0.94**	–	–	–
Nm	–	–	–	−0.59
Nmax	–	–	–	−0.55
Nt	**−0.97**	–	–	–
Variance explained (%)	38	22	12	10
Cumulative variance (%)	38	60	72	82

Significant variables with Eigen–values > 0.80.

3.4. Nitrate concentrations and discharge relationships

There is a scattered distribution of nitrate concentration versus discharge during flood response. The relationship between nitrate concentration and discharge within the 19 flood events observed revealed the existence of hysteresis effects with dominant anticlockwise behaviour in the Save catchment. However, clockwise patterns were produced when the nitrate concentration was high at the rising limb of the flood hydrograph, compared with the falling limb. Fig. 6 shows hysteresis patterns for selected seasonal flood events (winter, spring and autumn). The width and the slope of the patterns differed substantially. The autumn and winter loops (Fig. 6A and C) were flat and the increase in nitrate concentration over the initial (pre-event) nitrate concentration was very small, giving very slight variation in nitrate with changeable discharge; whereas, the spring loops (Fig. 6B) were wider due to significant variability in nitrate concentrations. The hysteresis patterns in the nitrate concentration and the discharge relationship during the hydrological response provided an indication of the nitrate sources and nitrate delivery process occurring within the catchment during flood events.

4. Discussion

4.1. Temporal variability of nitrate transport during hydrological response

Nitrate concentrations in streamwater of agricultural catchments often exhibit interannual variations, which are supposed to result from land use changes, as well as seasonal variations mainly explained by the effect of hydrological and biogeochemical cycles (Martin et al., 2004). Analysis of nitrate concentrations collected during all hydrological conditions in the Save catchment provided an insight into the characteristics of nitrate transport variability in this large agricultural catchment during flood events. Hydrological response caused an increased variability of nitrate and raised stream nitrate concentrations (Fig. 4). Maximum nitrate concentrations generally increased during flood events and crop fertilisation periods (Fig. 4). However, the increase of nitrate concentration following the small flood event on 11 Dec 2007 and that during the autumn floods (Fig. 4) are similarly high to that during winter and spring floods. The high concentration could be linked with extreme meteorological conditions which occurred from summer to early autumn with lack of precipitation and low flow conditions (Rusjan et al., 2008).

Table 3
Pearson correlation matrix of all variables (n = 19).

	Fd	Tr	If	Pt	Imax	P1d	P5d	P10d	Qa	Qb	Qm	Qmax	Wt	Nm	Nmax	Nt
Fd	1.00															
Tr	0.33	1.00														
If	***0.49***	−0.37	1.00													
Pt	**0.74**	***0.47***	***0.48***	1.00												
Imax	0.21	−0.13	**0.61**	***0.53***	1.00											
P1d	0.16	***−0.51***	0.45	0.04	0.31	1.00										
P5d	0.07	−0.37	0.40	0.12	0.50	**0.76**	1.00									
P10d	−0.18	−0.42	0.39	−0.04	***0.48***	0.34	**0.62**	1.00								
Qa	0.13	0.07	0.20	0.17	0.03	−0.18	0.06	0.02	1.00							
Qb	0.02	−0.24	0.29	−0.15	−0.15	−0.28	−0.11	0.05	**0.61**	1.00						
Qm	**0.58**	0.21	**0.62**	**0.64**	0.17	−0.14	−0.11	−0.03	***0.46***	***0.50***	1.00					
Qmax	**0.75**	0.32	**0.63**	**0.76**	0.17	−0.07	−0.12	−0.13	0.32	0.31	**0.95**	1.00				
Wt	**0.78**	0.37	0.55	**0.79**	0.18	−0.01	−0.09	−0.19	0.29	0.19	**0.89**	**0.97**	1.00			
Nm	0.14	−0.20	0.27	0.04	−0.04	0.18	0.13	0.01	0.16	0.19	0.17	0.14	0.04	1.00		
Nmax	0.24	−0.40	**0.58**	0.18	0.19	0.30	0.19	0.06	0.13	0.13	0.25	0.27	0.18	**0.75**	1.00	
Nt	**0.79**	0.32	**0.60**	**0.78**	0.19	0.05	−0.04	−0.15	0.31	0.21	**0.90**	**0.97**	**0.99**	0.18	0.27	1.00

Correlations significant at $P<0.01$ marked in bold and at $P<0.05$ marked in italics.

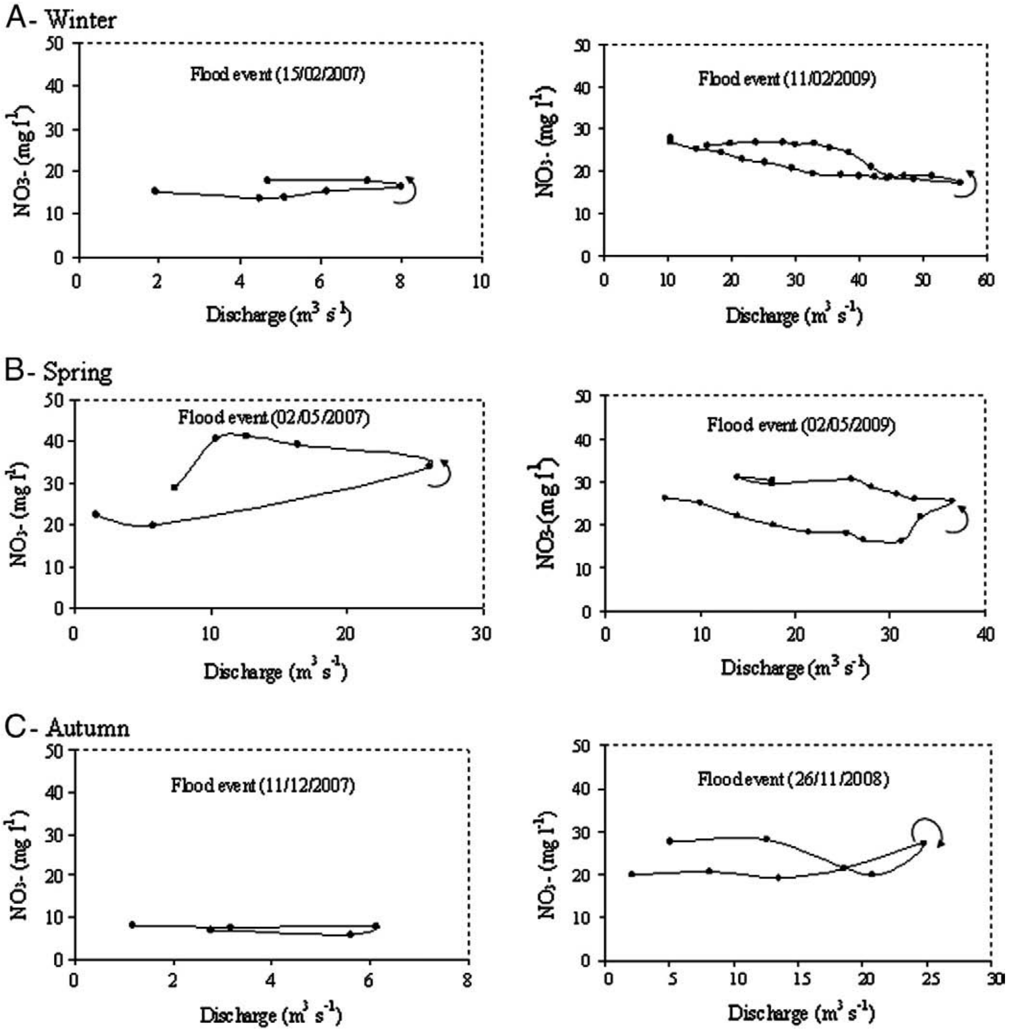

Fig. 6. Examples of different types of hysteresis patterns observed in the Save catchment during the study period.

Hydrologically, nitrate could not be mobilized from the soil horizons until the occurrence of floods in autumn (November to December). When the early seasonal rainfall starts, the saturation zone rises towards upper soil layers enriched by the accumulated nitrate pool during the previous seasons, more nitrate is flushed into the river (Sánchez–Pérez et al., 2003a).

The responses of different flood discharge magnitudes showed little variability in concentrations, indicating that the level of discharge increase did not control the increase in nitrate concentration (similar nitrate peaks were caused by different peak discharges). This can be observed in flood on 02 May 2007 ($Q\max = 30.36\ m^3\ s^{-1}$; $N\max = 41.1\ mg\ l^{-1}$), on 01 June 2008 ($Q\max = 44.02\ m^3\ s^{-1}$; $N\max = 40\ mg\ l^{-1}$), on 27 Jan 2009 ($Q\max = 112.60\ m^3\ s^{-1}$; $N\max = 30.7\ mg\ l^{-1}$) and on 14 April 2009 ($Q\max = 23.80\ m^3\ s^{-1}$; $N\max = 32.2\ mg\ l^{-1}$). A weak statistical relationship was found between peak discharge and peak nitrate concentration ($R = 0.27$), due to the peak nitrate concentration mainly occurring after the peak discharge. During the study period, the Neste canal at the upstream area has very slight nitrate contribution to the main river since the canal water originates from the Piedmont of Pyrenean Mountain with nitrate concentration of approximately $1\ mg\ l^{-1}$only. Rusjan et al. (2008) showed in a study on a $42.1\ km^2$ catchment that the nitrate concentration peaks during all hydrological flood events were reached with a certain delay after the occurrence of discharge peaks. However, the strong relationship observed between peak discharge and peak nitrate in that study indicates there is probably a mechanism controlling the temporal transport of nitrate on catchment level beyond the interactive behaviour of hydrological and biogeochemical settings. In particular, groundwater fluctuation in the riparian zone near the catchment outlet and in a relatively shallower zone may be critical factors contributing to streamwater nitrate (Ohte et al., 2003). Various studies have reported that nutrients are flushed out of the landscape during hydrologically active periods particularly during flood events, while they are retained in drier periods (Creed et al., 1996; Sickman et al., 2003; Burns, 2005; Rozemeijer and Broers, 2007). However, some authors emphasize the hydrological connectivity (Pringle, 2003), which refers to the spatially and temporally variable hydrological pathways along which matter is transferred from the land surface to the catchment outlet (Haag and Kaupenjohann, 2001; Mitchell, 2001; Weng et al., 2003; Inamdar et al., 2004). Several field studies (Band et al., 2001; McHale et al., 2002; Inamdar et al., 2004) have addressed the flushing of nitrate during flood events but the actual mechanisms responsible for the rapid nitrate export during flood events remain relatively uncertain (Weiler and McDonnell, 2006).

The different sources of nitrate and rainfall distribution in the Save catchment could be key factors determining the nitrate variability in stream water during hydrological flood events. Variable source areas that expand and contract laterally during the hydrological events can be ascribed to the topographical framework, as proposed by Creed and Band (1998) and tested on hillslope scale by Weiler and McDonnell (2006). Nutrient concentrations are often found to decrease markedly with depth in the soil profile (Bishop et al., 2004). The rising limb of the flood is accompanied by lateral expansion of variable source areas (which can also be described as areas of saturated soil profile), intensifying the transport of nitrate from soil horizons.

Although the nitrate concentrations did not vary greatly from one flood event to another in the present study, the nitrate transport during these flood events varied significantly, from 12 t to 909 t. The maximum quantity of nitrate transport occurred on 27 Jan 2009, when the flood was the largest of all 19 floods observed. Statistical analysis revealed a strong correlation between nitrate transport (Nt) and total precipitation, flood duration discharge, peak discharge and total water yield. These variables could be the main factors controlling nitrate export in water from the Save catchment. The quantity of nitrate transported during the two full hydrological years studied was slightly different (2514 t in 2007 and 3047 t in 2008). As can be seen from Fig. 5, the trend of cumulative nitrate load transport was similar in both years until late spring but differed in late autumn due to increasing flood events in autumn 2008, while autumn 2007 had only one small flood contributing little nitrate load. In contrast, Oeurng et al. (2010) found that suspended sediment transport within the Save catchment during the same hydrological periods was significantly different between 2007 and 2008 (16 614 t in 2007 and 77 960 t in 2008). Additionally, nitrate loads during flood events represented approximately 60% of the annual load in both hydrological years, whereas sediment load transport represented about 90%. There is therefore a significant difference in the transport behaviour of nitrate and suspended sediment within the same catchment. Nitrate variations could be attributed to the effect of both hydrological and biogeochemical cycles (Martin et al., 2004) but suspended sediment transport is physically dependent of land use practices, hydrological driving force as well as physiographic factors.

The average rate of nitrate exportation during the two-year study ($2.5\,\mathrm{t\,km^{-12}\,y^{-1}}$) was within the range reported previously for the Garonne river ($1–5\,\mathrm{t\,km^{-12}\,y^{-1}}$) (Probst, 1985). In the downstream area of the Save catchment, where sunflower, winter wheat and corn are grown, the specific yield of nitrate locally can exceed the specific yield of the whole catchment. It can be therefore assumed that nitrate export from the upstream part of the Save catchment, which is mainly dominated by pasture receiving limited amounts of fertilisers and by small forests receiving no fertilisers, is smaller than the nitrate contribution at the downstream where intensive agriculture is mainly adopted. The N fertiliser doses commonly applied to agricultural pastures in the Save catchment ($20–100\,\mathrm{kg\,N\,ha^{-1}}$) are low compared with some areas of the world that have application rates of more than $500\,\mathrm{kg\,N\,ha^{-1}\,y^{-1}}$(Chapin et al., 2002). In this case, to have a better understanding of the nitrate source contribution between the downstream and upstream area, another sampling station could be considered in the section which separates these different land use areas. The specific nitrate yield of the Save catchment ($2.5\,\mathrm{t\,km^{-12}\,y^{-1}}$) was much higher than that of a $13\,000\,\mathrm{km^2}$ agriculture-dominated catchment in south-east Spain ($0.88\,\mathrm{t\,km^{-12}\,y^{-1}}$) (Lorite-Herrera et al., 2009). This was due to the lower total rainfall in the latter (mean annual value 418 mm) contributing less streamflow than in the Save catchment.

4.2. Nitrate concentrations and discharge relationships

A clockwise pattern indicates that nitrate is rapidly transported to the catchment outlet during flood events, implying that the nitrate load comes from either within the river channel itself or from catchment sources that are rapidly transported to the catchment outlet (Bowes et al., 2009). It could also indicate a depletion of nitrate supply possibly resulting from a consequence of dilution effect during flood event. However, anticlockwise patterns were mainly found in most seasons within the Save catchment. It can be concluded, as suggested by Butturini et al. (2006), that the runoff component is not the prevailing contributor to nitrate load and that intensive solution flushing proceeds during the recession discharge limbs. The anticlockwise patterns may be associated with limited mobilisation of nitrate in the antecedent dry periods (summer) and therefore low concentrations of nitrate in the stream and accumulation of nitrate during summer periods were hydrologically disconnected in upper soil horizons. The loops (Fig. 6B) became steeper and wider during floods in spring due to the high variability of nitrate concentrations. The high concentrations during the spring season can be associated with nutrient availability through fertiliser application from January to April in downstream catchment areas where arable crops are grown (Fig. 1). They can also be attributed to the flood magnitude in the spring season reaching the capacity to mobilise nitrate from deeper soil horizons containing high $\mathrm{NO_3^-}$ concentrations in the soil solution as a result of crop fertilisation and nitrate leaching in soil with percolating rainfall (Sánchez–Pérez et al., 2003b). The predominantly anticlockwise hysteresis in the Save catchment could be explained by increasing nitrate concentrations at the recession flood from distant source areas within the catchment and nitrate delivery being slowly mobilised from deep soil horizons to the sampling station. This could occur when the rainfall event takes place in upstream areas since the travel time of water (and its nitrate load) is slow within this long thin catchment. Moreover, the discharge of shallow groundwater could influence nitrate dynamics since various studies (Ohte et al., 2003; Martin et al., 2004; Lapworth et al., 2008) have demonstrated the role of shallow groundwater influencing the stream nitrate variability. Therefore, it could be also the case in the Save catchment where shallow groundwater contributed more nitrate to the streamwater during the recession period of flood events after the rise of the saturation zone towards upper soil layers enriched by the accumulated nitrate pool.

However, identification of the nitrate sources in the Save catchment with spatial variability in land use from the nitrate delivery process using hysteresis patterns is rather unclear, since it is difficult to interpret nitrate sources when the hysteresis shape is mostly flat with slight variations in nitrate concentration during autumn and winter. The hysteresis study just only provides some basic understanding of probable nitrate sources referring to the sampling location. Moreover, water sampling was only carried out at the outlet of this long thin catchment and to better understand the nitrate transport process, the dynamics in the river at the mid-point of the catchment should be considered.

5. Conclusions

This study of temporal nitrate transport through hydrological response during floods in a large agricultural catchment showed significant nitrate transport (12–909 t) during flood events, even though the nitrate concentration did not vary significantly with changes in peak discharge. Nitrate transport during flood events amounted to 1600 t (64% of annual load; 16% of annual duration) in 2007 and 1872 t (62% of annual load; 20% of annual duration) in 2008. Annual nitrate transport amounted to 2514 t ($2.26\,\mathrm{t\,km^{-12}}$) in 2007 and 3047 t ($2.74\,\mathrm{t\,km^{-12}}$) in 2008, with average specific yield of $2.5\,\mathrm{t\,km^{-12}\,y^{-1}}$. Statistical analysis revealed strong correlations between nitrate transport and total precipitation, flood duration, peak discharge and total water yield, indicating that these four variables may be the main factors controlling nitrate exports from the Save catchment. Therefore, hydrological response during flood events proved to be important for nitrate load delivery from the catchment.

The relationship between nitrate and discharge (hysteresis patterns) investigated through flood events in this study was mainly dominated by anticlockwise behaviour, with wide and steep patterns in spring due to increasing nitrate concentration variability over the falling limb of the flood hydrograph. The hysteresis pattern during autumn and winter was flat because of low variation in nitrate concentrations. The dominance of anticlockwise hysteresis was attributed to distant source areas within the catchment and the process of slow mobilisation of nitrate from deeper soil horizons. The interpretation of nitrate sources based on discharge and nitrate concentration relationship is still uncertain because of the difficulty in interpreting nitrate sources when the hysteresis shape is mostly flat during autumn and winter.

With only 2.5 years of data collection, it is difficult to characterise long-term interannual variability of nitrate transport in a large agricultural catchment like the Save since it is difficult to obtain long-term datasets from field work. Additionally, the accurate sources of nitrate cannot be clearly determined without taking into account the spatial variability of the land use and additional spatially explicit sampling locations in such a large catchment with strong variability. However, the data collection with high frequency at the catchment outlet during this study will be necessarily served for future modelling work in order to characterise long-term nitrate variability and to identify the spatial contribution of nitrate sources within this catchment.

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