Seasonal variability of NO_3^- mobilization during flood events in a Mediterranean catchment: The influence of intensive agricultural irrigation

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Abstract

The temporal variability, hysteresis loops and various factors involved in the mobilization of nitrates (NO_3^-) have been studied for a 3-year period at the Flumen River basin. Multivariate techniques (Cluster Analysis and Pearson Correlation Matrix) were used to establish the relationship between the water discharge and NO_3^- flushing, as well as identify the agricultural and hydrometeorological parameters that influence its different mobilization trends. The relationship between changes in the NO_3^- concentration (ΔC) and the overall dynamic of each hysteresis loop (ΔR) was also analyzed in order to describe the NO_3^- trends according to the water discharge. A general dilution pattern of the NO_3^- concentration was noted in the Flumen River with respect to the degree of water discharge caused by irrigation return flows. While fertilization increased the NO_3^- concentration, the beginning of the irrigation season contributed to its dilution. However, in case of the NO_3^- load, the maximum values occurred during high flow periods in the irrigation period, which suggested the influence of the irrigation flow on the NO_3^- mass. The NO_3^- load increased to 2753 t and 1059 t during the first and second phases of the study period, respectively, with an average specific yield of 1.33 t km^{-2} y^{-1}. The NO_3^- transport in the first phase of the study was 1722 t during the irrigation season and 1031 t during the non-irrigation period. Only 348 t (13%) of NO_3^- was exported during the flood events. However, in the course of the second phase of the study, the NO_3^- load was 733 t during the irrigation season and 326 t during the non-irrigation period. In this case, 610 t (57%) of nitrate was transported during the floods. These results revealed the clear influence of irrigation return flows on the NO_3^- response in Flumen River.

1. Introduction

Concentrations of nitrogen (N) are elevated in rivers across large areas of Europe (Sutton et al., 2011). The European Water Framework Directive (WFD, EC, 2000) gives priority to watersheds and water bodies as reference units to achieve a “good ecological status” in 2015. For this, knowledge of the transfer of pollutants in catchment areas is essential when taking measures to mitigate the degradation of water quality. The dynamics of N loss from catchments has been studied in different environments, at different spatial scales and at different sampling frequencies (Ferrant et al., 2013). A substantial portion of excess N is exported from terrestrial ecosystems to aquatic ecosystems (Seitzinger and Harrison, 2008). The potential for NO_3^- leaching is a function of the soil type, weather conditions and the crop management system (Martin-Queller et al., 2010) but under similar conditions, the export of N increases with the percentage of the agricultural area in the watershed (Kaushal et al., 2008). In irrigated agriculture, irrigation return flows (IRF) are important factors that influence the NO_3^- concentration in the surface water (Causapé et al., 2006). IRF are mixtures of surface drainage water composed of overflow or bypass water, surface runoff or tail water, and collected subsurface drainage water (Skogerboe and Walker, 1981). IRF also have the potential for disrupting the natural hydrologic water balance of river basins (Haddeland et al., 2006). However, weather conditions also influence the NO_3^- mobilization.

Hydrologically active periods, particularly flood events, are important because the addition of new water sources during such events mobilizes distinctly new and different sources of nutrients from the catchment (Buda and DeWalle, 2009). Several studies have showed that the relationship between pollutant concentration (c) and water discharge (q) during storm events follows cyclic trajectories (Hill, 1993). This feature has been commonly studied using an approach called hysteresis analysis of river flows and pollutants, in which the physical processes of suspended and dissolved material transport are qualitatively identified in terms of the direction of a hysteresis loop (de Boer and Campbell, 1989). In a pollutant concentration vs. water discharge plot (c-q relation), hysteresis analysis may be used as a technique for determining the source of chemicals measured in streams and changes in the forms of nutrients through storm events (Stutter et al., 2008). Some studies focused on sediment transport reported that for most streams, clockwise hysteresis patterns are produced when higher concentrations occur on the rising limb of the hydrograph and lower concentrations occur on the recessional limb (Glysson, 1987). Otherwise, counter clockwise hysteresis loops have been explained by a delayed source from tributaries or due to a bank collapse on the recessional limb of the hydrograph (Rinaldi et al., 2004). With respect to nutrients, these patterns can be produced by either a dominant nutrient supply that is mobilized slowly during a storm event or could indicate a rapid input of the nutrient from a source with a concentration of the nutrient that is lower than that in the river (Bowes et al., 2009). In the case of NO_3^-, besides the weather factor, it is necessary to take into account the flow dynamics related to the land use within a watershed. Jiang et al. (2012) reported a significant positive correlation between the agricultural area and the peak of NO_3^--N concentrations during rainfall events. However, because of the multiplicity of factors affecting the NO_3^- mobilization in agricultural catchments, a sampling design that includes both high frequency sample collection and monitoring of the sporadic flood events is required.

A study of these characteristics was needed in the Flumen River basin to acquire a comprehensive understanding of the NO_3^- transport and the factors involved in this process. A monitoring program for water quality was carried out in Flumen River Basin for a 3-year period, with the aim to get a high data rate that would include the spatiotemporal, weather and agricultural factors affecting NO_3^- transfer. The objectives of this study were: (i) to study the variability of NO_3^- patterns in relation to water flow dynamics and hydro-meteorological variables; (ii) to determine the factors affecting NO_3^- transport during flood events; and (iii) characterize the types of events in the Flumen watershed according to the different agricultural seasons and the IRF.

2. Methods

2.1. Study area

The Flumen River is located in the province of Huesca (Aragón, Spain) in the north-central part of the Ebro River basin (80,093 km^2, NE Spain) (Fig. 1). The river originates at 1,250 m.a.s.l. in Sierra Guara, which is a calcareous pre-Pyrenean mountain chain. This river is 120 km long, and together with its tributary, the Isuela River, drains a watershed area of 1,430 km^2. After exiting the mountainous part of the basin, the Flumen River flows through flat plains that have intensive agricultural uses to its confluence with the Alcanadre River at 240 m.a.s.l.

In its final route, the river crosses quaternary glacis and alluvial fans that overlay a tertiary structure composed of conglomerates, sandstones and clays (Quirantes, 1978). Saline mudstones and gypsum deposits observed in the lower part of the basin influence the water quality of the river at its lower reaches (Martín-Queller et al., 2010). The Isuela River, which runs parallel to the upper north part of the Flumen River, is its only perennial tributary and joins the Flumen River in the flat area of the basin. Other seasonal streams discharge water only during the agricultural irrigation period (April-October).

A Mediterranean climate with irregular seasonal and interannual rainfall is a common feature of the entire basin (Comín and Williams, 1994), although a decreasing rainfall gradient of 77.6 mm for every 100 m of altitude change exists from the north mountain region to the flat southern region of the basin. The average annual rainfall in the basin is 581 mm (Pedrocchi, 1998).

In the Flumen River basin, the percentage of the agricultural zone reaches 71% of the total area. In this agricultural area, 70% are irrigated crops. In the lower region of the watershed, the principal land use is irrigated agriculture, in which rice (*Oryza sativa*), corn (*Zea mays)* and alfalfa (*Medicago sativa*) are the most representative crops (Fig. 1). Cereals such as wheat (*Triticum spp.)* and barley (*Hordeum vulgare)* are also cultivated as rainfed crops in the external areas of the watershed (Common Agricultural Policy, 2009-2011). Information on agricultural activities performed in the study area was obtained through farmers and agricultural cooperatives and is shown in Table ST1. Irrigation season takes place from April to October, but the summer months are those with the greatest irrigation activity. In the lower half of the basin, the so-called Northern Monegros County, there is a complex system of small irrigation canals that distribute the water transported by a large irrigation canal, the Monegros canal. The hydrological regime of the river is, especially in its last section, highly altered by the IRF. Thus, the water discharge is higher during irrigation season due to the contribution of the irrigation runoff. The maximum water flow recorded in the Flumen River during 2003-2012 was 146.5 $m^3 \cdot s^{-1}$ (22 October 2012), and the mean annual discharge (2003-2012) was 5.2 $m^3 \cdot s^{-1}$ (SAIHEbro, 2013).

2.2. Instrumentation, sampling strategy and water sample analysis

The sampling strategy was developed in two phases. The first phase was carried out to compare the NO_3^- patterns both in flood events and in stable hydrometeorological conditions. This stage was performed by means of weekly manual samplings and through samples and data collected by an automatic water sampler (AWS Eco Tech 2002-YSI) and a sonde YSI 6920 multiparameter probe (YSI Incorporated, Ohio, USA).

The second phase was conducted in order to continue studying the flood events and for comparison with the results obtained during the first phase. In this sampling stage only were used the automatic water sampling and the sonde probe.

The first phase was carried out from December 2009 to June 2011.The sonde probe and the automatic water sampler were installed at the lowest part of Flumen River in December 2009 to continuously monitor the water quality. Their location is next to a gauging station of the Ebro Water Authority and near the confluence with the Alcanadre River. The sonde probe was connected to the automatic water sampler and placed inside the water. Likewise, the automatic water sampler was programmed to activate the water pump based on the water level variations in a range from 10 cm to 20 cm, depending on the season and on the expected weather conditions. The inlet water from the pump was placed next to the sonde probe. Manual samples were collected near the sonde probe location under stable flow conditions.

The second sampling stage was developed from January to December 2012 using the automatic water sampler and the sonde probe under the same conditions mentioned above, but manual samplings were not conducted.

Approximately 200 water samples were collected through automatic and manual sampling during the study period. In the laboratory, the water samples were filtered using pre-weighted glass microfiber filter paper (Whatman GF/F 0.7 µm) in order to retain the suspended matter. Each filtered water sample was stored at 4 °C until analysis could be performed as soon as possible not later than one week after filtration. The NO_3^- concentration was determined by ion chromatography with a chemical suppressor method using a Metrohm 861 Advanced Compact IC ion chromatograph (APHA, 2012).

2.3. Statistical analysis

A Pearson Correlation Matrix and a Cluster Analysis (CA) were conducted using the R software (R Development Core Team, 2011) because of its versatility in terms of functions.

CA was carried out to classify the flood events. To conduct this analysis with the R software, the HCLUST package and the DIST function were used to perform the hierarchical classification and to compute the matrix of distances respectively. The Ward method was applied in order to achieve the optimal classification (Kuiper and Fisher, 1975)**.** The Euclidean distance was used because is the recommended measure for Ward's method of clustering (Hair, et al., 2006). It was represented by the difference between the analytical values from the samples and aimed to reveal the similarity between samples. Data were previously standardized through a z-scale transformation to eliminate the influence of different units of measurements.

The variables used to characterize flood events and to perform statistical analyses are shown in Table ST2.

2.4. Data sources and treatment

The mean total precipitation and the precipitation intensity throughout the basin were determined using the Thiessen polygons method with the information from seven meteorological stations (AEMET, 2013; Oficina del Regante del Gobierno de Aragón, 2013). The hourly water discharges in the Flumen River were obtained from the Albalatillo gauging station belonging to the Ebro Confederation (A094) (SAIHEbro, 2013) and next to the automatic water sampler installation and the sonde. The river water discharge was calculated from the recorded water level. The rating curve (water level-discharge relationship) was obtained through the control station section and a rule graduated. The NO_3^- load for each flood event was calculated using the Walling and Webb (1985) method:

$$NO_3^- \text{ Load} = V \times (\Sigma^{n}_{i=1} (Ci \times Qi) / \Sigma^{n}_{i=1} Qi) \quad \text{(eq.1)}$$

, where Ci is the instantaneous concentration associated with each individual sample ($mg \cdot l^{-1}$), Qi is the hourly discharge at each individual sample ($m^3 \cdot s^{-1}$) and V is the water volume during the flood period. This is the preferred method for estimating the flux given the available data (Littlewood, 1992).

Based on the methodology proposed by Butturini et al. (2006), two parameters were used to study the hysteresis loops corresponding to the relationship between the nitrate concentration and the water flow for every flood event:

ΔC (%) describes the relative changes in the NO_3^- concentration and the hysteresis loop trend from the following equation:

$$\Delta C = (Cs - Cb) / Cmax * 100 \quad \text{(eq. 2)}$$

, where Cs and Cb correspond to the NO_3^- concentrations during the peak flow and the base flow, respectively, and Cmax is the maximum concentration observed during the flood event. ΔC varies between -100 and 100. Negative values indicate NO_3^- dilution, and positive values indicate an increase in the NO_3^- concentration during the flood.

ΔR (%) incorporates information relating to the hysteresis loop area and the hysteresis rotational pattern using the following equation:

$$\Delta R = R * A_h * 100 \quad \text{(eq. 3)}$$

,where A_h is the area of the hysteresis loop. In order to estimate the area, it is necessary to standardize the flow and concentration values to unity. The term R is related to the c-q relation and corresponds to the hysteresis rotational pattern; if the direction is clockwise, then R = 1, and if the direction is counter clockwise, then R = -1. In some cases, if the meaning is not clear or if the hysteresis is absent, it is considered that R = 0. The ΔR parameter also varies between -100 and 100 and it is considered that ΔR values between -20% and 20% have a relatively small area. Detailed data for ΔR calculation are described in Butturini et al. (2006).

Previous equations (eq. 2 and eq. 3) for each event were plotted on a ΔC vs. ΔR graph composed of four quadrants. In Region A ($\Delta C > 0$, $\Delta R > 0$), clockwise hysteresis loops with an overall positive trend (increase in the concentration of the component during the ascending limb of the hydrograph) were located. Region B ($\Delta C <0$, $\Delta R > 0$) describes clockwise hysteresis but with a negative trend (NO_3^- dilution during the descending limb of the hydrograph). Region C ($\Delta C < 0$, $\Delta R < 0$) showed anti-clockwise hysteresis loops and a negative trend (NO_3^- dilution during the ascending limb of the hydrograph). Finally, region D ($\Delta C > 0$ $\Delta R < 0$) indicated a counterclockwise hysteresis rate and an overall positive trend (increase in the NO_3^- concentration during the descending limb of the hydrograph.

3. Results

3.1. Temporal distribution of flood events and NO_3^- discharges

During the study period, 12 flood events were studied (3 in winter, 4 in spring, 4 in autumn and 1 in summer) (Fig. 2). There was a lower frequency of these episodes during the summer season. The total annual precipitation during the study period amounted to 1016 mm (53 mm in December 2009, 345 mm in 2010, 222 mm in the period from January to June 2011 and 396 mm in 2012). The major rainfall events generally occurred in spring (March to June) and autumn (October to December).

Based on the results of the first phase of the study (Fig. 2), it was observed that during the high irrigation period, the NO_3^- concentrations were lower while the highest concentrations occurred in April-May and November. A NO_3^- increase that, in general, was considerably higher in the case of non-irrigation floods was noted (Table 1). Data of the analyzed variables for each event are shown in Table 1.

The NO_3^- loads amounted to 2753 t and 1059 t during the first and second phases of the study period, respectively, with an average specific yield of 1.33 t km^{-2} y^{-1}. In the first phase, the NO_3^- transport reached 1722 t in irrigation season and 1031 t in the non-irrigation period. Only 348 t (13%) was exported during the flood events. In the course of the second phase of the study, the NO_3^- load was 733 t in the irrigation season and 326 t in the non-irrigation season. In this case, 610 t (57%) of nitrate was transported during the floods.

3.2. Relationship between NO_3^- and hydrometeorological events

In order to assess the relationship between the NO_3^- response during the floods and the different variables that influence these events, a Pearson correlation matrix was performed. This analysis was carried out with the variables shown in Table ST2 for the 12 flood events captured. The total precipitation (Pt) showed a strong correlation with the maximum water discharge (Qmax) (R = 0.97), the mean discharge (Qm) (R = 0.96) and the total water yield (Wt) (R = 0.93). A slightly weaker correlation was observed between the total precipitation and the maximum rainfall intensity of the flood and the flood intensity (Imax and If) (R = 0.79 and R = 0.84, respectively). The NO_3^- load was strongly correlated with the maximum rainfall intensity during the flood (Imax) (R = 0.81), the flood intensity (If) (R = 0.76) and the total water yield (Wt) (R = 0.89), but its highest significant correlations occurred with the mean discharge (Qm) (R = 0.94), the maximum discharge (Qmax) (R = 0.98) and the total precipitation (Pt) (R = 0.94). However, the mean and maximum NO_3^- concentrations showed weak correlations with these variables. The mean NO_3^- concentration (Nm) only had a good correlation with the accumulated precipitation 5 days before the flood (P5d) (R = 0.76) and, in turn, the maximum NO_3^- concentration (Nmax) was strongly correlated with the mean NO_3^- concentration (Nm) (R = 0.85). Flood duration (Fd) was well correlated with the time to rise (Tr) (R = 0.88) and showed a weak correlation with the total water yield (Wt) (R = 0.59). P5d showed a slightly higher correlation with Qa (R = 0.72) and Nm (0.76).

3.3. NO_3^- concentration, water discharge and flood events classification

The study of the relationship between the water discharge and the NO_3^- concentration within the 12 observed flood events revealed different hysteresis patterns in the Flumen catchment. Five of these floods occurred during non-irrigation season while the remaining 7 occurred during irrigation season. The distribution of the hysteresis patterns was equitable: 6 flood events followed a clockwise pattern while the remaining 6 floods showed counterclockwise trend. 3 of the 5 floods in the non-irrigation period followed a counterclockwise pattern, and 3 of the 7 floods in the irrigation period showed also a counter clockwise pattern (Fig. 3).

In trying to understand the NO_3^- pattern during flood events, the methodology proposed by Butturini et al. (2006) was followed. Table 1 displays the values obtained for the c-q descriptors, and Fig. 4 (unity plane) shows the plot of ΔC vs. ΔR as well as a summary of the hysteresis curves for each flood event.

It is important to emphasize that, except for "event 8" all of the floods had ΔR values between -20% and 20%. In this case, it is considered that the area of the hysteresis loop is small (Butturini et al., 2006). In Region A, events 2, 7 (irrigation season, R) and 6 (non-irrigation season, NR) were located, and the NO_3^- concentration increased during the ascending limb of the hydrograph and followed a clockwise trend. In quadrant B ($\Delta C < 0$, $\Delta R > 0$), floods events nº 10, 11 (R) and 5 (NR) were found. In this case, there was NO_3^- dilution during the descending limb of the hydrograph, and the direction of the hysteresis loop was clockwise. In quadrant C events nº 9, 8 (R) and 12 (NR) ($\Delta C < 0$, $\Delta R < 0$) were situated. Here, dilution of the NO_3^- concentration occurred in the ascending limb of the hydrograph, and the hysteresis trend was counterclockwise. In the region D ($\Delta C > 0$, $\Delta R < 0$), events nº 1, 3 (NR) and 4 and 7 (R) were placed. In this instance, the hysteresis loops indicated an increase in the NO_3^-concentration over the descending limb of the hydrograph and a counterclockwise direction.

Hierarchical cluster analysis (Fig. 3) resulted in a dendrogram that exhibited a division first into two groups. The first cluster only contained “event 11” which took place in October-12 (R). The other group was composed of two minor clusters. The first one included 4 floods: events 12, 6, 1 and 4 that occurred in NR (November-12, March-11, February-10 and November-10, respectively). The other minor cluster included 7 floods: events 2, 3, 7, 5, 8, 9 and 10. All of them took place in R (June-10, October-10, May-10, April-12, May-12 and July-12, respectively) except for “event 5” (March-11). The results of this hierarchical cluster analysis revealed a clear differentiation of the flood events according to the agricultural practices of irrigation or non-irrigation.

4. Discussion

4.1. Seasonal variability of the NO_3^- mobilization related to hydrological changes

In general, the export of NO_3^- is significantly related to the presence of local N sources, which vary according to the land use distribution in the catchment (Yevenes and Mannaerts, 2011). Nevertheless, Causapé et al. (2004a) reported an increase in the

NO_3^- concentration in rivers receiving irrigation runoff in semi-arid conditions. During the development of the present study, we tried to identify the factors that influence NO_3^- discharge into the Flumen River.

During the first phase of the study period (December 2009 to June 2011, Fig. 2), a relationship between the NO_3^- concentration and the flood events was observed. The maximum NO_3^- concentration (Nmax) for different flood discharge magnitudes was not clear. Holz (2010) reported that the NO_3^- concentration decreased as the water flow increased indicating either or both an immediate depletion at the source from surface flow or the dilution of the base flow. Moreover, Oeurng et al. (2010) showed that similar NO_3^- concentrations were caused by different water discharge magnitudes. A dilution effect was observed in some events with higher peak discharges, but compared with other events; there was no clear relationship between both of these variables (Table 1). Furthermore, the Pearson Correlation Matrix did not show strong correlations between NO_3^- concentration and water discharge and precipitation variables (Table 2). Only the accumulated precipitation 5 days before the flood (P5D) showed a strong correlation (R^2 = 0.764) with the mean NO_3^- concentration (Nm). This result could indicate that antecedent rainfall caused the NO_3^- mobilization while the rainfall occurring the day before the flood could contribute to the dilution of the NO_3^- concentration. In this regard, Rusjan et al. (2008) reported that the highest NO_3^- concentrations can be characterized by a lack of precipitation and low flow conditions, and Abrahao et al. (2011) showed a significant negative relationship between precipitation and the NO_3^- concentration.

In the present study, differences were observed between irrigation and non-irrigation periods. In the Flumen River, we only found a significant negative relationship (R^2 = 0.744) between the average NO_3^- concentration (Nm) and the total precipitation (Pt) in the case of floods occurring during the non-irrigation period (Fig. 5 A and B). Likewise, when constructing the graphic without data from "event 11", a negative relationship was also found during the irrigation season ($R^2 = 0.507$) (Fig. 5 C). In flood "event 11", due to high total precipitation (PT = 105.58 mm) throughout the entire basin, the storm caused an increase in the riverine concentration by transporting point and non-point source pollutants via runoff (Chen et al., 2012).

In the southern part of the Flumen basin, irrigation season starts in April and ends in October. Top dressing for wheat and barley is carried out in March, and basal dressing for maize and rice is performed in April (Table ST1). The results (Fig. 2) showed that, in general, the NO_3^- concentration was higher during these months both in 2011 and in 2012 without the occurrence of significant variations in the water discharge. The NO_3^- concentration followed the same pattern in November when base dressing for barley and wheat is performed. Thus, the high NO_3^- concentrations observed during certain times of the year can be linked with the nutrient availability through fertilizer application (Oeurng et al., 2010) (Table ST1) and lower river flows that minimize the dilution of the NO_3^- concentration. Throughout the rest of the year, the NO_3^- concentration was lower including for flood events. Interannual variations in the NO_3^- concentration (Fig. 2) and regression results between the NO_3^- mean concentration (Nm) and the total precipitation (Pt) in irrigation and non-irrigation floods (Fig. 5) showed the importance of IRF in the dilution of pollutant concentrations.

However, the NO_3^- transport (Nt) varied greatly. During the various events occurring in the study period, the Nt ranged from 9.75 t to 477.62 t (Table 1). The maximum NO_3^- transport (Nt) occurred in "event 11" (October 2012). This flood event was caused by an explosive cyclogenesis that took place in some areas of the Ebro River basin from 19 to 21 October 2012 (SAIHEbro, 2013). Explosive cyclone development has been traditionally characterized by a central pressure fall of 20 hPa over a 24-h period in mid-latitudes (Sanders and Gyakum, 1980). This type of disturbance can produce strong winds and heavy rainfall, as a result of this rapid change of central pressure. The Pearson Correlation Matrix revealed a strong correlation between NO_3^- transport (Nt) and Total precipitation (PT), Maximum Rainfall Intensity of the flood (Imax), Flood intensity (If), Total Water Yield, Mean discharge (Qm) and Maximum discharge (Qm). These variables could be those that regulate the transport of NO_3^- (Nt) in the Flumen River Basin (Table 2) during the flood events. Differences were also observed between the irrigation period, with a highly significant relationship between Nt and Qmax, and the non-irrigation period (R^2 = 0.991 and R^2 = 0.822 respectively) (Fig. 6). Maximum NO_3^- loads occurred during high flows in the irrigation period; although, higher concentrations were observed when the water discharge was lower. 75% of the NO_3^- load is exported in floods that happened in the irrigation season. The influence of "event 11" heavily increased this percentage, but in the overall calculations of the study period, 64% of the NO_3^- load belonged to the irrigation season while 36% corresponded to the non-irrigation period. These results suggest that besides the combined input of hydrological and biogeochemical processes, there is also a joint influence of irrigation and fertilization on the mass of NO_3^- exported (Power et al., 2001; Zotarelli et al., 2007; Gheysari et al., 2009), and irrigation has an impact of on the pollutants trends.

4.2. NO_3^- concentration patterns in relation to changes in the water discharge

The difficulty in separating the cause and effect of NO_3^- flushing in field studies arises from discrepancies in the spatial hydrological units studied caused by spatial heterogeneities in the soil properties, a reduced ability to detect flow pathways within the soil, and other unknowns (Rusjan et al., 2008). The trends of a pollutant during a hydrological event may help to determine its origin and allow for the interpretation of its patterns.

A clockwise hysteresis pattern indicates the rapid transport of NO_3^-. It could also indicate a depletion of the NO_3^- supply possibly as a consequence of the dilution effect during flood events (Williams, 1989). An anticlockwise hysteresis pattern could be linked with the limited mobilization of NO_3^- in antecedent dry periods, and therefore, low concentrations of NO_3^- in the stream and the accumulation of NO_3^- during summer periods were hydrologically disconnected in the upper soil horizons (Oeurng et al., 2010). For the analysis of hysteresis loops; i.e. the interpretation of the NO_3^- sources and patterns, the characteristics of the time scale under study, either annual or seasonal, and weather conditions that occur at different stages should be particularly observed.

In the Cluster Analysis (CA), 3 major groups of NO_3^- hysteresis were observed (Fig. 3). The first one only contained “event 11”. This flood event was situated in region B of the unity plane (Fig. 4); therefore, it was a clockwise hysteresis that resulted in a dilution in the NO_3^- concentration as the flow rate decreased. The location of this event in the dendrogram, without being grouped with any other flood, is logical due to its special characteristics. This was an extremely large event with a maximum water discharge (Qmax) of 146.55 $m^3 \cdot s^{-1}$ and a duration (Fd) of 150 h. In the Aragonese Pyrenees there are important antecedents of heavy rainfall with flood events characterized by a rapid and huge water discharge into the rivers (García-Ruíz et al., 2000). This type of event can be described as extreme. The low atmospheric pressure isolated at high levels that affected the central part of the Ebro Basin produced flows that corresponded to extraordinary floods with return periods of 100 years in some of the basin areas (SAIHEbro, 2013). In this flood event, the NO_3^- concentration is diluted with increasing water discharge and hereby, the hysteresis loop followed a clockwise pattern. This result agreed with the study by Williams (1989) that linked clockwise hysteresis loops to long-lasting floods.

In the Flumen River basin, IRF occur primarily in the lower 40 km of the river and lead to changes in the hydrologic dynamics relative to the upper reaches of the river (Martin-Queller et al., 2010). Water flow is higher during the irrigation season (April to October) than during the non-irrigation period (November to March) (Fig. 2). In addition to punctual flood events, runoff from agriculture irrigation has a greater influence on the river flow increase than the occurrence of rain or snow. This fact could be related to the separation occurring in the dendrogram between non-irrigation and irrigation floods (Fig. 3).

The second cluster was composed of two minor groups. The first one contained events nº 12 (4/11/2012), nº 6 (15/3/2011), nº 1 (17/2/2010) and nº 4 (20/11/2010). All of these floods occurred in the non-irrigation period and followed an anticlockwise pattern except for "event 6" (Figures 4 and 7). Floods that followed a counterclockwise pattern in non-irrigation season occurred in November and February. At this time, the basal and top dressing for wheat and barley were carried out in the study area (November and February, respectively) (Table ST1). This could be the cause of a higher NO_3^- concentration. In these events, the following maximum NO_3^- concentrations (Nmax) were found: "event 2" = 32.12 $mg \cdot l^{-1}$, "event 4" = 34.17 $mg \cdot l^{-1}$ and "event 12" = 30.28 $mg \cdot l^{-1}$ (Table 1). The combined effect of fertilization and the absence of irrigation may cause the accumulation of NO_3^- in the soil, which is then leached by the rains and slowly mobilized to the river. Due to these two reasons, the peak NO_3^- concentration comes later than the water discharge peak and produces a loop with a counterclockwise direction (Williams, 1989).

"Event 6" was also in this group but followed a clockwise pattern (Figures 4 and 7). Only two days passed between "event 5" and "event 6" (12 March 2011 and 15 March 2011, respectively) and formed a composed flood (Fig. 7). "Event 6" took place at the end of non-irrigation season (15 March 2011). This fact was also shown in its position in the dendrogram (Fig. 3). However, unlike the rest of the events in this group, this flood followed a clockwise pattern. A long duration (Fd = 141 h) and an elevated total rainfall along the entire basin (Pt = 29.74 mm) could have caused a depletion of the available NO_3^- before the water discharge has peaked, resulting from a consequence of the dilution effect during the flood event and causing a clockwise pattern in this flood (Williams, 1989). Considering the summary table (Table 1), the maximum NO_3^- concentration was 31.92 $mg \cdot l^{-1}$, but this concentration occurred at the end of the flood (Fig. 7) when flow had decreased and the rains had stopped. This high maximum NO_3^- concentration could be related to the top-dressing fertilization for wheat and barley that occurred at this time (Table ST1).

The other cluster is formed by events 2, 3, 7, 8, 9 and 10. All of them took place during the irrigation season. However, "event 5", which occurred in March 2011 (non-irrigation season), is also grouped together with these events.

When the maximum NO_3^- concentration (Nt) in "event 5" (Nmax = 19.18 $mg \cdot l^{-1}$) (Table 1) was compared with the other floods, it was observed that the concentration range of this event was more similar to those occurring in the irrigation season than the non-irrigation floods. This result suggests that heavy rains occurring throughout the basin could have caused the rapid mobilization of NO_3^- and its dilution. In this case, the combined influence of the total rainfall (Pt = 20.72 mm) and the intensity (If = 0.50 $m^3 \cdot min^{-2}$) of the flood event could have caused a dilution effect on the NO_3^- concentration and produced a clockwise pattern. As in "event 6", the last sample showed an elevation of the NO_3^- concentration (19.18 mg·l^{-1}) (Fig. 7) in the flow recession limb but in this case, is considerably lower than in the other floods. During the period in which both events took place, the NO_3^- concentrations were high because of the agricultural fertilization performed in that season (Table ST1), but precipitation along the entire basin (PT = 20.72 mm and PT = 29.74 mm in events 5 and 6, respectively) induced a dilution effect. At the end of the rains and with a decreasing water discharge, the NO_3^- concentration was again high. This could be the cause of the location in the dendrogram of both events.

Previously, the different groupings of non-irrigation and irrigation floods in the dendrogram have been discussed, but within the irrigation floods, the volume of the IRF could also influence the pollutants pattern. Our results agreed with those of Causapé et al. (2004b). In their study, they divided the agricultural periods into the following 3 groups: non-irrigation (winter), low-irrigation (spring-autumn) and high irrigation (summer) and stated that irrigation is a key factor in determining the level and temporal variability of NO_3^-. Likewise, in our research, events that happened in low-irrigation season (event 3, Oct 2010; event 8, Apr 2012; and event 9, Apr 2012) followed anticlockwise loops, and high-irrigation events (event 2, Jun 2010; event 7, May-Jun 2011; and event 10, Jul 2012) had a clockwise conduct (Figures 4 and 7). The antecedent wet conditions were reported to result in the peak NO_3^- concentration occurring before the discharge peak (clockwise patterns), whereas dry antecedent soil moisture was related to the NO_3^- flush occurring after the discharge peak (anticlockwise patterns) (Christopher et al., 2008; McNamara et al., 2008; Jiang et al., 2010).

Other authors have studied the shape and width of the hysteresis loops relating these parameters with pollutant sources and the season of the year in which these events take place (Rusjan et al., 2008; Oeurng et al., 2010). In this regard, differences were observed between the flood events studied. Among some of hysteresis loops obtained, the widest widths (difference between the NO_3^- concentrations) were found in "events 1 and 6" (February 2010 and March 2011, respectively) (Nmin = 17.27 mg·l^{-1}, Nmax = 32.12 mg·l^{-1} in event 1 and Nmin = 10.56 mg·l^{-1}, Nmax = 31.92 mg·l^{-1} in event 6) (Fig. 7). Otherwise, "events 3 and 7" (October 2010 and June 2011) were those with the smallest widths. In general, the differences between the NO_3^- concentrations were greater in non-irrigation season floods. During the irrigation period, the widths decreased and flatter shapes were found. The lower differences within the NO_3^- concentrations in flood events occurring in irrigation season were probably due to the influence of IRF, which contributed to increases in the water discharge and induced dilution of the NO_3^- concentration in the river throughout the season. In the case of non-irrigation season floods, NO_3^- concentrations were lower due to the increased water flow caused by the rain. In low flow periods, NO_3^- concentrations were higher (Fig. 2). This suggests that for the Flumen River, IRF significantly influence the NO_3^- concentrations and the flood patterns as well as the hydrologic regime of the river.

5. Conclusions

A general dilution pattern of the NO_3^- concentration was observed in the Flumen River in relation to an increase in the water discharge caused by agricultural IRF (April-October), while the NO_3^- concentration in the river was higher during the fertilization period (November-March). However, the maximum NO_3^- loads occurred during high flows in irrigation periods, which suggest that IRF have an intense influence on NO_3 discharges into the river.

The Pearson Correlation Matrix showed that the Total Precipitation (Pt), the Maximum rainfall intensity of the flood (Imax), the Flood intensity (If), the Mean discharge (Qm) and the Maximum discharge (Qmax) were key factors for the export of NO_3^- in the Flumen River Basin.

Even though the c-q analysis found that, in general, hysteresis taking place in the Flumen River had a small area; the cluster analysis (CA) showed that the NO_3^- trends during floods was highly influenced by the seasonality of agricultural activities. The type of flood event is different in irrigation and non-irrigation seasons. While anticlockwise patterns are common in non-irrigation season, clockwise trends are usual during the irrigation season or high increases in the water discharge.

Due to the multiplicity of factors that influence the transport of pollutants within a watershed, it is difficult to determine its origin and the conditions that affect its patterns, but agricultural land use and especially the irrigation return flows (IRF) are essential for interpreting the trends of NO_3^- mobilization in Mediterranean basins. However, the continuous monitoring of water quality conducted in this study, the high frequency data obtained and the knowledge of the land use seasonality within the watershed will be essential to characterize and understand the long-term NO_3^- variability in different hydrological and climatic circumstances and to identify its sources. Also, this information will be crucial when taking measures to minimize the effects of water pollution and for these measures are effective.

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Table captions

Table 1. Characteristics of flood events that occurred in the Flumen basin during the study period (the abbreviations correspond to those variables presented in Table ST2).

Table 2. Pearson correlation matrix of analysed variables

Table ST1. Times of agricultural activities in the Flumen River catchment.

Table ST2. Variables and units used to characterize flood events and to perform statistical analyses.

Figure captions

Fig. 1 Location and land use of the Flumen River basin

Fig. 2 Temporal variability of the NO_3^- concentrations during the first phase of the study period. The numbers indicate each flood event studied.

Fig. 3 Dendrogram classifying all of the flood events that occurred during the study period.

Fig. 4 Representation of the c-q hysteresis characteristics of NO_3^- in the unity plane ΔC vs. ΔR.

Fig. 5 Correlation between the NO_3^- concentration and Total Precipitation in non-irrigation events (A), irrigation events (B) and irrigation events without the “event 11” data (C).

Fig. 6 Correlation between the NO_3^- load and the water discharge in non-irrigation events (A) and irrigation events (B).

Fig. 7 Hysteresis patterns in the Flumen River basin during the study period