

1 **Seasonal variability of NO₃⁻ mobilization during flood events in a Mediterranean**
2 **catchment: The influence of intensive agricultural irrigation**

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25

26 **Abstract**

27 The temporal variability, hysteresis loops and various factors involved in the
28 mobilization of nitrates (NO_3^-) have been studied for a 3-year period at the Flumen
29 River basin. Multivariate techniques (Cluster Analysis and Pearson Correlation Matrix)
30 were used to establish the relationship between the water discharge and NO_3^- flushing,
31 as well as identify the agricultural and hydrometeorological parameters that influence its
32 different mobilization trends. The relationship between changes in the NO_3^-
33 concentration (ΔC) and the overall dynamic of each hysteresis loop (ΔR) was also
34 analyzed in order to describe the NO_3^- trends according to the water discharge. A
35 general dilution pattern of the NO_3^- concentration was noted in the Flumen River with
36 respect to the degree of water discharge caused by irrigation return flows. While
37 fertilization increased the NO_3^- concentration, the beginning of the irrigation season
38 contributed to its dilution. However, in case of the NO_3^- load, the maximum values
39 occurred during high flow periods in the irrigation period, which suggested the
40 influence of the irrigation flow on the NO_3^- mass. The NO_3^- load increased to 2753 t and
41 1059 t during the first and second phases of the study period, respectively, with an
42 average specific yield of $1.33 \text{ t km}^{-2} \text{ y}^{-1}$. The NO_3^- transport in the first phase of the
43 study was 1722 t during the irrigation season and 1031 t during the non-irrigation
44 period. Only 348 t (13%) of NO_3^- was exported during the flood events. However, in
45 the course of the second phase of the study, the NO_3^- load was 733 t during the irrigation
46 season and 326 t during the non-irrigation period. In this case, 610 t (57%) of nitrate
47 was transported during the floods. These results revealed the clear influence of
48 irrigation return flows on the NO_3^- response in Flumen River.

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51 **1. Introduction**

52 Concentrations of nitrogen (N) are elevated in rivers across large areas of
53 Europe (Sutton et al., 2011). The European Water Framework Directive (WFD, EC,
54 2000) gives priority to watersheds and water bodies as reference units to achieve a
55 “good ecological status” in 2015. For this, knowledge of the transfer of pollutants in
56 catchment areas is essential when taking measures to mitigate the degradation of water
57 quality. The dynamics of N loss from catchments has been studied in different
58 environments, at different spatial scales and at different sampling frequencies (Ferrant et
59 al., 2013). A substantial portion of excess N is exported from terrestrial ecosystems to
60 aquatic ecosystems (Seitzinger and Harrison, 2008). The potential for NO_3^- leaching is a
61 function of the soil type, weather conditions and the crop management system (Martin-
62 Queller et al., 2010) but under similar conditions, the export of N increases with the
63 percentage of the agricultural area in the watershed (Kaushal et al., 2008). In irrigated
64 agriculture, irrigation return flows (IRF) are important factors that influence the NO_3^-
65 concentration in the surface water (Causapé et al., 2006). IRF are mixtures of surface
66 drainage water composed of overflow or bypass water, surface runoff or tail water, and
67 collected subsurface drainage water (Skogerboe and Walker, 1981). IRF also have the
68 potential for disrupting the natural hydrologic water balance of river basins (Haddeland
69 et al., 2006). However, weather conditions also influence the NO_3^- mobilization.

70 Hydrologically active periods, particularly flood events, are important because
71 the addition of new water sources during such events mobilizes distinctly new and
72 different sources of nutrients from the catchment (Buda and DeWalle, 2009). Several
73 studies have showed that the relationship between pollutant concentration (c) and water
74 discharge (q) during storm events follows cyclic trajectories (Hill, 1993). This feature
75 has been commonly studied using an approach called hysteresis analysis of river flows

76 and pollutants, in which the physical processes of suspended and dissolved material
77 transport are qualitatively identified in terms of the direction of a hysteresis loop (de
78 Boer and Campbell, 1989). In a pollutant concentration vs. water discharge plot (c-q
79 relation), hysteresis analysis may be used as a technique for determining the source of
80 chemicals measured in streams and changes in the forms of nutrients through storm
81 events (Stutter et al., 2008). Some studies focused on sediment transport reported that
82 for most streams, clockwise hysteresis patterns are produced when higher
83 concentrations occur on the rising limb of the hydrograph and lower concentrations
84 occur on the recessional limb (Glysson, 1987). Otherwise, counter clockwise hysteresis
85 loops have been explained by a delayed source from tributaries or due to a bank
86 collapse on the recessional limb of the hydrograph (Rinaldi et al., 2004). With respect to
87 nutrients, these patterns can be produced by either a dominant nutrient supply that is
88 mobilized slowly during a storm event or could indicate a rapid input of the nutrient
89 from a source with a concentration of the nutrient that is lower than that in the river
90 (Bowes et al., 2009). In the case of NO_3^- , besides the weather factor, it is necessary to
91 take into account the flow dynamics related to the land use within a watershed. Jiang et
92 al. (2012) reported a significant positive correlation between the agricultural area and
93 the peak of NO_3^- -N concentrations during rainfall events. However, because of the
94 multiplicity of factors affecting the NO_3^- mobilization in agricultural catchments, a
95 sampling design that includes both high frequency sample collection and monitoring of
96 the sporadic flood events is required.

97 A study of these characteristics was needed in the Flumen River basin to acquire
98 a comprehensive understanding of the NO_3^- transport and the factors involved in this
99 process. A monitoring program for water quality was carried out in Flumen River Basin
100 for a 3-year period, with the aim to get a high data rate that would include the spatio-

101 temporal, weather and agricultural factors affecting NO_3^- transfer. The objectives of this
102 study were: (i) to study the variability of NO_3^- patterns in relation to water flow
103 dynamics and hydro-meteorological variables; (ii) to determine the factors affecting
104 NO_3^- transport during flood events; and (iii) characterize the types of events in the
105 Flumen watershed according to the different agricultural seasons and the IRF.

106 **2. Methods**

107 **2.1. Study area**

108 The Flumen River is located in the province of Huesca (Aragón, Spain) in the
109 north-central part of the Ebro River basin (80,093 km², NE Spain) (Fig. 1). The river
110 originates at 1,250 m.a.s.l. in Sierra Guara, which is a calcareous pre-Pyrenean
111 mountain chain. This river is 120 km long, and together with its tributary, the Isuela
112 River, drains a watershed area of 1,430 km². After exiting the mountainous part of the
113 basin, the Flumen River flows through flat plains that have intensive agricultural uses to
114 its confluence with the Alcanadre River at 240 m.a.s.l.

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

123 A Mediterranean climate with irregular seasonal and interannual rainfall is a
124 common feature of the entire basin (Comín and Williams, 1994), although a decreasing
125 rainfall gradient of 77.6 mm for every 100 m of altitude change exists from the north

126 mountain region to the flat southern region of the basin. The average annual rainfall in
127 the basin is 581 mm (Pedrocchi, 1998).

128 In the Flumen River basin, the percentage of the agricultural zone reaches 71%
129 of the total area. In this agricultural area, 70% are irrigated crops. In the lower region of
130 the watershed, the principal land use is irrigated agriculture, in which rice (*Oryza*
131 *sativa*), corn (*Zea mays*) and alfalfa (*Medicago sativa*) are the most representative crops
132 (Fig. 1). Cereals such as wheat (*Triticum spp.*) and barley (*Hordeum vulgare*) are also
133 cultivated as rainfed crops in the external areas of the watershed (Common Agricultural
134 Policy, 2009-2011). Information on agricultural activities performed in the study area
135 was obtained through farmers and agricultural cooperatives and is shown in Table ST1.
136 Irrigation season takes place from April to October, but the summer months are those
137 with the greatest irrigation activity. In the lower half of the basin, the so-called Northern
138 Monegros County, there is a complex system of small irrigation canals that distribute
139 the water transported by a large irrigation canal, the Monegros canal. The hydrological
140 regime of the river is, especially in its last section, highly altered by the IRF. Thus, the
141 water discharge is higher during irrigation season due to the contribution of the
142 irrigation runoff. The maximum water flow recorded in the Flumen River during 2003-
143 2012 was $146.5 \text{ m}^3 \cdot \text{s}^{-1}$ (22 October 2012), and the mean annual discharge (2003-2012)
144 was $5.2 \text{ m}^3 \cdot \text{s}^{-1}$ (SAIHEbro, 2013).

145 **2.2. Instrumentation, sampling strategy and water sample analysis**

146 The sampling strategy was developed in two phases. The first phase was carried
147 out to compare the NO_3^- patterns both in flood events and in stable hydrometeorological
148 conditions. This stage was performed by means of weekly manual samplings and
149 through samples and data collected by an automatic water sampler (AWS Eco Tech
150 2002-YSI) and a sonde YSI 6920 multiparameter probe (YSI Incorporated, Ohio, USA).

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

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

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

167 Approximately 200 water samples were collected through automatic and manual
168 sampling during the study period. In the laboratory, the water samples were filtered
169 using pre-weighted glass microfiber filter paper (Whatman GF/F 0.7 μm) in order to
170 retain the suspended matter. Each filtered water sample was stored at 4 °C until analysis
171 could be performed as soon as possible not later than one week after filtration. The NO_3^-
172 concentration was determined by ion chromatography with a chemical suppressor
173 method using a Metrohm 861 Advanced Compact IC ion chromatograph (APHA,
174 2012).

175

176 **2.3. Statistical analysis**

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

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

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

191 **2.4. Data sources and treatment**

192 The mean total precipitation and the precipitation intensity throughout the basin
193 were determined using the Thiessen polygons method with the information from seven
194 meteorological stations (AEMET, 2013; Oficina del Regante del Gobierno de Aragón,
195 2013). The hourly water discharges in the Flumen River were obtained from the
196 Albalatillo gauging station belonging to the Ebro Confederation (A094) (SAIHEbro,
197 2013) and next to the automatic water sampler installation and the sonde. The river
198 water discharge was calculated from the recorded water level. The rating curve (water
199 level-discharge relationship) was obtained through the control station section and a rule

200 graduated. The NO_3^- load for each flood event was calculated using the Walling and
201 Webb (1985) method:

202

$$203 \quad \text{NO}_3^- \text{ Load} = V \times (\sum_{i=1}^{n_i} (C_i \times Q_i) / \sum_{i=1}^{n_i} Q_i) \quad (\text{eq.1})$$

204

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

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

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

214

$$215 \quad \Delta C = (C_s - C_b) / C_{\text{max}} * 100 \quad (\text{eq. 2})$$

216

217 , where C_s and C_b correspond to the NO_3^- concentrations during the peak flow and the
218 base flow, respectively, and C_{max} is the maximum concentration observed during the
219 flood event. ΔC varies between -100 and 100. Negative values indicate NO_3^- dilution,
220 and positive values indicate an increase in the NO_3^- concentration during the flood.

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

223

$$224 \quad \Delta R = R * A_n * 100 \quad (\text{eq. 3})$$

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

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

243 **3. Results**

244 **3.1. Temporal distribution of flood events and NO_3^- discharges**

245 During the study period, 12 flood events were studied (3 in winter, 4 in spring, 4
246 in autumn and 1 in summer) (Fig. 2). There was a lower frequency of these episodes
247 during the summer season. The total annual precipitation during the study period
248 amounted to 1016 mm (53 mm in December 2009, 345 mm in 2010, 222 mm in the

249 period from January to June 2011 and 396 mm in 2012). The major rainfall events
250 generally occurred in spring (March to June) and autumn (October to December).

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

256 The NO_3^- loads amounted to 2753 t and 1059 t during the first and second phases
257 of the study period, respectively, with an average specific yield of $1.33 \text{ t km}^{-2} \text{ y}^{-1}$. In the
258 first phase, the NO_3^- transport reached 1722 t in irrigation season and 1031 t in the non-
259 irrigation period. Only 348 t (13%) was exported during the flood events. In the course
260 of the second phase of the study, the NO_3^- load was 733 t in the irrigation season and
261 326 t in the non-irrigation season. In this case, 610 t (57%) of nitrate was transported
262 during the floods.

263 **3.2. Relationship between NO_3^- and hydrometeorological events**

264 In order to assess the relationship between the NO_3^- response during the floods
265 and the different variables that influence these events, a Pearson correlation matrix was
266 performed. This analysis was carried out with the variables shown in Table ST2 for the
267 12 flood events captured. The total precipitation (Pt) showed a strong correlation with
268 the maximum water discharge (Q_{max}) ($R = 0.97$), the mean discharge (Q_{m}) ($R = 0.96$)
269 and the total water yield (Wt) ($R = 0.93$). A slightly weaker correlation was observed
270 between the total precipitation and the maximum rainfall intensity of the flood and the
271 flood intensity (I_{max} and I_{f}) ($R = 0.79$ and $R = 0.84$, respectively). The NO_3^- load was
272 strongly correlated with the maximum rainfall intensity during the flood (I_{max}) ($R =$
273 0.81), the flood intensity (I_{f}) ($R = 0.76$) and the total water yield (Wt) ($R = 0.89$), but its

274 highest significant correlations occurred with the mean discharge (Q_m) ($R = 0.94$), the
275 maximum discharge (Q_{max}) ($R = 0.98$) and the total precipitation (P_t) ($R = 0.94$).
276 However, the mean and maximum NO_3^- concentrations showed weak correlations with
277 these variables. The mean NO_3^- concentration (N_m) only had a good correlation with
278 the accumulated precipitation 5 days before the flood (P_{5d}) ($R = 0.76$) and, in turn, the
279 maximum NO_3^- concentration (N_{max}) was strongly correlated with the mean NO_3^-
280 concentration (N_m) ($R = 0.85$). Flood duration (F_d) was well correlated with the time to
281 rise (T_r) ($R = 0.88$) and showed a weak correlation with the total water yield (W_t) ($R =$
282 0.59). P_{5d} showed a slightly higher correlation with Q_a ($R = 0.72$) and N_m (0.76).

283 **3.3. NO_3^- concentration, water discharge and flood events classification**

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

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

296 It is important to emphasize that, except for “event 8” all of the floods had ΔR
297 values between -20% and 20%. In this case, it is considered that the area of the
298 hysteresis loop is small (Butturini et al., 2006). In Region A, events 2, 7 (irrigation

299 season, R) and 6 (non-irrigation season, NR) were located, and the NO_3^- concentration
300 increased during the ascending limb of the hydrograph and followed a clockwise trend.
301 In quadrant B ($\Delta C < 0$, $\Delta R > 0$), floods events n° 10, 11 (R) and 5 (NR) were found. In
302 this case, there was NO_3^- dilution during the descending limb of the hydrograph, and the
303 direction of the hysteresis loop was clockwise. In quadrant C events n° 9, 8 (R) and 12
304 (NR) ($\Delta C < 0$, $\Delta R < 0$) were situated. Here, dilution of the NO_3^- concentration occurred
305 in the ascending limb of the hydrograph, and the hysteresis trend was counterclockwise.
306 In the region D ($\Delta C > 0$, $\Delta R < 0$), events n° 1, 3 (NR) and 4 and 7 (R) were placed. In
307 this instance, the hysteresis loops indicated an increase in the NO_3^- concentration over
308 the descending limb of the hydrograph and a counterclockwise direction.

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

319 **4. Discussion**

320 **4.1. Seasonal variability of the NO_3^- mobilization related to hydrological changes**

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

324 NO₃⁻ concentration in rivers receiving irrigation runoff in semi-arid conditions. During
325 the development of the present study, we tried to identify the factors that influence NO₃⁻
326 discharge into the Flumen River.

327 During the first phase of the study period (December 2009 to June 2011, Fig. 2),
328 a relationship between the NO₃⁻ concentration and the flood events was observed. The
329 maximum NO₃⁻ concentration (N_{max}) for different flood discharge magnitudes was not
330 clear. Holz (2010) reported that the NO₃⁻ concentration decreased as the water flow
331 increased indicating either or both an immediate depletion at the source from surface
332 flow or the dilution of the base flow. Moreover, Oeurng et al. (2010) showed that
333 similar NO₃⁻ concentrations were caused by different water discharge magnitudes. A
334 dilution effect was observed in some events with higher peak discharges, but compared
335 with other events; there was no clear relationship between both of these variables (Table
336 1). Furthermore, the Pearson Correlation Matrix did not show strong correlations
337 between NO₃⁻ concentration and water discharge and precipitation variables (Table 2).
338 Only the accumulated precipitation 5 days before the flood (P5D) showed a strong
339 correlation ($R^2 = 0.764$) with the mean NO₃⁻ concentration (N_m). This result could
340 indicate that antecedent rainfall caused the NO₃⁻ mobilization while the rainfall
341 occurring the day before the flood could contribute to the dilution of the NO₃⁻
342 concentration. In this regard, Rusjan et al. (2008) reported that the highest NO₃⁻
343 concentrations can be characterized by a lack of precipitation and low flow conditions,
344 and Abrahao et al. (2011) showed a significant negative relationship between
345 precipitation and the NO₃⁻ concentration.

346 In the present study, differences were observed between irrigation and non-
347 irrigation periods. In the Flumen River, we only found a significant negative
348 relationship ($R^2 = 0.744$) between the average NO₃⁻ concentration (N_m) and the total

349 precipitation (Pt) in the case of floods occurring during the non-irrigation period (Fig. 5
350 A and B). Likewise, when constructing the graphic without data from “event 11”, a
351 negative relationship was also found during the irrigation season ($R^2 = 0.507$) (Fig. 5 C).
352 In flood “event 11”, due to high total precipitation (PT = 105.58 mm) throughout the
353 entire basin, the storm caused an increase in the riverine concentration by transporting
354 point and non-point source pollutants via runoff (Chen et al., 2012).

355 In the southern part of the Flumen basin, irrigation season starts in April and
356 ends in October. Top dressing for wheat and barley is carried out in March, and basal
357 dressing for maize and rice is performed in April (Table ST1). The results (Fig. 2)
358 showed that, in general, the NO_3^- concentration was higher during these months both in
359 2011 and in 2012 without the occurrence of significant variations in the water
360 discharge. The NO_3^- concentration followed the same pattern in November when base
361 dressing for barley and wheat is performed. Thus, the high NO_3^- concentrations
362 observed during certain times of the year can be linked with the nutrient availability
363 through fertilizer application (Oeurng et al., 2010) (Table ST1) and lower river flows
364 that minimize the dilution of the NO_3^- concentration. Throughout the rest of the year,
365 the NO_3^- concentration was lower including for flood events. Interannual variations in
366 the NO_3^- concentration (Fig. 2) and regression results between the NO_3^- mean
367 concentration (Nm) and the total precipitation (Pt) in irrigation and non-irrigation floods
368 (Fig. 5) showed the importance of IRF in the dilution of pollutant concentrations.

369 However, the NO_3^- transport (Nt) varied greatly. During the various events
370 occurring in the study period, the Nt ranged from 9.75 t to 477.62 t (Table 1). The
371 maximum NO_3^- transport (Nt) occurred in “event 11” (October 2012). This flood event
372 was caused by an explosive cyclogenesis that took place in some areas of the Ebro
373 River basin from 19 to 21 October 2012 (SAIHEbro, 2013). Explosive cyclone

374 development has been traditionally characterized by a central pressure fall of 20 hPa
375 over a 24-h period in mid-latitudes (Sanders and Gyakum, 1980). This type of
376 disturbance can produce strong winds and heavy rainfall, as a result of this rapid change
377 of central pressure. The Pearson Correlation Matrix revealed a strong correlation
378 between NO_3^- transport (Nt) and Total precipitation (PT), Maximum Rainfall Intensity
379 of the flood (Imax), Flood intensity (If), Total Water Yield, Mean discharge (Qm) and
380 Maximum discharge (Qm). These variables could be those that regulate the transport of
381 NO_3^- (Nt) in the Flumen River Basin (Table 2) during the flood events. Differences
382 were also observed between the irrigation period, with a highly significant relationship
383 between Nt and Qmax, and the non-irrigation period ($R^2 = 0.991$ and $R^2 = 0.822$
384 respectively) (Fig. 6). Maximum NO_3^- loads occurred during high flows in the irrigation
385 period; although, higher concentrations were observed when the water discharge was
386 lower. 75% of the NO_3^- load is exported in floods that happened in the irrigation season.
387 The influence of “event 11” heavily increased this percentage, but in the overall
388 calculations of the study period, 64% of the NO_3^- load belonged to the irrigation season
389 while 36% corresponded to the non-irrigation period. These results suggest that besides
390 the combined input of hydrological and biogeochemical processes, there is also a joint
391 influence of irrigation and fertilization on the mass of NO_3^- exported (Power et al.,
392 2001; Zotarelli et al., 2007; Gheysari et al., 2009), and irrigation has an impact of on the
393 pollutants trends.

394 **4.2. NO_3^- concentration patterns in relation to changes in the water discharge**

395 The difficulty in separating the cause and effect of NO_3^- flushing in field studies
396 arises from discrepancies in the spatial hydrological units studied caused by spatial
397 heterogeneities in the soil properties, a reduced ability to detect flow pathways within
398 the soil, and other unknowns (Rusjan et al., 2008). The trends of a pollutant during a

399 hydrological event may help to determine its origin and allow for the interpretation of
400 its patterns.

401 A clockwise hysteresis pattern indicates the rapid transport of NO_3^- . It could also
402 indicate a depletion of the NO_3^- supply possibly as a consequence of the dilution effect
403 during flood events (Williams, 1989). An anticlockwise hysteresis pattern could be
404 linked with the limited mobilization of NO_3^- in antecedent dry periods, and therefore,
405 low concentrations of NO_3^- in the stream and the accumulation of NO_3^- during summer
406 periods were hydrologically disconnected in the upper soil horizons (Oeurng et al.,
407 2010). For the analysis of hysteresis loops; i.e. the interpretation of the NO_3^- sources
408 and patterns, the characteristics of the time scale under study, either annual or seasonal,
409 and weather conditions that occur at different stages should be particularly observed.

410 In the Cluster Analysis (CA), 3 major groups of NO_3^- hysteresis were observed
411 (Fig. 3). The first one only contained “event 11”. This flood event was situated in region
412 B of the unity plane (Fig. 4); therefore, it was a clockwise hysteresis that resulted in a
413 dilution in the NO_3^- concentration as the flow rate decreased. The location of this event
414 in the dendrogram, without being grouped with any other flood, is logical due to its
415 special characteristics. This was an extremely large event with a maximum water
416 discharge (Q_{max}) of $146.55 \text{ m}^3 \cdot \text{s}^{-1}$ and a duration (F_d) of 150 h. In the Aragonese
417 Pyrenees there are important antecedents of heavy rainfall with flood events
418 characterized by a rapid and huge water discharge into the rivers (García-Ruíz et al.,
419 2000). This type of event can be described as extreme. The low atmospheric pressure
420 isolated at high levels that affected the central part of the Ebro Basin produced flows
421 that corresponded to extraordinary floods with return periods of 100 years in some of
422 the basin areas (SAIHEbro, 2013). In this flood event, the NO_3^- concentration is diluted
423 with increasing water discharge and hereby, the hysteresis loop followed a clockwise

424 pattern. This result agreed with the study by Williams (1989) that linked clockwise
425 hysteresis loops to long-lasting floods.

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

434 The second cluster was composed of two minor groups. The first one contained
435 events n° 12 (4/11/2012), n° 6 (15/3/2011), n° 1 (17/2/2010) and n° 4 (20/11/2010). All
436 of these floods occurred in the non-irrigation period and followed an anticlockwise
437 pattern except for “event 6” (Figures 4 and 7). Floods that followed a counterclockwise
438 pattern in non-irrigation season occurred in November and February. At this time, the
439 basal and top dressing for wheat and barley were carried out in the study area
440 (November and February, respectively) (Table ST1). This could be the cause of a higher
441 NO_3^- concentration. In these events, the following maximum NO_3^- concentrations
442 (Nmax) were found: “event 2” = $32.12 \text{ mg}\cdot\text{l}^{-1}$, “event 4” = $34.17 \text{ mg}\cdot\text{l}^{-1}$ and “event 12”
443 = $30.28 \text{ mg}\cdot\text{l}^{-1}$ (Table 1). The combined effect of fertilization and the absence of
444 irrigation may cause the accumulation of NO_3^- in the soil, which is then leached by the
445 rains and slowly mobilized to the river. Due to these two reasons, the peak NO_3^-
446 concentration comes later than the water discharge peak and produces a loop with a
447 counterclockwise direction (Williams, 1989).

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

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

465 When the maximum NO_3^- concentration (N_t) in “event 5” ($N_{\text{max}} = 19.18 \text{ mg}\cdot\text{l}^{-1}$)
466 (Table 1) was compared with the other floods, it was observed that the concentration
467 range of this event was more similar to those occurring in the irrigation season than the
468 non-irrigation floods. This result suggests that heavy rains occurring throughout the
469 basin could have caused the rapid mobilization of NO_3^- and its dilution. In this case, the
470 combined influence of the total rainfall ($P_t = 20.72$ mm) and the intensity ($I_f = 0.50$
471 $\text{m}^3\cdot\text{min}^{-2}$) of the flood event could have caused a dilution effect on the NO_3^-
472 concentration and produced a clockwise pattern. As in “event 6”, the last sample

473 showed an elevation of the NO_3^- concentration ($19.18 \text{ mg}\cdot\text{l}^{-1}$) (Fig. 7) in the flow
474 recession limb but in this case, is considerably lower than in the other floods. During the
475 period in which both events took place, the NO_3^- concentrations were high because of
476 the agricultural fertilization performed in that season (Table ST1), but precipitation
477 along the entire basin (PT = 20.72 mm and PT = 29.74 mm in events 5 and 6,
478 respectively) induced a dilution effect. At the end of the rains and with a decreasing
479 water discharge, the NO_3^- concentration was again high. This could be the cause of the
480 location in the dendrogram of both events.

481 Previously, the different groupings of non-irrigation and irrigation floods in the
482 dendrogram have been discussed, but within the irrigation floods, the volume of the IRF
483 could also influence the pollutants pattern. Our results agreed with those of Causapé et
484 al. (2004b). In their study, they divided the agricultural periods into the following 3
485 groups: non-irrigation (winter), low-irrigation (spring-autumn) and high irrigation
486 (summer) and stated that irrigation is a key factor in determining the level and temporal
487 variability of NO_3^- . Likewise, in our research, events that happened in low-irrigation
488 season (event 3, Oct 2010; event 8, Apr 2012; and event 9, Apr 2012) followed
489 anticlockwise loops, and high-irrigation events (event 2, Jun 2010; event 7, May-Jun
490 2011; and event 10, Jul 2012) had a clockwise conduct (Figures 4 and 7). The
491 antecedent wet conditions were reported to result in the peak NO_3^- concentration
492 occurring before the discharge peak (clockwise patterns), whereas dry antecedent soil
493 moisture was related to the NO_3^- flush occurring after the discharge peak (anticlockwise
494 patterns) (Christopher et al., 2008; McNamara et al., 2008; Jiang et al., 2010).

495 Other authors have studied the shape and width of the hysteresis loops relating
496 these parameters with pollutant sources and the season of the year in which these events
497 take place (Rusjan et al., 2008; Oeurng et al., 2010). In this regard, differences were

498 observed between the flood events studied. Among some of hysteresis loops obtained,
499 the widest widths (difference between the NO_3^- concentrations) were found in “events 1
500 and 6” (February 2010 and March 2011, respectively) ($N_{\min} = 17.27 \text{ mg}\cdot\text{l}^{-1}$, $N_{\max} =$
501 $32.12 \text{ mg}\cdot\text{l}^{-1}$ in event 1 and $N_{\min} = 10.56 \text{ mg}\cdot\text{l}^{-1}$, $N_{\max} = 31.92 \text{ mg}\cdot\text{l}^{-1}$ in event 6) (Fig.
502 7). Otherwise, “events 3 and 7” (October 2010 and June 2011) were those with the
503 smallest widths. In general, the differences between the NO_3^- concentrations were
504 greater in non-irrigation season floods. During the irrigation period, the widths
505 decreased and flatter shapes were found. The lower differences within the NO_3^-
506 concentrations in flood events occurring in irrigation season were probably due to the
507 influence of IRF, which contributed to increases in the water discharge and induced
508 dilution of the NO_3^- concentration in the river throughout the season. In the case of non-
509 irrigation season floods, NO_3^- concentrations were lower due to the increased water flow
510 caused by the rain. In low flow periods, NO_3^- concentrations were higher (Fig. 2). This
511 suggests that for the Flumen River, IRF significantly influence the NO_3^- concentrations
512 and the flood patterns as well as the hydrologic regime of the river.

513 **5. Conclusions**

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

520 The Pearson Correlation Matrix showed that the Total Precipitation (Pt), the
521 Maximum rainfall intensity of the flood (I_{\max}), the Flood intensity (I_f), the Mean

522 discharge (Q_m) and the Maximum discharge (Q_{max}) were key factors for the export of
523 NO_3^- in the Flumen River Basin.

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

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

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726

727 **Table captions**

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

730 **Table 2.** Pearson correlation matrix of analysed variables

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

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

734

735 **Figure captions**

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

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

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

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

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

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

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

749