

1 **Identifying spatial and seasonal patterns of river water quality in a semiarid irrigated agricultural**  
2 **Mediterranean basin**

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4 **Nadia Darwiche-Criado<sup>a\*</sup>, Juan José Jiménez<sup>a</sup>, Francisco A. Comín<sup>b</sup>, Ricardo Sorando<sup>b</sup>, José**  
5 **Miguel Sánchez-Pérez<sup>c,d</sup>**

6

7 <sup>a</sup> Instituto Pirenaico de Ecología (IPE-CSIC), Av. Nuestra Señora de la Victoria s/n, 22700. Jaca  
8 (Huesca). SPAIN

9 <sup>b</sup> Instituto Pirenaico de Ecología (IPE-CSIC), Av. Montañana 1005. 50192 Zaragoza. SPAIN

10 <sup>c</sup> Université de Toulouse, INPT, UPS, ECOLAB (Laboratoire Ecologie Fonctionnelle et Environnement),  
11 Ecole Nationale Supérieure Agronomique de Toulouse (ENSAT), Avenue de l'Agrobiopole BP 32607  
12 Auzeville Tolosane, 31326 CASTANET TOLOSAN Cedex, France

13 <sup>d</sup> CNRS, ECOLAB (Laboratoire Ecologie Fonctionnelle), 31326 CASTANET TOLOSAN Cedex, France

14

15 **\*Corresponding author:** Nadia Darwiche-Criado. Phone number: +34 976369393 Ext: 881133. Fax  
16 number: +34 974363222. [nadiadarcri@hotmail.com](mailto:nadiadarcri@hotmail.com), [darwiche@ipe.csic.es](mailto:darwiche@ipe.csic.es)

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19 **Abstract**

20 A detailed understanding of the study area is essential to achieve key information and optimizing the  
21 monitoring, analysis and evaluation of water quality of natural ecosystems that have been highly  
22 transformed into agricultural areas. Using classification techniques like the hierarchical cluster analysis  
23 (CA) and partial triadic analysis (PTA), we assessed the sources of water pollution and the seasonal  
24 influence of human activities in water composition in a river basin from North-eastern Spain. The results  
25 suggested that a strong connection existed between water quality and the seasonality of the human  
26 activities. The CA showed the spatial relationship between water chemistry and the adjacent land uses.  
27 The PTA associated the analyzed variables to their pollutant source. Electrical conductivity (EC), Cl<sup>-</sup>,  
28 SO<sub>4</sub><sup>2-</sup>-S, Na<sup>+</sup> and Mg<sup>2+</sup> ions were related with agricultural sources, whereas NH<sub>4</sub><sup>+</sup>-N, PT and PO<sub>4</sub><sup>3-</sup>-P  
29 were linked with urban polluted sites. Concentration of NO<sub>3</sub><sup>-</sup>-N was associated with urban land use.  
30 Differences in water composition according to the irrigation intensity were also found during the  
31 irrigation season. The statistical tools used in this work, especially the PTA, allowed us to jointly analyze  
32 the spatial and seasonal components of water pollutant trends. We obtained a more comprehensive  
33 knowledge of water quality patterns in the study area, which will be essential when taking measures to  
34 minimize the effects of water pollution.

35 **Keywords:** Water quality, Land use, Spatial analysis, Agricultural Intensification, Irrigation, Partial  
36 Triadic Analysis

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## 1 **1. Introduction**

2 Human activities are a major factor that impacts the quality of surface water and groundwater  
3 through atmospheric pollution, effluent discharges, the utilization of agricultural chemicals, eroded soils  
4 and land use (Niemi et al. 1990). In recent years, research on the ecological impacts of land use changes  
5 has increased with numerous studies suggesting that surface water is affected by land cover  
6 characteristics in the basin drainage areas of streams (Limburg and Schmidt 1990; Jones et al. 1999; Bis  
7 et al. 2000; Riva-Murray et al. 2002; Woodcock et al. 2006). This result indicates that changes in land use  
8 and management practices can have considerable impacts on the quality of water (Brainwood et al. 2004).  
9 As an example, forest land use plays an important role in mitigating the degradation of water quality,  
10 while urban land use substantially modifies the chemical properties of river water by increasing the  
11 concentration of certain elements (Sliva and Williams 2001). Previous studies have shown that  
12 agricultural land uses are one of the primary contributors to the degradation of water quality (Lenat and  
13 Crawford 1994; Tong and Chen 2002) and the primary source of nitrogen in European aquatic  
14 environments (Grizzetti et al. 2005). Excessive utilization of mineral fertilizers and the disposal of  
15 manure cause irrigation agriculture to be identified as one of the primary nutrient sources worldwide  
16 (Baker, 1992). In addition, different studies have investigated the spatial and seasonal variability of water  
17 quality. These studies have reported that water quality issues, such as eutrophication, which are  
18 considerably dependent on land use patterns, are influenced by basin runoff discharge (Caccia and Boyer  
19 2005; Zhang et al. 2007).

20 The interaction of a wide range of human influenced variables, such as land use, fertilizer  
21 utilization, soil type and the hydrological pathways linking the land to a certain stream is difficult to  
22 analyze (Casey and Clarke 1979; Dermine and Lamberts 1987). Moreover, the degradation of water  
23 quality results from multiple land use activities, including both point and non-point sources. While point-  
24 source pollution can be easily identified, non-point source pollution from land uses is a diffuse source of  
25 contamination and it is often difficult to attribute to a single location (Seeboonruang 2012) and depends  
26 on several factors that are easily variable (Causapé et al. 2004). Nevertheless, the temporal patterns of  
27 non-point source pollutants can help us to understand the transport characteristics associated with  
28 hydrological processes (Kang and Lin 2007). In this research, we have studied the Flumen River basin,  
29 which belongs to the Ebro River catchment, in order to identify the spatial and seasonal trends of different  
30 variables and we search for the relationship between the spatio-temporal trends and the land uses present  
31 in the basin. The application of multivariate statistical tools as Partial Triadic Analysis (PTA) allowed us  
32 to improve the evaluation of the water quality patterns, including both the spatial and seasonal factors in a  
33 single analysis. Accordingly, we can optimize the water quality monitoring and obtain a more  
34 comprehensive understanding of the pollutants tendencies.

35 This study aimed to obtain a general overview of the spatial and temporal variability of water  
36 quality and its relationship with the human activities and land uses in the Flumen River basin, in order to  
37 acquire the essential information to perform an appropriate management of the water pollution issue. For  
38 this, (i) we have obtained the characterization of the catchment in terms of water quality and based on the  
39 land uses impacts and (ii) we have identified the sources (both point and non-point inputs) of pollution,  
40 determining its spatial and seasonal patterns.

## 41 **2. Materials and methods**

### 42 **2.1. Study Area**

43 The Flumen River is located in the province of Huesca (Aragón, Spain) in the north-central part  
44 of the Ebro River basin (NE Spain) (Fig. 1). This river is 120 km long and together with its tributary, the  
45 Isuela River, drains a basin area of 1,430 km<sup>2</sup>. The river originates in Guara Sierra, which is a calcareous  
46 pre-Pyrenean mountain chain (1,250 m.a.s.l.). After exiting the mountainous part of the basin, the Flumen  
47 River flows through flat plains that have an increasingly agricultural landscape to its confluence with the  
48 Alcanadre River (240 m.a.s.l.). In this final route, the river crosses quaternary glacia and alluvial fans that  
49 overlay a tertiary structure composed of conglomerates, sandstones and clays (Quirantes 1978). Saline  
50 mudstones and gypsum deposits observed in the lower part of the basin influence the water quality of the  
51 river at lower reaches (Martín-Queller et al. 2010). The Isuela River, which runs parallel to the Flumen  
52 River for one third of its length, is the only perennial tributary and joins the Flumen River in the flat area  
53 of the basin. Other affluents are intermittent discharging water only during big rain storm events and  
54 during the irrigation period.

1 A Mediterranean climate with irregular seasonal and interannual rainfall is a common feature to  
2 the entire basin (Comín and Williams 1993), although a decreasing rainfall gradient of 77.6 mm for every  
3 100 m of altitude change exists from the north mountain region to the flat southern region of the basin.  
4 The average annual rainfall in the basin is 581 mm (Pedrocchi 1998; AEMET 2010).

5 The most important urban areas within the basin include Huesca (52,354 inhabitants), which is  
6 crossed by the Isuela River and discharges effluents from its wastewater treatment plant into it, Sariñena  
7 (4,428 inhabitants) and Grañén (2,038 inhabitants), which both contain wastewater treatment plants, and  
8 Lalueza (1,149 inhabitants), which discharges its wastewater effluents into the Flumen River.

9 The upper part of the study zone is dominated by oak woods and shrublands. The city of Huesca  
10 is located in the middle part but this area also has substantial animal farming and some agricultural  
11 activity. In the lower region, the so-called Northern Monegros County, the principal land use is irrigated  
12 agriculture, in which rice (*Oryza sativa*), corn (*Zea mays*) and alfalfa (*Medicago sativa*) are the most  
13 representative crops. Cereals such as *Triticum spp.* and *Hordeum vulgare* are also cultivated (Fig. 1). In  
14 the study area, the irrigation season occurs from April to October.

15 The Flumen River flows are managed by three reservoirs (Santa Maria de Belsué, Cienfuens and  
16 Montearagón (Fig. 1), which have water storage capacities of 13, 1 and 51 hm<sup>3</sup>, respectively) that are  
17 located in the upper third part of the river. The Isuela River is regulated by the Arguis reservoir (2.7 hm<sup>3</sup>),  
18 which is also located in the upper part of the river. Furthermore, in the lower half of the basin, the so-  
19 called Northern Monegros County, there is a complex system of small irrigation canals that distribute the  
20 water transported by a large irrigation canal: the Monegros canal. The Monegros canal is created by  
21 joining the waters supplied by another two large canals that transport water from two rivers (Cinca and  
22 Gállego) outside the Flumen basin. In this lower part of the basin, there are many small artificial ponds  
23 that store rain and canal water to be used later for irrigation purposes.

## 24 2.2. Water sampling and analytical methods

25 A two-step sampling was employed.

- 26 1. Sampling A: water samples were collected in different places throughout the entire basin  
27 (November 2009, January and February 2010) in order to obtain an overall perspective of the  
28 land uses influence on water quality during the non-irrigation season. A total of 15 samples were  
29 collected on each date, including 9 from the Flumen River (F1-F9) and 6 from the Isuela River  
30 (I1-I6) (Fig. 1). F1, I1 and I2 are located in the northern part of the basin area, upstream from the  
31 principal urban and agricultural inputs. F2 and F3 are situated at the surrounding areas of  
32 villages near Huesca. I3 is located at the entry of Huesca city, and I4 and I5 are placed before  
33 and after the sewage treatment plant respectively. Finally, the last group of sampling stations,  
34 from F4 to F9 and I6, were located in the agricultural part of the basin.
- 35 2. Sampling B: After describing the whole basing in terms of water quality, several sites were  
36 selected according to their potential pollution vulnerability during the warm and hot periods of  
37 the year in which agriculture is intensively irrigated. Six sampling times were established: April,  
38 June, July, August, September and October 2010. A total of 11 samples were collected during  
39 each sampling date, including 6 samples from the Flumen River (F4-F9) and 5 samples from the  
40 Isuela River (I2-I6). Two new sampling stations located in irrigation canals (IC1 and IC2) were  
41 included to determine the influence of irrigation return flows on the water quality of the river  
42 (Fig. 1). Samples were also collected from another sampling station, named IW, which  
43 corresponds to the discharge from the sewage treatment plant on the Isuela River.

44 The sampling stations were chosen regarding to the spatial distribution of major land uses in the  
45 basin, including forest, urban and agricultural land uses (Fig. 1). The sampling dates were selected  
46 according to the agricultural activities of the study area, which were based on the dates for irrigation and  
47 the application of fertilizers for each crop (table 1).

48 Direct measurements of water temperature (T), pH, electrical conductivity (EC) and dissolved  
49 oxygen (DO) were determined in the river sampling sites using a calibrated multi-parameter probe. Water  
50 samples from the same sites were collected in polyethylene bottles that were previously rinsed three times  
51 with distilled water. After collection, the samples were transported to the lab and filtered with a Whatman

1 GF/F 0.7  $\mu\text{m}$  fiberglass filter. The samples were stored at 4°C within 12 hours for later (within one  
2 month) analysis of suspended solids (SS), ammonium ( $\text{NH}_4^+\text{-N}$ ), nitrite ( $\text{NO}_2\text{-N}$ ), nitrate ( $\text{NO}_3^-\text{-N}$ ),  
3 phosphate ( $\text{PO}_4^{3-}\text{-P}$ ), total dissolved phosphorus (TDP), chloride ( $\text{Cl}^-$ ), sulphate ( $\text{SO}_4^{2-}\text{-S}$ ), sodium ( $\text{Na}^+$ ),  
4 potassium ( $\text{K}^+$ ), calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), dissolved organic carbon (DOC), total dissolved  
5 nitrogen (TDN), fluoride ( $\text{F}^-$ ) and bromide ( $\text{Br}^-$ ) using standard methods (APHA, 2012). The analysis of  
6 suspended solids (SS) was performed by means the weight difference of the filter before and after  
7 filtering. The total phosphorous (TP) and the alkalinity (Alk) were determined using an unfiltered water  
8 sample.

## 9 **2.3. Data Analysis**

### 10 **2.3.1. Hierarchical cluster analysis**

11 Hierarchical cluster analysis (CA) was used to obtain the spatial grouping of all sampling sites in  
12 the entire basin during non-irrigation season (Sampling A). This analysis was conducted using the R  
13 software (R Development Core Team, 2011) and the HCLUST package and the DIST function were used  
14 to perform the hierarchical classification and to compute the matrix of distances respectively. The Ward  
15 method was applied in order to achieve the optimal classification (Kuiper and Fisher 1975). The  
16 Euclidean distance was used because is the recommended measure when Ward's method of clustering is  
17 applied (Hair et al. 2006). It was represented by the difference between the analytical values from the  
18 samples and aimed to reveal the similarity between samples. Data were previously standardized through a  
19 z-scale transformation to eliminate the influence of different units of measurements.

20 The CA was conducted with data obtained from “Sampling A” in order to obtain a land use  
21 classification within the basin based on water quality of each sampling station.

### 22 **2.3.2. Partial Triadic Analysis (PTA)**

23 Multivariate statistical approaches rely mainly on Principal Component Analysis (PCA) for  
24 assessment of hydrological patterns in basins (Valder et al. 2012). In this study we used Partial Triadic  
25 Analysis (PTA) (Thioulouse and Chessel 1987; Kroonenberg 1989), that allows analyses of data matrices  
26 with a cubic structure, i.e. variables  $\times$  sites  $\times$  time (Thioulouse and Chessel 1987; Kroonenberg 1989;  
27 Rossi 2003). This analysis aims at extracting the common multivariate structure from the sampling dates  
28 and describes dominant patterns in its first axes that are retained for interpretation (Rossi 2003).

29 The first step is the Inter-structure analysis which determines the information that is common to  
30 all the samples dates using a PCA, i.e. provides a global description of sampling points as a function of  
31 the typology of the sampling dates (Jiménez et al. 2006). The comparison of the sampling dates is  
32 performed with calculation of a vectorial correlation coefficient matrix ( $R_V$ ) between samples dates and  
33 the representation of the proximity between dates that depend on the analyzed variables.

34 The second step is the Compromise analysis where a mean matrix of maximum inertia (referred  
35 to as the compromise matrix) is constructed. This matrix is derived from the initial temporal sub-matrices  
36 in proportion to their weight. A dimensionless value is obtained, the  $\cos^2$ , indicates how much the  
37 compromise expresses the information contained in each sub-matrix. This new matrix that represents the  
38 vectorial correlations between the different sampling dates and sub-matrices ( $R_V$  coefficients) reveals the  
39 intensity of the linkages among the different temporal sub-matrices (Rolland et al. 2009). This step allows  
40 a description of sampling sites as functions of the typology of variables and the identification of the  
41 variables responsible for similar patterns at different dates (Jiménez et al. 2006).

42 The PTA was carried out with data obtained from “Sampling B”. This analysis was focused on  
43 the agricultural part of the basin defined by CA in order to obtain the water quality patterns during the  
44 irrigation season. Six temporal matrices were used: April, June, July, August, September and October  
45 2010.

46 The PTA was conducted with the ADE4 package in the software R 2.13.0 (R Development Core  
47 Team 2011).

### 1 3. Results

2 The mean values of all variables analyzed in each sampling station are listed in table 2.

#### 3 3.1. Spatial distribution of river water characteristics

4 The CA resulted in a dendrogram that exhibited a first division with two big clusters (Fig. 2).

5 Cluster 1 included the sampling stations F1 and I2. These sites are located in the upper part of  
6 the basin are primarily covered by forest and thus, are less affected by pollution from urban and  
7 agricultural uses.

8 Cluster 2 revealed a change in land use from the mountain area to urban or agricultural zones and  
9 also denoted a change in water quality. Cluster 2 was composed of two minor groups. The first one  
10 included the sampling stations I3, I4 and I5, which are located in the surrounding of urban environments.  
11 Sampling stations located in agricultural areas were congregated in the other cluster. This last group was  
12 also composed of two minor clusters of sampling stations differentiated by the type of agricultural  
13 practices. The first one was composed of I1, F2 and F3, which are located in areas with small farms,  
14 rainfed crops and small towns. The other cluster was formed of sampling stations F4, F5, F6, F7, I6, F8  
15 and F9, which are located in the southern part of the basin in which intensive irrigated agriculture occurs.  
16 Additionally, there was a distinction between the group of sampling stations F4, F5 and F6, which are  
17 located in the initial part of the irrigated agricultural area, and the group formed by the sampling stations  
18 F7, F8 and F9, which are located in the final part of the basin in which the most intensive irrigation and  
19 water drainage associated with rice fields occur.

#### 20 3.2. Spatiotemporal pattern in the agricultural zone of the basin during irrigation season

##### 21 3.2.1. Inter-structure Analysis

22 The Inter-structure analysis revealed that the first two axes of the PCA retained 69.3 and 9.7 %  
23 of total variance, respectively. The structure extracted in axis I indicated a common spatial pattern across  
24 the different dates during the study period. The representation of the sampling dates onto the factorial  
25 plane revealed a strong common temporal structure, i.e., no inversion of the temporal structure of the  
26 analyzed variables was observed. In axis II, the inter-structure analysis emphasized the segregation of the  
27 information corresponding to every date in three groups. This result indicated differences in the dynamics  
28 of the variables measured in each group of dates. The first group included only October 2010, the second  
29 group included April, June and September 2010 and the third group included July and August 2010 (Fig.  
30 3A). The remaining eigenvectors explained only a small part of the inertia, but such distribution in the  
31 Euclidean space suggested the existence of three main alternatives in the identified temporal pattern.  
32 Matrix of vectorial correlation coefficients between the tables showed the strongest correlation ( $R_V =$   
33  $0.737$ ) between June and April, whereas the weakest correlation ( $R_V = 0.307$ ) occurred between August  
34 and October (table 3). Based on the information revealed by  $\cos^2$ , it was observed that the matrix  
35 corresponding to September-2010 contributed most to the temporal dynamics of the analyzed variables  
36 (Fig. 3D).

##### 37 3.2.2. Compromise Analysis

38 In the compromise analysis, the screen plot of eigenvalues showed that the two first axes  
39 accounted for 70.9 % of total inertia. Axis I of PCA (44.5 % of total inertia) revealed a clear organization  
40 of variables related to salinity ( $Mg^{2+}$ ,  $SO_4^{2-}$ -S, Alk, EC,  $Cl^-$ ,  $Na^+$ ,  $Br^-$  and  $F^-$ ) and nitrogen compounds  
41 (TDN and  $NO_3^-$ -N). Axis II accounted for 26.4 % of the total inertia and was related with nutrients like  
42  $NH_4^+$ -N,  $PO_4^{3-}$ -P and TP. T,  $NO_2^-$ -N, DOC and DO were close to the origin of both axes. No particular  
43 pattern was observed for SS and pH (Fig. 3B).

44 Map of factorial coordinates of the 10 sampling stations (Fig. 3C) also revealed a clear spatial  
45 variation. Sampling stations located in intensive agricultural zone (IC1, F8, F9, IC2) were linked to  
46 variables related to salinity ( $Na^+$ ,  $Cl^-$ , EC,  $Br^-$ ,  $F^-$ ), whereas sampling station IW, which represents the  
47 discharge from the wastewater treatment plant, and I6, which is in the Isuela river downstream from the  
48 wastewater treatment plan, were associated with TDN and  $NO_3^-$ -N and  $NH_4^+$ -N, TP and  $K^+$  respectively.

49

## 1 4. Discussion

### 2 4.1. General ordination of sampling sites

3 A few studies have shown that land use near rivers is a better indicator of water quality than land  
4 use of the entire basin (Osborne and Wiley 1988; Hunsaker and Levine 1995). These results agree with  
5 those of our study because the dendrogram obtained with “Sampling A” data revealed the grouping of  
6 sampling stations based on their adjacent land use (Fig. 3B). Two major areas of the Flumen River basin  
7 could be distinguished after the CA (Fig. 2): the northern part, which had a better water quality in the  
8 upper mountainous basin, and the mid-south area, which had a higher level of water pollution in the lower  
9 agricultural area of the basin.

10 But dendrogram also revealed a differentiation based on the source of pollution, either urban or  
11 agricultural. Our results were consistent with those reported by Martín-Queller et al. (2010), who  
12 indicated that the primary sources of contamination in the Flumen River were the discharges from the city  
13 of Huesca and those from the agricultural area. Group 2 contained sampling stations located in urban  
14 areas (I3, I4 and I5). And group 3 was formed by F2, F3 and I1 that are situated near small towns with no  
15 industrial activity. In this case, water quality was found to be only moderately polluted by agricultural  
16 practices (Jain 2002). Nevertheless, grouping of F2, F3 and I1 could be due to the regulation of water  
17 flow by the nearby reservoirs (Fig. 1).

18 It was also possible to note a new division in two subgroups related to the level of water  
19 pollution and to the increasing intensity of agricultural practices. F6, F4, and F5 are placed at the upper  
20 part of the agricultural area and still reflected non-intensive agricultural practices. Moreover, F7, F8 and  
21 F9 are found in the southernmost part of the basin and corresponded to typical river locations in areas  
22 with intensive irrigated agriculture. I6 is the final sampling station belonging to the Isuela River after  
23 crossing the urban area and before it flows into the Flumen River. This sampling station could be grouped  
24 with this cluster because it had similar high  $\text{NO}_3^-$ -N concentrations and EC (table 2), probably caused by  
25 inputs of Huesca and wastewater treatment plant.

26 The clustering distribution of the sampling stations followed a spatial pattern from the upper  
27 mountain to the lower agricultural parts of the river. This distribution is not simply a change of the river  
28 water characteristics as water progresses through the basin contributing to dissolve ions and particulate  
29 compounds. This fact reflects the impacts from land uses as significantly increased concentrations of  
30 variables associated to agricultural land use practices (e.g.,  $\text{NO}_3^-$ -N).

### 31 4.2. Spatiotemporal variability of water quality during irrigation season

32 Human activities on land use changes could influence the types and degree of pollution (Bu et al.  
33 2014). In this regard, the analysis of inter-structure and distribution of variables in the Euclidean space  
34 revealed the relationship between the physico-chemical parameters and the agricultural practices  
35 performed at each sampling date. The analysis of inter-structure showed the clustering of sampling dates  
36 based on agricultural periods (Fig. 3A). This grouping was related to the different agricultural seasons in  
37 the study area (Causapé et al. 2004): non-irrigation (Oct-10, since this sampling was performed at the end  
38 of the irrigation season), low-irrigation (Jun-10, Apr-10 and Sep-10) and high irrigation or summer (Jul-  
39 10 and Aug-10). Causapé et al. (2004) reported high irrigation volumes, low EC and moderate  $\text{NO}_3^-$ -N  
40 concentrations during high irrigation period. The low irrigation period had similar EC and  $\text{NO}_3^-$ -N values  
41 but much lowers volumes of irrigation and finally, the non-irrigation period was characterized by lack of  
42 irrigation and the highest EC and  $\text{NO}_3^-$ -N values, indicating the inefficient flood-irrigation management  
43 that generates high return flows with relatively low salt and nitrate contents. This fact reported that  
44 irrigation is a key factor in water composition and its seasonality. Our results agreed with those of  
45 Causapé et al. (2004), but our study also indicated a relationship between water quality and other  
46 agricultural practices conducted in the study area. The distribution of variables in the Euclidean space was  
47 dependent on sampling date (Fig. 3B). The  $R_v$  coefficient matrix allowed the comparison of the sampling  
48 dates and the representation of proximity between dates depending on the analyzed variables. This matrix  
49 exhibited the strongest correlation between Apr-10 and Jun-10 ( $R_v = 0.737$ , table 3). It is during these  
50 months when base dressing for rice and corn is performed (April and June respectively, table 1). As  
51 shown in similar research of the study area (Darwiche-Criado et al. 2015), these results indicated that the  
52 analyzed variables followed a spatiotemporal pattern influenced by the seasonality of adjacent land uses.

1 In the analysis of compromise, axis I explained the influence of agriculture on water quality in  
2 the southern part of the catchment. Sampling stations with highest values on axis I were those located in  
3 the agricultural zone of the basin (F8, F9, IC1 and IC2), and were related to  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ -S,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  
4 EC (Fig. 3B and C). This fact exposed the influence of agricultural activities on water pollution and is  
5 also related with soil sanitization of agricultural areas in the southern part of the basin (Pedrocchi 1998).  
6 Nevertheless, other saline compounds were not associated with this axis and this could be due to the  
7 period in which "Sampling B" was carried out (irrigation season) and thus, to the influence of irrigation  
8 return flows. In Monegros County, high-irrigation season occurs in the summer month's causing a  
9 dilution of salts concentrations (Causapé et al. 2004). Similar studies performed at the lower part of the  
10 basin (Martín-Queller et al. 2010) have reported results of  $\text{EC} = 450 \mu\text{S}\cdot\text{cm}^{-1}$  during irrigation season and  
11  $\text{EC} = 1550 \mu\text{S}\cdot\text{cm}^{-1}$  during non-irrigation season. This fact could explain the different position in the  
12 Euclidean space of these saline compounds.

13  $\text{NO}_3^-$ -N also contributed to the definition of axis I. Monteagudo et al. (2012) reported the greater  
14 influence of irrigation practices in  $\text{NO}_3^-$ -N export than non-irrigated agriculture. However and due to its  
15 location in the Euclidean space, our results showed this sampling site was linked with an urban origin:  
16 Huesca wastewater contribution (IW) (Fig.4B and C). In this regard, other studies (Osborne and Wiley  
17 1988; Sliva and Williams 2001; Ngoye and Machiwa 2004) also noted elevated  $\text{NO}_3^-$ -N concentrations in  
18 the streams of urbanized areas.

19 The variables  $\text{NH}_4^+$ -N, TP and  $\text{PO}_4^{3-}$ -P positively contributed to the definition of axis II and  
20 could represent the influence of urban inputs on water quality too. These variables were related to  
21 sampling stations I6 and F6, which received inputs from the city of Huesca. Previous studies have  
22 reported that the primary source of P and  $\text{NH}_4^+$ -N are the urban inputs (Mendiguchía et al. 2007; Neal et  
23 al. 2000; Sánchez-Pérez et al. 2009) and similarly for case of  $\text{NO}_2^-$ -N (Martín-Queller et al. 2010).  
24 Braimwood et al. (2004) also observed that urban basins were highly correlated with  $\text{NH}_4^+$  ions and  
25 reactive  $\text{PO}_4^{3-}$ -P. Perona et al. (1999) considered that in spring and summer, presence of holiday-makers  
26 leads to a high population density in the residential buildings and recreation areas influencing the nutrient  
27 content of the river. But besides the influence of seasonal component, different distribution of variables  
28 with an urban origin could also indicate dissimilar sources of urban pollution. For instance, while  $\text{NO}_3^-$ -N  
29 could be originated from a point source of pollution (IW, discharge from the wastewater treatment plant  
30 of Huesca city),  $\text{NH}_4^+$ -N, PT and  $\text{PO}_4^{3-}$ -P may arise from different urban runoffs and thus from a non-  
31 point source (Sliva and Williams 2001).

32 In the case of SS, Rovira and Batalla (2006) reported that at the annual scale, the SS  
33 concentration exhibits a high inter-annual variability according to the number of floods recorded yearly  
34 because almost all the suspended load is transported during these events. This result could be the reason  
35 for why the SS location in the Euclidean space is separate from the other variables. This parameter is  
36 more closely linked to punctual flood events that to the seasonal variations. Oeurng et al. (2011) also  
37 reported similar effects.

## 38 5. Conclusions

39 The results of this study revealed the influence of human activities on water quality. The  
40 analyses carried out in this study allowed characterizing spatial and seasonal impacts of land uses in  
41 Flumen River basin. In urban and agricultural areas, the analyzed variables followed spatio-temporal  
42 patterns caused by seasonal variability of the adjacent land uses. In addition to the type of land use, its  
43 seasonality was an essential component that influenced the behavior and the pollutants concentration.  
44 During the irrigation season, differences in water composition according to the irrigation intensity were  
45 found. We also identified the pollutant sources and we distinguished its point or non-point character.

46 The proper management of this environmental problem must come from the overall knowledge  
47 of the river basin and its processes, as well as factors and underlying causes. The information acquired  
48 throughout this work will be crucial when taking measures to minimize the effects of water pollution.

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33 **Table captions**

34 **Table 1.** Times of agricultural activities in the Flumen River basin.

35 **Table 2.** Mean values of analyzed variables in each sampling station.

36 **Table 3.** Matrix of vectorial correlation coefficients between the tables (RV).

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1 **Figure captions**

2 **Fig. 1** Location of the Flumen River catchment in the Ebro basin, land use distribution and sampling  
3 stations within the study area.

4 **Fig. 2** Dendrogram of Cluster Analysis classifying sampling stations corresponding to “Sampling A”.

5 **Fig. 3** Ordination of sampling dates on the factorial plane defined by the first two axes of the PCA on the  
6 inter-structure matrix in PTA-1(A). The compromise analysis. Coordinates of analyzed variables in the  
7 first plane (axes I–II) of the compromise and histogram of eigenvalues identifying the prominence of the  
8 two first axes that define the average spatial structure (B). Projections of the sampling stations in the first  
9 plane (axes I–II) of the compromise (C). Weight of each table ( $\alpha_k$ ) in the construction of the compromise,  
10 and quality index of the compromise’s structure ( $\cos^2$ ) for each sampling date (D).