Runoff, nutrients, sediment and salt yields in an irrigated watershed in southern Navarre (Spain)


ABSTRACT

The environmental impact of irrigated agriculture on water quality was assessed in Landazuria watershed (Navarre, northeast Spain), a 479.5 ha watershed with 53% of irrigated agricultural land. In the framework of a long-term monitoring program, precipitation and discharge were measured at 10-minutes intervals and compound daily water samples were collected during the agricultural years (September to August) 2007-2016, and analysed for nitrate (NO₃⁻), phosphate (PO₄³⁻), sediment and total dissolved solids (TDS) concentrations. Typical agricultural management (including crop surfaces, irrigation and fertilization rates) was obtained from inquiries to farmers. Concentration and yield of the studied variables presented a high degree of variation, both intra- and inter-annual. Median concentration for the entire study period were 185, <0.05, 31 and 2284 mg L⁻¹ for NO₃⁻, PO₄³⁻, sediment and TDS, respectively. NO₃⁻-N and PO₄³⁻-P yields averaged 74 and 0.04 kg ha⁻¹ year⁻¹, respectively. NO₃⁻-N yield was higher than in other...
agricultural land uses in Navarre and in the order of magnitude of other irrigated areas in the Middle Ebro Valley. PO$_4^{3-}$-P yield was in the same order of magnitude than in rainfed watersheds in Navarre but lower than in intensively grazed watersheds. Sediment yield was extremely variable, averaging 360 kg ha$^{-1}$ year$^{-1}$, with 44 % of the total measured load recorded in a few days. It was in the lower range of those measured in Navarre for rainfed agriculture and similar to those estimated in other irrigated areas of the Middle Ebro River. TDS concentration presented a significant decreasing trend since available salts were being washed out, while TDS yield averaged 1.8 Mg ha$^{-1}$ year$^{-1}$. Long-term monitoring of irrigated areas is required to understand pollution processes in these agroecosystems and to adequately characterize the environmental impact of current agricultural practices on water quality, in order to implement, and adequately assess, measures to reduce agricultural pollution.

**Keywords:** watershed, agricultural pollution, nitrate, phosphate, soil loss, TDS.
1. Introduction

More than 1.5 billion ha (about 12% of the world’s land area) are used for crop production. Rainfed agriculture is the predominant agricultural production system, but increasing climate variability is bringing greater uncertainty in the production levels. Current productivity in rainfed systems is, on average, little more than half of its potential (FAO, 2013). However, agricultural production has grown between 2 and 4% per year over the last 50 years, while the cultivated area has grown by only 1% annually. More than 40% of the increase in food production has come from irrigated areas.

Irrigation has many advantages over rainfed agriculture, such as increased productivity, higher diversity of crops, more reliable harvests, or regional economic security (e.g., Duncan et al., 2008). For these reasons, a global increase in irrigated surface has been observed, especially in developing countries, where it doubled between 1962 and 1998 (FAO, 2003a). In Spain, the increase of irrigated area has been moderate but significant, with 7% more irrigated land between 1990 and 2009 according to the Spanish Ministry of Agriculture and Fisheries, Food and Environment (MAPAMA, 2017). In fact, irrigated agriculture has been a key factor in the agrarian Spanish system as it provides more than 50% of the final agrarian production with only 13% of the surface. According to official estimates, in Spain an irrigated hectare produces, on average, six times more than a rainfed hectare, and generates four times more income. In Navarre (10,391 km², northern Spain), irrigated surface has increased in recent years to over 110,000 ha (approximately 25% growth between 2000 and 2015; DDRMAAL, 2017), being pressurized districts those implemented in the new irrigated land.

There is no question about the value of irrigated agriculture but there is an increasing trend to make it accountable for its impacts on the environment (e.g., Stockle, 2001). Agricultural land use is regarded as the main source of diffuse pollution (Novotny, 1999), and it has a wide range of associated environmental impacts such as changes in
landscapes and plant and animal communities, and the deterioration of soil, water and air quality (Stoate et al., 2001; Merrington et al., 2002). Specifically, irrigated agriculture imposes severe pressure on the environment, as it accounts for the consumption of 70% of global water resources (FAO, 2003b), being the main reason behind the construction of most dams or aquifers overexploitation. Apart from the effects on the withdrawal water body, irrigation return flows can also cause hydrological changes in the receiving ones. Specific environmental problems in waters downstream of the irrigated areas are related, among others, to nutrients, sediments or salts.

Nitrate pollution is a major concern in irrigated areas since high nitrate concentrations have long been regarded as a threat for human health and ecosystems (e.g., Sutton et al., 2011). Despite the fact that nitrate leaching varies considerably with climatic conditions (e.g., Elmi et al., 2004), the actual impact of N pollution depends on specific features of the area such as the soil types (Kyllmar et al., 2014), the presence of reducing conditions in aquifers (Rivett et al., 2008) and the irrigation/fertilization management (Quemada et al., 2013). On the other hand, the mobility of phosphorus is rather limited, especially in arid or semi-arid regions (Brady and Weil, 2008). In these soils, only a small fraction of P is in soluble reactive form (phosphate) and can be incorporated into plants. For this reason, P losses are normally related to soil or sediment losses (Edwards and Withers, 1998). As a consequence, P pollution is greatly conditioned by erosion, especially in arid and semi-arid areas.

Erosion processes in agricultural land tend to be significantly higher than in other land uses (García-Ruiz et al., 2015). Erosion removes preferentially the fine fraction of soils, which is enriched in nutrients and organic matter (Merrington et al., 2002). Soil erosion rates are extremely variable (García-Ruiz et al., 2015) and depend on both natural factors (climate, slope, soils, bedrock…) and agronomic management (cover, tillage…). Finally, the leaching of salts is a requirement of irrigated agriculture (Letey et al., 2011)
since its build-up in soils can be deleterious for plants, decrease productivity and even force the abandonment of cultivation. However, leached salts will reach water bodies downstream, affecting its quality for human consumption or ecosystem uses (Nielsen et al., 2003). The amount of salts leached depends on different factors such as climate, hydrogeological conditions or irrigation management (Merchán et al., 2015c).

In Navarre, the environmental impact of agriculture is investigated in a network of experimental watersheds (Fig. 1) implemented by the former Department of Agriculture, Livestock and Food of the Government of Navarre. This network includes representative agricultural land-uses in the region (Casalí et al., 2008, 2010). An irrigated watershed (Landazuria) was included in the monitoring network in 2006. The climatic, geologic and agronomic characteristics of this watershed make it representative of the recent pressurized irrigated areas in the Middle Ebro Valley, with over 900,000 ha dedicated to irrigated agriculture, and approximately half of this surface being pressurized irrigation systems (CHE, 2017). In addition, in the framework of the project LIFE-Nitrates (LIFE+10 ENV/ES/478), a consortium of public institutions constituted by the Government of Navarre (GN), Environmental Management of Navarre (GAN), Navarre Institute of Agricultural and Food Technologies and Infrastructures (INTIA) and CRANA Foundation conducted a detailed study on the “Impacts of agricultural practices on nitrate pollution of continental waters” (www.life-nitratos.eu/). One of the study sites investigated in this project was the irrigated watershed monitored by the Government of Navarre.

In this paper we present the data obtained during the agricultural years 2007-2016 in the irrigated watershed (Landazuria). Given the high variability in climatic and agronomic conditions in specific study cases and the different processes affecting different pollutants, the analysis of detailed and long-term temporal series of a wide set of variables is paramount to better understand the pollution of water bodies as a consequence of agricultural land use, particularly in irrigated areas. The main objectives
were: (1) to estimate the effects of irrigated agriculture on water quality, specifically in terms of nitrate, phosphate, sediment and salts concentration in the watershed outlet and exported yields; (2) to determine the controlling factors explaining that behaviour; and (3) to contextualize the obtained estimations and inferred controlling factors with those reported in other irrigated and rainfed watersheds, paying especial attention to the difference between them.

2. Methods

2.1. Experimental watershed

Landazuria watershed covers an area of 479.5 ha and is located in southern Navarre (Fig. 1). It is relatively flat, with slopes between 3.5 and 5%. A single 1st order stream drains the watershed. The geographical coordinates of the watershed outlet are 42º15’3.5’’N and 1º35’3.4’’W. According to data collected for the period 1992-2016 around 5 km south (meteorological station Bardenas-El Yugo, Government of Navarra) the climate in the study zone is Dry Mediterranean. Average annual temperature is 14 ºC, but it can reach values as low as -8 ºC in winter and as high as 41 ºC in summer. Annual precipitation is 426 ± 114 mm (average ± standard deviation) whereas annual reference evapotranspiration (FAO Penman-Monteith, Allen et al., 1998) is 1369 ± 101 mm, i.e., more than three times higher and much less variable.

The geology in Landazuria is represented by Tertiary and Quaternary materials. The Tertiary materials appear as a bottom layer several hundred metres thick, composed of alternating gypsum, and red clays, with occasional intercalations of fine (centimetres to decimetres) limestone layers (DOPTC, 2003a, 2003b). The Quaternary materials cover in most of the watershed surface the Tertiary materials, and they are composed mainly by detrital sediments, gravels with some limestone clasts, alternating with sands, silt and clays (glacis) of Pleistocene-Holocene age. The synclinal structure and extremely low hydraulic conductivity of the Tertiary materials (<10⁻⁸ m s⁻¹; DOPTC, 2003a, 2003b) avoids deep percolation of water within the watershed.
According to a detailed survey including 78 direct observations (Government of Navarre, 2005), soils developed in Landazuria present mainly clay loam or silt loam textures and are deep, with the exception of eroded hills (Fig. 1c). The most common series correspond to Typic Haplustepts and Typic Calciustolls, although other series do appear (Fig. 2 and Table 1). Organic matter content ranged between 1.7 and 2.7 % while pH ranged between 8.1 and 8.9. Landazuria soils presented in general low salinity, with some slight to moderate salinity level in the valley bottoms and in soils developed over Tertiary marls.

Around 88.3 % of Landazuria is cultivated land and 11.7 % streams, riparian vegetation, bare soils, ways and rock outcrops (Fig. 1b). In the year 1999, a surface of 252.9 ha was equipped for pressurized irrigation (59.7 % of cultivated land) whereas the rest of the surface remained as rainfed agriculture (170.5 ha or 40.3 % of cultivated land). According to face-to-face farmers’ inquiries (INTIA, 2017), the main crops under irrigation where maize, winter cereal, tomatoes and onions (Table 1). Rainfed surface was dominated by barley, although it is worthy to mention that rainfed agriculture in Landazuria followed a cultivation system in which the land is left bare one out of two years (Table 1).

The irrigation system more widely used in Landazuria is solid-set sprinkler irrigation (89%), although minor surfaces of drip irrigation do exist (e.g., tomatoes). The pressure is provided by the difference in elevation between a reservoir or several distribution ponds and the agricultural plots. The origin of irrigation water is a neighbour watershed, so irrigation implies in an additional input in Landazuria. Irrigation volumes applied were estimated according to the recommendations provided by INTIA, based on the irrigation requirement of the crops. To this end, reference evapotranspiration ($ET_0$) computed by the FAO Penman-Monteith methodology (Allen el al., 1998) was used in combination with crop coefficients to obtain crop evapotranspiration ($ET_C = K_C \cdot ET_0$). The amount of
water provided by precipitation was considered and an irrigation efficiency of 85% and 
95% was assumed for sprinkler and drip irrigation systems, typical values used by the 
agricultural extension service in the region.

Fertilization practices varied widely among crops and, especially, between irrigated and 
rainfed surfaces. Detailed information about fertilization practices for the period 2007 – 
2013 was available for this study (Table 1). According to the aforementioned farmers 
inquiries (INTIA, 2017), nitrogen fertilization rates in the rainfed surface averaged 32 kg 
N ha⁻¹ year⁻¹, while in the irrigated surface they averaged 208 kg N ha⁻¹ year⁻¹, that is, 
6.5 times higher (Table 1). This fact combined with the fallow land proportion in the 
rainfed surface and the existence of double cropping patterns in irrigated surface (Table 
1) implies that rainfed crops fertilization accounted only for 4.3 % of N fertilization in the 
study area.

Maize was the crop with highest fertilization rates, between 224 and 423 kg N ha⁻¹ year⁻¹ (average of 285 kg N ha⁻¹ year⁻¹). Maize fertilization was carried in two steps in most of 
the cases, complex fertilizer as basal application (normally 18-46-0, 9-23-30 or 8-15-15) 
followed by urea or liquid fertilizers (e.g., N32 solution) as topdressing. Irrigated winter 
cereal (barley and wheat) received around 138 kg N ha⁻¹ year⁻¹ split in December and 
February-March. Tomato received 218 kg N ha⁻¹ year⁻¹ in several applications, normally 
complex fertilizers as basal application before seeding followed by two topdressing 
applications of liquid N32 (fertigation). Onion received 168 kg N ha⁻¹ year⁻¹ normally in 
two applications with significant contents of sulphur (e.g., ammonium nitrosulphate). 
Among rainfed crops, barley received 48 kg N ha⁻¹ year⁻¹ normally in a unique basal 
application as complex fertilizers. Fertilization rates regarding other nutrients such as P, 
K or S were not systematically collected since they were out of the scope of the LIFE-
Nitrates project. Only partial information was available (for instance, that recorded when
complex NPK fertilizer were applied) and therefore it was not analysed in detail in this study.

Considering all ploughing methods, for the period with available data, an average of 689 ha year\(^{-1}\) were ploughed, i.e., 63% more than the arable land, since several plots were ploughed in several occasions during the year (INTIA, 2017). 80.6% of the total ploughed surface was irrigated land, whereas 19.4% was rainfed land, what implies that, as an average, irrigated land was ploughed twice a year while rainfed land was not ploughed each year, as expected given the high proportion of fallow land. This fact together with the fertilization rates aforementioned denotes the intense use of irrigated land in Landazuria in comparison with that of rainfed land. Ploughing actuations were mainly carried out in two different periods: between February and April (47% of ploughed surface) and between August and October (22%). The remaining months in the year together accounted for 31% of the ploughed surface.

Average productions for the period 2007-2013 were 11,850 kg ha\(^{-1}\) for maize, over 90,000 kg ha\(^{-1}\) for tomato, 68,500 kg ha\(^{-1}\) for onion, 6,150 and 1,500 kg ha\(^{-1}\) for irrigated and rainfed wheat, respectively, and 5,600 and 2,100 kg ha\(^{-1}\) for irrigated and rainfed barley, respectively (INTIA, 2017). It is worthy to note the different productions attained under irrigated and rainfed conditions given the local conditions in Landazuria.

Although a great degree of variation is expected depending on the specific study site, due to its climatological, geological and agronomic characteristics, Landazuria watershed may be regarded as representative of the new pressurized irrigation districts that have been implemented in the Middle Ebro Valley during the last decades.

\textit{2.2. Data collection}
The former Department of Agriculture, Livestock and Food of the Government of Navarre installed a hydrological station at the watershed outlet in the summer of 2006. Since then, water level was recorded at 10 minutes intervals. The discharge measurement device consisted of an H-type flume. Discharge was calculated from water level data, which were monitored using a pressure probe and data logger. According to the hydraulic characteristics of the weir, the following rating curve was used to transform the water level ($h$, m) in discharge ($Q$, L s$^{-1}$):

$$Q = 449.11 \cdot h^3 + 622.19 \cdot h^2 + 8.4101 \cdot h + 0.2248$$  [Eq. 1]

Water discharge was also directly measured for verification using a propeller-type current meter and triangular and rectangular sharp-crested weirs. All measurement methods yielded consistent results.

Water samples were taken every 6 hours from a hemispheric hollow, 0.66 m in diameter, made in the downstream face of the H-type flume. For this purpose, an automatic programmable sampler was used, consisting of 24 bottles (500 mL). The four samples collected each day were mixed together prior to analysis to provide a representative daily average sample for determining sediment and nutrient concentration (Isidoro et al., 2003). Water samples were analysed following the standard methods for water quality parameter at the Agricultural Laboratory of the Department of Agriculture and Food of the Government of Navarre. Suspended sediment concentration and dissolved nitrate ($NO_3^-$) and phosphate ($PO_4^{3-}$) concentrations were determined as well as the pH (Cison 52-02 probe) and the major dissolved constituents ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $SO_4^{2-}$, $HCO_3^-$, $CO_3^{2-}$). Cations were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES); $Cl^-$, $SO_4^{2-}$ and $NO_3^-$ by ionic chromatography technique; $HCO_3^-$ and $CO_3^{2-}$ by acid-base volumetric technique; $PO_4^{3-}$ by spectrophotometry (ammonium molybdate); and suspended sediment by gravimetric technique (0.7 µm pore size). The charge balance of the samples was determined and found to be within ±10 % for most
of the samples, suggesting that all relevant constituents were considered. Total dissolved solids (TDS) was then computed by addition of the individual dissolved constituents.

2.3. Data treatment, statistical procedures and interpretation

10-minute meteorological and discharge values were processed to hourly, daily and monthly time-series for analysis. Daily discharge data and concentration was used to estimate the daily load of nitrate-nitrogen (NO$_3^-$-N), phosphate-phosphorus (PO$_4^{3-}$-P), sediment and salts. TDS is usually used to estimate salt content of a water sample. However, in Landazuria TDS was only determined in a subset of the available samples (1,721 out of 2,984). For this reason, the existing relationship between chloride and total dissolved solids (Fig. 2) was used to generate a TDS value for every sample. This value was used in the estimation of salt loads.

Several problems produced missing samples for specific days (e.g., equipment malfunctioning, not enough flow for sample collection, etc.). In fact, for the 10-year study period (3,653 days), a total of 2,984 water samples were collected (82 %). As a consequence, in order to obtain monthly time-series, the following criteria was applied:

(1) To obtain monthly concentration values, the median was estimated with a 95% confidence interval using all available samples for that specific month;

(2) For monthly load values:

(a) If more than 33% of the days in the month had available samples, an estimation was computed assigning the median value for that month to the days without sample.

(b) No estimation of the load was obtained for those months with less than 33% of the days in the month with available samples.

For PO$_4^{3-}$ and sediments, a significant proportion of the samples were below detection limits (BDL), <0.05 mg L$^{-1}$ for PO$_4^{3-}$ and <5 mg L$^{-1}$ for sediments. To avoid bias in the
estimation of concentration and yields, robust methods were used to deal with concentrations BDL (Helsel and Hirsch, 2002).

As exposed previously, there were gaps in the time series due to different issues. For this reason, a temporal resolution of weeks was selected to study the correlation between the different variables. Out of the 10 year study period, 381 complete weeks were sampled (73%). For each week, the precipitation, irrigation, and fertilization amounts were computed or estimated. In addition, average concentration and total load exported of studied variables were computed. A correlation matrix was obtained using the non-parametric Spearman's rho test (Helsel and Hirsch, 2002).

3. Results and discussion

3.1. Precipitation, reference evapotranspiration, irrigation and runoff

During the study period (agricultural years 2007-2016), annual precipitation (P) ranged from 309 mm (2012) to 631 mm (2013), whereas reference evapotranspiration (ET₀) ranged from 1253 mm to 1558 mm in the years 2013 and 2009, respectively. Average values were 437 ± 97 mm and 1380 ± 85 mm for P and ET₀, respectively. There were no significant differences with the long-term data (section 2.1). In addition, no significant trends (Seasonal Kendall Test, Helsel and Hirsch, 2002) were detected for monthly or annual data of P or ET₀, neither in the study period nor in the long-term data. The lack of long-term trends suggest that the dynamics observed were representative of the natural variability in Landazuria.

P was, in some extent, evenly distributed throughout the year, with 29%, 25%, 29% and 17% of the annual value for autumn, winter, spring and summer, respectively (Table 2). In fact, although summer presented the lowest precipitation, there were no significant differences between seasons (p>0.05). In contrast, ET₀ was not evenly distributed, with
12%, 12%, 34% and 42%, respectively. Estimated irrigation volumes required for crops (I) averaged 337 mm year\(^{-1}\), with 2%, 4%, 31% and 62% of the annual value for autumn, winter, spring and summer, respectively. As a consequence of the irrigation volume distribution, an even distribution of discharge volume (Q) throughout the year was observed (Table 2, Fig. 3). In fact, Q tended to be higher during summer than during winter, with averages of 29 ± 9 mm and 22 ± 9 mm, respectively. However, the differences between summer and winter discharge were not significant (p>0.05).

During the irrigated season, a daily cycle in Landazuria discharge was detected (Fig. 4). Discharge reached a maximum around 9:00 hours and a minimum around 21:00 hours. This observation is related to the irrigation practice of farmers in Landazuria, who irrigate mainly during the night since wind speed and relative humidity were more favourable for sprinkler irrigation, minimizing evaporation and wind drift losses (Playán et al., 2005). Similar observations have been reported in other pressurized irrigation districts in the Middle Ebro Valley (e.g., Isidoro et al., 2003; Causapé et al., 2012).

Since the irrigation volumes required by crops were relatively constant during the years covered by this study, the differences in the distribution of the daily discharge were related to the precipitation regime of the different years (Table 3), i.e., the amount of precipitation and its distribution throughout the year. For instance, the dry year 2012 presented the lowest median and quartiles whereas the humid year 2015 presented the highest.

3.2. Nitrate concentrations and nitrate-nitrogen yields

Measured NO\(_3^-\) concentrations in Landazuria outlet were considerably high, over three times the European guideline for continental waters (50 mg L\(^{-1}\)) and even higher (Fig. 8). In several years, a sharp increase in NO\(_3^-\) concentration in early summer (May and June)
was observed coinciding with the high fertiliser applications in the irrigated plots. Similar observations have been reported in other irrigated watersheds in the Middle Ebro Valley (Isidoro et al., 2003; Merchán et al., 2013) where a crop with high N needs dominated the irrigated surface (such as maize in the case of Landazuria).

Significant differences in NO$_3^-$ concentration were observed between agricultural years (Fig. 8). For instance, the year 2013 presented the highest median and quartiles. This year combined high fertilization rates during the last years (Table 1) with a previous dry year (2012, the driest year covered in the study period; Table 3). Indeed, NO$_3^-$ concentration tends to be higher after dry years (Burt et al., 2012). In contrast, the years 2015 and 2016 presented the lowest NO$_3^-$ concentrations, being significantly lower than those recorded in any other year ($p<0.001$). Several explanation may justify this observation. Firstly, humid years (such as 2013 and 2015 in Landazuria) may deplete the NO$_3^-$ pool available in soils or phreatic layers, contributing to lower concentrations in following years. In addition, a subtle decrease in the surface of crops requiring high N fertilisation (maize) is observed in the last years (Table 1), what may have promoted increased NO$_3^-$ extractions. Finally, most of the farmers in the study area received training and attended informative sessions about Best Management Practices to reduce NO$_3^-$ leaching in the framework of the LIFE-Nitrates Project (INTIA and GAN, 2015a). Probably, a combination of these explanations is behind the lower concentration in the last two studied years. Unfortunately, there was not available information about the possible shift of fertilisation practices to adequately assess the contribution of each explanation.

Monthly nitrate-nitrogen (NO$_3^-$-N) loads varied widely intra- and inter-years, and in general they were heavily conditioned by discharge (Table 3). For those years in which a complete estimation was possible, an average NO$_3^-$-N yield of $39 \pm 13$ kg N ha$^{-1}$ year$^{-1}$. However, N fertilisers applied to the irrigated surface accounted for 96 % of total
applications (see section 2.1). Thus, considering negligible the nitrogen leached from rainfed and bare soils, yield averaged ca. 70 ± 24 kg N ha\(^{-1}\) year\(^{-1}\) for the irrigated surface. This figure implies that, as an average, a mass of about 35 % of applied N in the irrigated area leaves the watershed (Table 3). The yield reached up to 114 kg NO\(_3\)⁻-N ha\(^{-1}\) year\(^{-1}\) or ca. 50 % of applied fertilizers in 2013. This year combined high NO\(_3\)⁻ concentration, as previously discussed, with a humid year in which the base flow in the outlet was significantly higher than in most of the remaining years (Table 3). On the other hand, despite the high fertilization rates and NO\(_3\)⁻ concentration, the dry conditions in 2012 propitiated low flow and consequently NO\(_3\)⁻-N yield was 40 kg ha\(^{-1}\) year\(^{-1}\). Even this figure implies 18% of applied N fertilisers that year. NO\(_3\)⁻-N yields in 2015 and 2016 were close to the estimated average (81 and 53 kg ha\(^{-1}\) year\(^{-1}\) respectively), indicating that the low NO\(_3\)⁻ concentrations observed in those years were not associated with significantly less N being exported from the watershed.

According to fertilisation and soil N studies performed in several plots following typical agricultural management (Litago Munarriz, 2011; INTIA and GAN, 2015b), a significant oversupply of N fertilizers is applied to crops in Landazuria. In these studies, farmers did not take into account either available mineral nitrogen in soils before the crop cycle (86 kg N ha\(^{-1}\) as a representative value) or mineral nitrogen provided by organic matter mineralization (125 – 400 kg N ha\(^{-1}\) depending on site-specific conditions; INTIA and GAN, 2015b). Therefore, fertilisation rates should be adjusted considering both previously available N and expected organic matter mineralization rates in order to minimize N leaching.

Although other forms of N may contribute to N loads in Landazuria, NO\(_3\)⁻ constitutes the predominant form of nitrogen in eutrophic or hypertrophic waters, contributing with up to 90% of total N (Durand et al., 2011). In this sense, the N load estimated using NO\(_3\)⁻ may
be considered as a conservative but accurate estimation of total-N loads in this case study.

3.3. Phosphate concentration and phosphate-phosphorus yields

Measured PO$_4^{3-}$ concentrations in Landazuria outlet were below the detection limit (0.05 mg L$^{-1}$) in 63 % of collected samples (Fig. 10). In fact, PO$_4^{3-}$ was consistently detected only in specific periods, such as late summer and beginning of autumn, mainly in humid years. Significant differences were observed between years (Fig. 10). The year 2015 presented the highest concentrations, while the years 2007, 2009 and 2010 presented the lowest. It is hard to explain these pattern since no specific information about P fertilization was available for this study. In addition, P dynamics may be rather complex due to particulate or soluble transport pathways, and a wide range of storage and release processes occurring in soils, hillslopes, groundwater or wetlands (Sharpley et al., 2013).

Monthly phosphate-phosphorus (PO$_4^{3-}$-P) loads varied widely intra- and inter-years, and in general they were heavily conditioned by discharge (Table 3). For those years in which a complete estimation was possible, PO$_4^{3-}$-P yield ranged from 8 g P ha$^{-1}$ year$^{-1}$ in 2009, to 97 g P ha$^{-1}$ year$^{-1}$ in the humid year 2015. It averaged 39 ± 32 g P ha$^{-1}$ year$^{-1}$.

An important issue to consider is that, in contrast with the case of NO$_3^{-}$-N fractions of total N, PO$_4^{3-}$-P loads represent a partial estimate of total phosphorus load, since particulate-P can suppose 45 – 90 % of P load in agricultural land (Merrington et al., 2002). However, PO$_4^{3-}$ (also known as soluble reactive phosphorus, SRP) is the most readily bioavailable form of P, and, as a consequence, suppose the critical P pool in soils and waters (Merrington et al., 2002).
Although no specific information about P fertilization was available in this study, a build-up of soil P is reported to have occurred (and goes on) in agricultural soils all across Europe as a consequence of over-fertilization (Daniel et al., 1998). For instance, Skhiri and Dechmi (2012) reported an excess in P fertilization of about 16% of crop needs (44 kg P ha\(^{-1}\) year\(^{-1}\)) in a pressurized irrigated area in the Middle Ebro Valley. However, the loss of total P in the watershed outlet averaged 200 g P ha\(^{-1}\) year\(^{-1}\). The excessive P is likely being immobilized in soils, hillslopes, streams, etc., and can imply a long-term source of P in the future, or “P legacy” (Sharpley et al., 2013). This fact complicates the assessment of the effects of measures to reduce P leaching from agricultural soils.

3.4. Sediment concentration and yields

A significant proportion of the collected samples (14%) presented sediment concentrations below the quantification limit (0.005 g L\(^{-1}\)), coinciding with low flow conditions. In general, sediment concentration in the outlet was related to discharge. The higher the discharge, the higher the sediment concentration. There were some periods in the year in which this pattern was not followed (Fig. 12). For instance, high sediment concentrations were measured at the beginning of the irrigation season (March to June) and can be related with ploughing activities before seeding of a summer crop (INTIA, 2017). The highest concentrations were measured when these activities coincided with important precipitation events (such as in the years 2007, 2012 and 2015; Fig. 12). In fact, sediment concentrations were significantly higher in the years 2007 and 2015, humid years in which important precipitations occurred during the period when most of the plots had been recently ploughed. The median concentration of sediment for the whole study period was of 31 mg L\(^{-1}\).

Sediment yields were greatly conditioned by extraordinary precipitation events and periods (Table 3), such as that on October 4\(^{th}\) 2013 (55 mm in a day), October 20\(^{th}\) 2012
(48 mm) or September 2014, with moderate precipitations occurring after an
extraordinary wet summer (148 mm between June and August, twice the average in this
period). For those years in which a complete estimation was possible, sediment yield
averaged 360 kg ha⁻¹ year⁻¹, and it ranged from 42 to 1154 kg ha⁻¹ year⁻¹, being extremely
variable. For instance, only a few days in October 2013 accounted for 44% of the
sediment load for the whole study period. The importance of specific events in sediment
exports is a well-known fact (e.g., O’Brien et al., 2016). This is one of the main reasons
why long-term studies are required to adequately assess soil erosion rates (García-Ruiz
et al., 2015).

It is important to state that sediment concentration and yield data in Landazuria has to
be considered with caveats, since small wetlands are present upstream from the
hydrological station, adding a layer of complexity to the interpretation of sediment data.
The presence of these wetlands does not follow any human intervention, since they
developed in areas receiving irrigation return flows enriched in nutrients after the
transformation to irrigated land of the study area (farmer’s personal communication).
Wetlands are recognized as effective sediment tramps (USEPA, 2015). However, they
may become a net source of sediment under high-flow conditions. As a comparison,
Aryal and Reba (2017) reported sediment concentration between 293 and 434 mg L⁻¹ for
an irrigated season in two watersheds in Arkansas, an order of magnitude higher than
that observed in Landazuria.

3.5. Total dissolved solids concentrations and yields
TDS concentrations in Landazuria presented a marked intra annual pattern (Fig. 14),
with higher values each year between late winter and early spring (the end of the non-
irrigated season) and lower values in the summer months (July – September, the
irrigated season). In addition, significant decreasing trends (p<0.05) were detected for
every month applying the Seasonal Kendall Test (Helsel and Hirsch, 2002). Trend slopes varied between -130 and -77 mg L\(^{-1}\) year\(^{-1}\) for the different months, with an overall value of -106 mg L\(^{-1}\) year\(^{-1}\). In fact, the years 2015 and 2016 presented the lower TDS concentrations, being significantly lower than those recorded in any other year (\(p<0.001\); Fig. 14). Both the intra- and inter-annual observed pattern can be explained by the influence of irrigation water in TDS concentration. The intra annual pattern is related to the dilution originated by irrigation water in spring-summer months (Causapé et al., 2012). On the other hand, during the study period Landazuria was a relatively recently transformed irrigated area (irrigation began in the year 1999) implemented over geological materials rich in gypsum and other soluble salts. Thus, the implementation of irrigation mobilized salts stored in soils prior to irrigation due to prevailing semi-arid climatic conditions. In addition, salts present in the geological material at the bottom of Landazuria soils (marls and clays with gypsum) would be also mobilized. Consequently, the amount of salts readily available for dissolution by irrigation return flows have decreased with time. Similar processes have been documented in new irrigated soils (Wang et al, 2012) or watersheds (Merchán et al., 2013).

Monthly TDS loads varied widely intra and inter years, and in general they were heavily conditioned by discharge (Table 3). In fact, TDS loads followed a temporal distribution almost identical to that of discharge. For those years in which a complete estimation was possible, TDS yield ranged from 1.0 to 2.9 Mg ha\(^{-1}\) year\(^{-1}\) for the dry year 2012 and the humid 2013, respectively. The average value was 1.8 ± 0.7 Mg ha\(^{-1}\) year\(^{-1}\).

An estimation of the TDS mass provided by precipitation and irrigation water was obtained using its volumes and salinities. Although precipitation and irrigation water presented some variability in their TDS concentration, the highest values (80 mg L\(^{-1}\) and 300 mg L\(^{-1}\), respectively; CHE, 1996) were assigned to the volumes of both components of the water balance (Table 2), what implies a worst case scenario for a salt balance.
Under this assumption, an average of 0.35 and 1.01 Mg ha\(^{-1}\) year\(^{-1}\) of TDS were introduced in Landazuria by precipitation and irrigation waters, respectively. Neglecting minor components of the salt balance (such as salts incorporated by the crops or added in fertilization, Villalobos et al., 2016), an out/in ratio of around 1.3 was obtained. Thus, salts in the watershed were being washed and the feasibility of a build-up of soil salinity was negligible under current irrigation and weather conditions (Thayalakumaran et al., 2007).

3.6. Interaction between studied variables in Landazuria

Surprisingly, no significant correlation was detected between weather or agronomic variables and hydrological variables (not shown). Despite the fact that Landazuria is a first order watershed, a time gap does exist between any input in agricultural soils (precipitation or irrigation water, fertilization...) and outputs at the watershed outlet. These dynamics were not captured with the weekly resolution of the correlation analysis performed in this study, and deserve further analysis using more complex time series analysis. Such detailed analysis is out of the scope of the present study.

Regarding the hydrological variables themselves, the degree of correlation between discharge and concentrations was, in general, low or non-significant (Table 4). This may be a consequence of the amount of different processes involved and the different initial conditions for rainfall-runoff events, fertilisation season, etc. Only subtle significant relationships were detected between discharge and concentration of NO\(_3^-\) (-0.18) and sediment (+0.19). However, stronger correlations were detected between discharge and loads: high correlation coefficients were obtained for TDS and NO\(_3^-\)-N loads, while the correlation coefficients between PO\(_4^{3-}\)-P and sediment loads were lower. Isidoro et al. (2003) also detected low correlation between discharge and water quality parameters in other irrigated area of the Middle Ebro Valley.
In general, low correlation coefficients were obtained between the different water quality variables (Table 4), indicating different processes controlling each of them. Edwards and Withers (1998) also reported the differences in hydrological processes controlling each pollutant dynamics in agricultural watersheds in the UK. In Landazuria, high concentration of one parameter did not coincide with high concentrations in any other one. Some degree of correlation was detected between the soluble constituents (NO$_3^-$ vs. TDS = +0.41) and were probably due to dilution effects after strong precipitation events or under increased base flow conditions in the irrigated season. In contrast, higher correlation coefficients were obtained between the loads of different constituents. NO$_3^-$N and TDS loads were strongly related between them (+0.93) and more weakly related to the remaining constituents (+0.34 - +0.47). The relation between PO$_4^{3-}$-P and sediment loads was lower (+0.53). Although some studies have estimated that up to 90 % of P load occurs in particulate forms (Merrington et al., 2002), high P concentration in fine sediment mobilized under high flow conditions makes PO$_4^{3-}$ to desorb from the sediment into the water (Gibson, 1997). As a consequence, PO$_4^{3-}$-P load (and PO$_4^{3-}$ concentrations) tended to increase with sediment loads.

For soluble constituents, small correlation coefficients were obtained between each water quality variable (i.e., concentration) and the constituent load (Table 4), indicating that the higher loads did not coincide with the higher concentrations (+0.18 for NO$_3^-$ vs. NO$_3^-$-N Load, and +0.22 for TDS vs. TDS Load). In contrast, a strong correlation was founded between concentration and loads (+0.83 and +0.91 for P and sediments, respectively) indicating that high concentrations coincided with high loads events.

The observed relationships support the fact that different processes control the behaviour of these pollutants: NO$_3^-$ and TDS represent highly soluble components that were easily mobilized by flowing water, either under base flow or high flow conditions.
On the other hand, $\text{PO}_4^{3-}$ and sediment have low solubility and therefore their concentration was linked to specific high flow events that eroded soil particles in the fields, banks or bare soil areas (Aryal and Reba, 2017).

3.7. Agricultural pollution dynamics in irrigated areas in contrast with rainfed areas

Irrigated agriculture is mostly located in semi-arid areas, where the climatic conditions do not allow to achieve competitive agronomic production. Regions with Mediterranean climate, where the higher temperatures of summer coincide with the dry season, constitute a typical example (Ryan et al., 2009). Soils in semi-arid regions typically have a particular set of characteristics, such as lower organic matter content or higher pH and carbonate contents, in relation with soils in more humid regions (Brady and Weil, 2008; Ryan et al., 2009). In addition, climatic conditions imply, in general, low yield in these regions, especially for summer crops. As a consequence, winter crops such as wheat or barley are predominant (Ryan et al., 2009), and its productivity rely on climatic conditions. All these characteristics are present in Landazuria as reported in section 2.1: semi-arid conditions, especially with hot and dry summers; predominance of alkaline and calcareous soils; fallow-winter cereal as the typical rotation in the rainfed area, with low yield (ca. 2.5 and 4 times less yield in the rainfed surface in comparison with the irrigated one for barley and wheat, respectively).

Thus, irrigation in semi-arid soils produce a significant modification in the moisture conditions and the soil water balance, especially during summer when most of irrigation is applied. As a consequence, several properties of the soil are modified. For instance, the cultivation of more productive crops implies an increase in crop residues, and therefore organic matter in these soils (Apesteguía et al., 2015). In addition, summer high temperatures in combination with moisture provided by irrigation significantly increase organic matter mineralization rates (Arroita et al., 2013).
The water balance in watersheds with a significant proportion of irrigated surface is severely modified. However, the casuistic in watersheds receiving irrigation water from external sources is quite different to those in which irrigation water is obtained through dams, diversions or aquifers from the watershed itself. Indeed, in watersheds with external sources of irrigation water, excessive irrigation applied over the crop needs or summer rainfalls in already wet soils facilitates water leaching and, thus, increases aquifer recharge and/or baseflow contributions to nearby streams (e.g., Cameira et al., 2003; Sánchez-Pérez et al., 2003). In contrast, decreased flow of rivers or depleted aquifers are the main consequences when the irrigation water is obtained within the analysed watershed (e.g., Scanlon et al., 2007). In the rest of this discussion, we focus in the environmental issues in watersheds receiving irrigation water from external sources, such as Landazuria.

In fact, Landazuria exemplifies this modified water balance, with stable discharge throughout the year. In contrast, rainfed watersheds in Navarre, even in more humid areas, presented summer discharge values considerably lower than those observed in Landazuria (Casalí et al., 2008, 2010). Other studies have reported the severe modification of the water balance in irrigated areas (Barros et al., 2011; Andrés and Cuchí, 2014). In fact, in a watershed with similar conditions to that observed in Landazuria, Merchán et al. (2013) reported the shift from an ephemeral stream to a permanent one after the implementation of irrigation.

Water balance modification in semi-arid soils and watersheds has a huge relevance on its environmental impact since it controls pollutants exports to water bodies. Nitrate, as a readily soluble constituent of soil water, is particularly affected by modifications in the water balance. In fact, despite similar fertilization rates, nitrate-N yield from Landazuria irrigated surface (ca. 70 kg ha\(^{-1}\) year\(^{-1}\)) was higher than that in rainfed winter cereal watersheds in Navarre (16-37 kg ha\(^{-1}\) year\(^{-1}\), Casalí et al., 2008). While nitrate-N yield
in rainfed cereal watersheds occurred mostly during winters and was negligible during summer, in Landazuria it occurred throughout the year, as a consequence of the increased summer discharge due to irrigation return flows. In addition, more productive crops are usually grown under higher water availability (e.g., Gaydon et al., 2012), raising significantly the expected production and, consequently, fertilization rates. In Landazuria, the irrigated surface presented: (1) maize and vegetables such as tomato or onion as dominant crops; (2) a significant proportion of fields with two crops per year; and (3) an average fertilization rate seven times higher than that in the rainfed surface, where winter cereals were the dominant crops and cultivation took place one out of two years (Table 1).

A simple balance between average fertilization rates and nitrate-N yield in Landazuria suggested that around 35 % of N fertilizer being lost in drainage. Although a great range of variation is reported in the literature, similar figures have been reported in irrigated areas in Spain or Australia (Barros et al., 2012b; Thorburn et al., 2011). The variation in N losses fraction in drainage have been related to differences in terms of soils, crops grown and agricultural management. As extreme values, no significant N loss through drainage have been reported in irrigated clayey soils (Arauzo and Valladolid, 2013) whereas losses of up to 77 % of applied N fertilizer have been reported for humid areas with well-drained sandy soils intensively cropped in central Wisconsin, US (Kraft and Stites, 2003).

Irrigation by itself does not imply higher nitrate leaching. In fact, in more humid climates nitrate leaching is extremely variable, depending on climatic, soils or management conditions. For instance, in rainfed soils over terraces in Nepal, nitrate-N leaching ranged between 0-64 kg ha-1 year-1. In general, it was observed that the more fertilizer received, the more leaching (Pilbeam et al., 2004). In long-term monitored watersheds, the agricultural land exported 6-32 and 10-40 kg N ha-1 year-1 in Sweden and Estonia,
respectively (Kyllmar et al., 2014; Iital et al., 2014). However, even under humid conditions, nitrate-N leaching is expected to increase in irrigated and heavily fertilized areas (Kraft and Stites, 2003).

Due to the aforementioned calcareous soils, phosphate-P leaching is not particularly enhanced by irrigation in semi-arid regions, as the P-fixing capacity of these soils is considerable. For instance, phosphate-P yield in Landazuria (39 g ha-1 year-1) was in the order of magnitude of that estimated for rainfed winter cereal watersheds in Navarre (52 g ha-1 year-1; Casalí et al., 2008). However, a watershed with more humid conditions, neutral soils and manure application presented higher phosphate-P yield (120-250 g ha-1 year-1; Casalí et al., 2010). According to Withers and Sharpley (1995), soluble P makes up a greater component of P in runoff from sites that frequently receive applications of organic manures and slurries. In Alberta, Olson et al. (2010) related risk of P leaching with application rates of manure in irrigated soils. Thus, factors such as soil pH or organic fertilization, rather than irrigation, controls phosphate-P leaching in agricultural watersheds. Total P, in contrast, is greatly related to erosion and sediment losses from agricultural fields (Merrington et al., 2002). In fact, a significant relationship was detected between phosphate-P and sediment loads in Landazuria (section 3.6, Table 4).

Irrigation water quality and temperature, application rates or irrigation systems make irrigation-induced erosion a phenomenon quite different from rainfed erosion (Sojka et al., 2008). Unfortunately, there is scarce data about irrigation-induced erosion with a wide range of reported values in the available studies. Indeed, both rainfall- and irrigation-induced erosion contribute to soil loss in irrigated areas. Despite this, sediment yield in Landazuria (360 kg ha-1 year-1) was in the lower range of those estimated for the rainfed winter cereal watersheds in Navarre (230-1350 kg ha-1 year-1). The presence of wetlands (section 3.4) and the lower slopes in Landazuria (3–5%) in comparison with the
rainfed winter cereal watersheds (7–30%) were the most likely explanations for the
different behaviour. Although no much data was available for comparison, in a terraced
surface irrigated area of the Middle Ebro Valley, the sediment yield estimation was similar
to that obtained in this study (ca. 300 kg ha-1 year-1; García-Ruiz, 2010).

The clearing of natural vegetation for rainfed crop production, especially in arid to semi-
arid areas, is reported to increase mobilization of salts stored in the vadose zone over
millennia due to an increases in soil water leaching (Scanlon et al., 2007). The shift to
irrigated agriculture normally enhances this process due to an increase in available water
for leaching (Merchán et al., 2015a). The rate at which salts are washed out depends
mainly on the available amount of salts and the water leached. The amount of available
salts depends on the geological materials and the “recent” (in geological terms) history
of the soil. For instance, in many places of Australia, a great degree of irrigation induced
leaching of salts is reported as a consequence of prevailing climatic conditions during
recent times (Duncan et al., 2008). On the other hand, the amount of irrigation return
flows is controlled by the lack or existence of irrigation, and the system and/or
management of irrigation carried out. In this sense, higher irrigation efficiencies have
been related to lower salt loading (e.g., García-Garizábal and Causapé, 2010; Merchán
et al., 2015c).

3.8. Overview of management practices to mitigate the environmental impact of irrigated
areas in receiving water bodies

In a meta-analysis conducted over irrigated soils studies (Quemada et al., 2013),
improved water and fertilization management were reported as the most effective
practices in reducing nitrate leaching, with average decreases of 58 % and 39 %,
respectively. Alternative practices such as use of cover crops or improved fertilization
technologies presented, in general, lower reductions in leaching (Quemada et al., 2013).
This behaviour is also detected at the watershed scale. For instance, improved surface
irrigation management decreased the yield of soluble constituents such as nitrate and salts (Barros et al. 2012a,b; García-Garizábal et al., 2012, 2014). In general, sprinkler irrigation presented lower yields of nitrate and salts than surface irrigation (Merchán et al., 2015c).

Nitrogen fertilization rates should be adapted to the necessities of the crops, both in total amount applied and temporal distribution (Quemada et al., 2013), as these measures significantly reduced nitrate leaching with minimal impact on yield. Reduced fertilization rates decreased leaching but also yield, while fertigation did not always reduce leaching and it decreased in ca. 6 % yield (Quemada et al., 2013). In addition, the mineral N available at the beginning of the crop cycle along with that provided by organic matter mineralisation should be accounted for (Cameira et al., 2003; INTIA, 2017). Regarding phosphorus, applications in manure and slurries, rather than irrigation, usually controls phosphate leaching (e.g., Olson et al., 2010).

Since irrigated areas are subject to both rainfall- and irrigation-induced erosion, a wide range of management practices can be applied to decrease soil loss and sediment yield in irrigated areas. Apart from those typical of rainfed areas, practices such as improved water management, tailwater elimination/reuse or low-pressure wide-area sprays are recommended to curb irrigation-induced erosion (Sojka et al., 2008). For instance, Campo-Bescós et al. (2015) reported the beneficial effects of improved irrigation management and vegetative filter strips in the sediment exported in furrow-irrigated fields.

Although detailed information about irrigation management was not available for Landazuria, the higher discharge in summer with respect to winter suggest there is some margin of improvement in irrigation management that would probably decrease the environmental impact in terms of nitrate and salt yield. N fertilisation management clearly
needs to be optimized since the average loss of N in the watershed was about one third of N applied in fertilisers. Phosphate and sediment yield were not considered especially problematic in this study, probably due to the low use of organic fertilization and the presence of semi-natural wetlands and relatively low slopes in Landazuria.

4. Conclusion

In this study, a detailed and long-term dataset collected in the watershed outlet is used to estimate pollutant loads and behaviour in an area under pressurized irrigation typical in north-eastern Spain. While the inclusion of several variables provides an integrated picture of the studied system, the length of the obtained record (including both normal and extreme climatic and agronomic conditions) provided reliable estimates on the environmental effects of irrigation in this particular study case. This estimates are then contextualized in the broad field of agricultural pollution of water bodies.

Irrigation modified the water regime of Landazuria stream, providing a higher base flow during summer months along with a relatively constant discharge throughout the year. Median concentration in daily water samples collected at the watershed outlet for ten agricultural years were: NO$_3^-$, 185 mg L$^{-1}$; PO$_4^{3-}$ (or SRP) <0.05 mg L$^{-1}$; sediment, 31 mg L$^{-1}$; TDS, 2284 mg L$^{-1}$. Estimated annual yields averaged 39 kg NO$_3^-$-N ha$^{-1}$, 39 g PO$_4^{3-}$-P ha$^{-1}$, 360 kg sediment ha$^{-1}$ and 1.8 Mg TDS ha$^{-1}$. For both concentration and loads, a high degree of intra- and inter-annual variation was observed, conditioned by different weather conditions, the behaviour of highly soluble constituents (NO$_3^-$ and TDS) or particulate driven constituents (sediment and PO$_4^{3-}$), and agronomic management. In these sense, NO$_3^-$ and TDS behaved conservatively with respect to water whereas PO$_4^{3-}$ and sediment dynamics were related to high flow events.
Our results were put into a broader context, especially regarding differences between rainfed and irrigated agricultural systems in semi-arid areas receiving irrigation water from external sources (neighbouring watersheds). In this sense, irrigation water supposes an additional water input, increasing aquifer recharge and baseflow of nearby streams. It implies a shift to more productive and N-fertilizer demanding crops, and consequently tends to increase nitrate leaching in these soils. In addition, salt stored in the vadose zone are mobilized by irrigation return flows, increasing salinity in downstream water bodies. Phosphorus fixing capacity of semi-arid soils implies that phosphate leaching is not particularly enhanced by irrigation, while erosion and sediment yield from irrigated areas depends greatly in site-specific characteristics.

Given the high variability in both concentration and loads imposed by the precipitation regime and agronomic management, long-term monitoring in well characterized agricultural watersheds is essential to understand the dynamics of pollution processes. In addition, it can provide an accurate estimation of the pollution “base level”, which is needed in order to assess the effects of preventive or corrective measures undertaken to improve the water quality downstream.

Acknowledgements

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[Accessed March 2017, Spanish]


<table>
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<th>09</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
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<td>25</td>
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² Surface with two different crops in a single agricultural year (the sum of crops surfaces exceeds 100%).

n.a.: not available.
Table 2. Some characteristics of precipitation, irrigation (estimated) and discharge recorded at Landazuria. Runoff coefficient = Discharge / (Precipitation + Irrigation).

<table>
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S.D.: Standard deviation.

Table 3. Values of discharge, nitrate (NO3-), phosphate (PO43-), sediment and total dissolved solids (TDS) yields for the hydrological years. Estimated values representative of the whole study period are presented in the line 2007-2016.

<table>
<thead>
<tr>
<th>Agric. year (Sep-Aug)</th>
<th>Discharge [mm]</th>
<th>NO3-N yield [kg ha(^{-1})]</th>
<th>PO4-P yield [g ha(^{-1})]</th>
<th>Sediment yield [kg ha(^{-1})]</th>
<th>TDS yield [kg ha(^{-1})]</th>
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<tr>
<td>2014</td>
<td>88</td>
<td>33.9</td>
<td>52</td>
<td>1154</td>
<td>1,703</td>
</tr>
<tr>
<td>2015</td>
<td>147</td>
<td>45.2</td>
<td>97</td>
<td>740</td>
<td>2,640</td>
</tr>
<tr>
<td>2016</td>
<td>96</td>
<td>29.3</td>
<td>24</td>
<td>42</td>
<td>1,711</td>
</tr>
<tr>
<td>Average (S.D.)</td>
<td>102</td>
<td>38.8 (13.2)</td>
<td>39 (32)</td>
<td>360 (473)</td>
<td>1,798 (680)</td>
</tr>
</tbody>
</table>

S.D.: Standard deviation
n.a.: not available (not enough reliable data for an adequate estimation).
Table 4. Correlation matrix among selected variables using the non-parametric Spearman’s rho (Helsel and Hirsch, 2002). Only significant correlations (p<0.05) are presented. The case of the Spearman’s rho coefficient is selected according with the strength of the correlation (absolute values of rho: <0.40; 0.40-0.70; >0.70).

<table>
<thead>
<tr>
<th></th>
<th>Q</th>
<th>NO₃⁻</th>
<th>PO₄³⁻</th>
<th>Sed.</th>
<th>TDS</th>
<th>N-L</th>
<th>P-L</th>
<th>Sed.-L</th>
<th>TDS-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>-0.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>-0.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sed.</td>
<td>+0.19</td>
<td>-0.13</td>
<td>+0.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>TDS</td>
<td></td>
<td>+0.41</td>
<td>-0.39</td>
<td>-0.17</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>N-L</td>
<td></td>
<td>+0.92</td>
<td>+0.18</td>
<td>-0.11</td>
<td>+0.12</td>
<td></td>
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<tr>
<td>P-L</td>
<td></td>
<td>+0.46</td>
<td>-0.29</td>
<td>+0.83</td>
<td>+0.39</td>
<td>-0.39</td>
<td>+0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sed.-L</td>
<td></td>
<td>+0.54</td>
<td>-0.17</td>
<td>+0.28</td>
<td>+0.91</td>
<td>-0.18</td>
<td>+0.45</td>
<td>+0.53</td>
<td></td>
</tr>
<tr>
<td>TDS-L</td>
<td></td>
<td>+0.94</td>
<td>-0.12</td>
<td>+0.14</td>
<td>+0.22</td>
<td>+0.93</td>
<td>+0.34</td>
<td>+0.47</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. A) Network of experimental watersheds in Navarre (Spain). Main rivers (blue lines) and irrigated surface (green). B) Agricultural plots in Landazuria. C) Soil map following Soil Survey Staff (2014). Source: Government of Navarre (2005) and IDENA (2017).
Figure 2. Relationship between chloride (Cl⁻) and total dissolved solids (TDS) concentrations in Landazuria outlet.

\[
\text{TDS} = 2.7915 \times [\text{Cl}^{-}] + 881.27 \\
R^2 = 0.8957 \\
N = 1721
\]
Figure 3. Monthly average discharge, precipitation and irrigation. Vertical bars indicate standard deviation.

Figure 4. Selected two-month periods during the non-irrigated (A) and the irrigated (B) seasons of the year 2016 in which the influence of daily irrigation schedules was clearly observed.
Figure 5. Nitrate concentration (NO$_3^-$; 95%-confidence interval on the monthly median) and daily average discharge in Landazuria outlet.

Figure 6. Phosphate concentration (PO$_4^{3-}$; 95%-confidence interval on the monthly median) and daily average discharge in Landazuria outlet.
Figure 7. Sediment concentration (95%-confidence interval on the monthly median) and daily average discharge in Landazuria outlet.

Figure 8. Total suspended solids concentration (TDS; 95%-confidence interval on the monthly median) and daily average discharge in Landazuria outlet.