ASSESSMENT OF THE MAIN FACTORS AFFECTING THE DYNAMICS OF NUTRIENTS IN TWO RAINFED CEREAL WATERSHEDS

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Abstract

Nutrient dynamics and factors that control nutrient exports were observed in two watersheds, namely Latxaga and La Tejería, with similar climatic and management characteristics throughout 10 years (2007-2016).

Similar patterns were observed in intra-annual and inter-annual dynamics with higher NO_3^- concentration and NO_3^--N yield during the humid seasons (i.e., winters and hydrological year 2013). Regarding concentration, Latxaga showed a higher decrease of nitrate due to a higher development of vegetated areas. High discharge events produced nitrate dilution due to the presence of tile-drainage at La Tejeria. At Latxaga, where tile-drainage was not observed, an increase in concentration occurred as a response to high discharge events. Comparing both watersheds, La Tejería presented ca. 73 ± 25 mg NO_3^- L^{-1} while at Latxaga, the concentration observed was almost three times lower, with ca. 21 ± 15 mg NO_3^- L^{-1} throughout the study period. Similar patterns were observed for the NO_3^--N yield, with 32 kg NO_3^--N ha^{-1} $year^{-1}$ and 17 kg NO_3^--N ha^{-1} $year^{-1}$ at La Tejería and Latxaga, respectively.

Regarding phosphorous, the observed concentrations were 0.20 ± 0.72 mg PO_4^{3-} L^{-1} and 0.06 ± 0.38 mg PO_4^{3-} L^{-1} at La Tejería and Latxaga, respectively, with PO_4^{3-}–P yields being 71 kg PO_4^{3-}–P ha^{-1} $year^{-1}$ and 33 kg PO_4^{3-}–P ha^{-1} $year^{-1}$. Annual phosphate-P yield distribution in both watersheds followed similar patterns to those observed for the nitrate-N yield, with higher yields in the humid season. Regarding concentration, highly erosive rainfall that occurred in summer, mobilizing sediments and probably generating desorption of phosphorous in the stream channel, increased phosphate concentration.

This research adds to the knowledge base regarding the dynamics of nutrients and the controlling factors in complex agricultural systems with Mediterranean characteristics.

Keywords:

Water quality, Tile-Drainage, Riparian vegetation, Nitrate, Phosphate

1. INTRODUCTION

The intensification of agricultural activity throughout the world is, at least partially, responsible for the decline of water quality and, as a consequence, of the deterioration of freshwater and coastal ecosystems (Berka et al., 2001; Van Meter et al., 2016). In particular, the application of fertilization doses above crop necessities and/or the intensification of livestock production are usually associated with a surplus of nutrients in soils. This means an excess of available nutrients that are subject to losses via runoff and/or leaching, plus the aforementioned off-site effects (Durand et al., 2011; Merrington et al., 2002).

Nitrogen is considered the nutrient that generates one of the best crop responses, increasing yields. Therefore, nitrogenous fertilization is the most employed in the world, with over 100 million tonnes applied each year (Delgado et al., 2016). N fertilizers are available in a range of forms (straight, such as urea or ammonium, compound forms such as di-ammonium phosphate, or organic fertilization with manure). Soil N is mainly lost in the form of nitrate, via leaching (Billen et al., 2011; Oelmann et al., 2007; Wang et al., 2018), although other types of losses can also be significant (Huang et al., 2016; Liu et al., 2003). Nitrate loss is relevant both from a farmer's perspective, as it entails a loss of economic resources, and due to environmental reasons, worsening water quality for human supply (World Health Organization 2011) or contributing to eutrophication (Merrington et al., 2002; Le Moal et al., 2019). Other environmental impacts have been reported, such as air pollution or greenhouse gas emissions (Butterbach-Bahl et al., 2011; Moldanová et al., 2011).

In contrast, the effects of phosphorus (P) on the environment are mostly associated with eutrophication, being habitually the limiting nutrient in inland water ecosystems. An increase of 0.01 mg L^{-1} has been reported as sufficient to transform oligotrophic inland waters into eutrophic (Merrington et al., 2002). P exportation is controlled by soil erosion and sediment exports, as a considerable proportion of P is fixed or precipitated due to prevailing soil pH values (Withers and Jarvie, 2008). Although wastewater is commonly the main P-contributor to inland waters, especially in developing countries, agriculture is a proven, but variable, contributor of P to many affected waters (Sharpley, 1995).

There are multiple factors that influence nutrient export processes. Riparian vegetation located near the water bodies act as filters or sinks of sediments and nutrients (Chase et al., 2016; Dosskey et al., 2010; Tabacchi et al., 2000; Neilen et al., 2017). In particular, width, density, and diversity of riparian vegetation have been reported to affect nutrient transport to streams (Broadmeadow and Nisbet, 2004; de Souza et al., 2013). For instance, herbaceous vegetation improves water infiltration and protects from runoff and erosion while woody vegetation protects streambanks from mass failure, and, in the case of senescent species, its leaves increase the soil roughness, reducing runoff (Dosskey et al., 2010). Besides riparian vegetation, the presence of aquatic vegetation can influence the export of nutrients altering the amount in the watershed outlet (Soana et al., 2019). A greater sinuosity of the stream causes a higher interaction of water with the hyporheic zone of the bed (Peterson and Benning, 2013), increasing the potential of denitrification and nitrogen uptake in riparian areas. Soil characteristics such as cracks and tile drainage also influence nitrogen exports, reducing the residence times of dissolved nutrients and decreasing denitrification (Arenas Amado et al., 2017; Brady and Weil, 2008; Randall and Goss, 2008). In addition, other factors have been also reported to significantly influence nutrient export, such as soil pH (Merrington et al., 2002) and climatic conditions (Chen et al., 2002), for example.

These factors, plus other physical factors, can trigger biogeochemical processes such as denitrification (Mastrocicco et al., 2019). Denitrification is the process where microbial activity reduces compounds, namely nitrate, to gaseous forms found in the environment. Denitrification occurs mainly when denitrifying microorganisms do not have sufficient oxygen, and therefore carry out anaerobic respiration, transforming soluble nitrogen compounds into gases such as nitrous oxide and nitrogen (Martens, 2004; Skiba, 2008). Assessment of these factors can underpin the extension of knowledge on the different pathways of nutrients in diverse watersheds.

Rainfed winter cereal is the most extended agricultural land use around the world, representing approximately 20% of the cultivated area (FAO, 2011). For instance, in Europe and Spain, the main rainfed winter crops, wheat, and barley, occupy ca. 36% and 40 % of the total arable area, respectively (EUROSTAT, 2016; MAPAMA, 2018). Although this land use is considered essential to the agriculture sector, the effects on water quality are widely acknowledged (e.g., Durand et al., 2011). The European Union has even promoted the Nitrates Directive to address pollution from agricultural sources (91/676/EEC). Many European countries have implemented networks of agricultural watersheds to investigate diffuse source pollution (e.g., Fučík et al., 2017; Hooda et al., 1997; Kyllmar et al., 2006; Lagzdins et al., 2012; Lloyd et al., 2016; Ockenden et al., 2016; Povilaitis et al., 2014). However, there is an apparent under-representation of watersheds in Mediterranean climate conditions, which presumably present remarkable differences in nutrient dynamics and exports. In fact, to the best of our knowledge, only a few studies have reported nutrient dynamics for the Mediterranean climate or in locations under its influence (De Girolamo et al., 2017a; Ferrant et al., 2011; Lassaletta et al., 2012). The Mediterranean climate is characterized by mild, wet winters and hot, dry summers. Evapotranspiration is high in summer, with crop management being a challenge, and irrigated agriculture is a frequent practice. Besides, rainfed cereal fertilization in Mediterranean areas occurs at approximately the same period in which most of the runoff is generated. Therefore, its contribution to nutrient exports is significant.

In Navarre (northern Spain), the impact of agriculture on soil erosion and water quality has been analysed in a network of small watersheds implemented by the former Department of Agriculture, Livestock, and Food of the Government of Navarre. These studies have mainly focused on the characterization of hydrological and erosion (Casalí et al., 2008, 2010), factors controlling sediment exports (Giménez et al., 2012), assessment of the AnnAGNPS model for runoff and sediment yield simulation (Chahor et al., 2014), and the dynamics of dissolved solids and suspended sediment (Merchán et al., 2019). Specific work on nutrient dynamics was also conducted at one of these watersheds (Merchán et al., 2018), although some information regarding nutrient dynamics in the remaining watersheds was presented in Casalí et al. (2008, 2010). In a study conducted at two watersheds representing rainfed cereal land use under relatively similar management conditions, surprising different behaviours were reported for nutrient exports (especially nitrate). Although no detailed study was carried out, differences in the watersheds' morphology, riparian and stream channel vegetation were proposed to be the leading causes of the differences observed (Casalí et al., 2008).

This paper builds upon and extends the work of Casalí et al. (2008) by elaborating on nutrient concentration and export dynamics in two relatively similar watersheds, which were expected to behave similarly. However, the watersheds presented distinct behaviours, as previously reported. In this study, we aim to improve the knowledge base on the nutrient dynamics in rainfed agricultural watersheds under the Mediterranean climate and, mainly, on the factors that could explain the differences observed between two similarly managed watersheds. The specific objectives were: (a) to characterize the behaviour of both watersheds, in terms of concentration and exports of nitrate and phosphate, for a range of temporal scales (in response to rainfall events, seasonally, and inter-annually); (b) to estimate a long-term (10 years) average nitrate-N and phosphate-P concentration and yield in each of the watersheds; and (c) to gain insight on the controlling factors influencing these processes, through comparisons between the watersheds and with information available in scientific literature.

2. METHODS

2.1. Experimental watersheds

This section describes the monitored watersheds selected, namely Latxaga and La Tejería, within the agricultural watershed network monitored by the former Department of Agriculture, Livestock, and Food of the Government of Navarre. The main characteristics of these two watersheds can be observed in Table. 1.

2.1.1. Latxaga experimental watershed

The watershed of Latxaga, with an extension of 207 ha, is located in the east of Navarre, in Spain (Fig. 1). At Latxaga, the average rainfall is 861 mm per year, with an average temperature of 11.8 ºC, according to data collected by the weather station located at the watershed (Government of Navarre, 2019). The average altitude of the watershed is 576 m, with an average slope of 17%. The predominant geology is composed of flysch and marls with levels of 50 cm of thickness, alternating with sandstones 1-3 cm thick (Government of Navarre, 1994). A detailed soil map was developed at La Tejería, where Paralithic Xerorthent (SSS, 2014) was the prevailing soil (Government of Navarre, 2005).

Although the predominant land use at this watershed is rainfed cereal, approximately the 11% of the area of the watershed is occupied by non-cultivated plots with natural grassland vegetation and emerging forests (Fig. 2A). The riparian vegetation of Latxaga is considered dense and developed for a Navarrese agro-system. The presence of woody species around all the streambanks is usual. The most common tree species are *Salix alba*, *Populus nigra,* and *Fraxinus angustifolia* (Government of Navarre, 2005), occupying a continuum in the streambanks and generating a canopy in the channel. Multiple herbaceous and shrubs species appeared around the channel, where *Buxus semprevirens*, *Rosa Sp*., *Rubus ulmifolius,* and *Cornus Sanguinea* predominate (Government of Navarre, 2005). The width of the riparian vegetation at Latxaga varied between 2 and 5 meters, being wider at the lower part of the watershed. Due to the seasonality of the stream channel, no aquatic vegetation was found at this watershed. Channel sinuosity (i.e., ratio between channel length and a straight line) was 1.13 m m^{-1}.

The fertilization rate of the arable land at Latxaga was ca. 170 kg N ha^{-1}, as reported by the agricultural extension services (Government of Navarre, 2018). Fertilization was divided into two stages: the first application occurred at the beginning of tillering, generally in January, with an application of 60 kg N ha^{-1} from urea fertilizer, and the second application occurred approximately in March (Casalí et al., 2008) with an application of 110 kg N ha^{-1} from urea fertilizer. Phosphorous was applied in the sowing stage (November) with di-ammonium phosphate, with a biennial or triennial periodicity (Casalí et al., 2008).

The productivity of the watershed, considering the production of the region to be representative of the study area, was 5,000 kg ha^{-1} for common wheat and 4,700 kg ha^{-1} for barley, considering the period 2000-2016 (Government of Navarre, 2018). The average N surplus was 41.9 kg N ha^{-1}, computed through the balance of fertilization applied and the nitrogen fraction of the production of each year, based on data provided by the Government of Navarre.

2.1.2. La Tejería experimental watershed

The experimental watershed of La Tejería covers an area of 169 ha and is located in the central Western part of the Navarre region in Spain (Fig. 1). At this watershed, the average rainfall is 755 mm per year, with an average temperature of 12.3 ºC (Government of Navarre, 2019). The average altitude at La Tejería is 577 m, with an average slope of 15.5%. The predominant geology of the area includes yellow silts and clays with occasional alternation of sandstones of the Middle Miocene, and silt, gravels, sands in valleys, and colluvial material in hillslopes (Government of Navarre, 1994). As well as for Latxaga, a detailed soil map was developed at La Tejería, where Vertic Haploxerept (SSS, 2014) was the prevailing soil at the watershed (Government of Navarre, 2005).

The predominant land use in this watershed was rainfed cereal, with a surface of 93%. There is also a reduced area (2.3%) of the watershed with non-cultivated areas (Figure 2.B). In contrast with Latxaga, the riparian vegetation at La Tejería is poorly developed. The banks of the stream are not densely vegetated. Most of the agricultural plots developed in detriment of riparian vegetation, with only a few trees of *Salix alba* and *Populus nigra,* and some herbaceous vegetation constituted of prickly plants, where the most predominant genus is *Rubus* (Government of Navarre, 2005). The width of the riparian vegetation was always under two meters and inexistent in more than half of the watershed's stream. Unlike Latxaga, tile drainage was observed in this watershed, with an estimated density of ca. 25 m ha^{-1} (field observations). Channel sinuosity was lower than that observed in Latxaga, with a sinuosity value of 1.04 m m^{-1}.

According to agricultural extension services, the fertilization rate of the arable land at La Tejería was 190 kg N ha^{-1} (Government of Navarre, 2018), divided into the same two stages described previously for Latxaga, with 67 kg N ha^{-1} in January, and 123 kg N ha^{-1} in March (urea fertilizer). Phosphorous was applied in the sowing stage, with di-ammonium phosphate, of biennial or triennial periodicity (Casalí et al., 2008).

The productivity of La Tejería, considering the production of the study area as being representative of the region, was 4,500 kg ha^{-1} for common wheat and 4,100 kg ha^{-1} for barley, considering the period 2000-2016 (Government of Navarre, 2018). The average N surplus was 46.7 kg N ha^{-1}, based on data provided by the Government of Navarre.

2.2. Data Collection

The former Department of Agriculture, Livestock, and Food of the Government of Navarre monitored the two watersheds to measure the agricultural impacts on water quality, with the following equipment:

An automatic meteorological station, which recorded meteorological data every 10 minutes. The parameters registered by this station are air temperature, rainfall, relative air moisture, wind speed, wind direction, soil temperature, and solar radiation.

A hydrological station installed at the watershed outlet, where water level was recorded at 10–minute intervals. The water discharge measurement was obtained through V-notch weir devices (Fig. 3A). Water level measurements were used for the calculation of runoff, which was monitored with a pressure probe and a data logger.

Water quality was monitored by collecting samples at the outlet of the watershed. Samples were collected every six hours, four times a day, and mixed to generate a single composite sample per day, to avoid possible concentration fluctuations that could have occurred during the day. The four daily samples were collected from a hemispheric hollow located just after the V-notch weir, as shown in Fig. 3A. The daily samples collected throughout the day were stored in a sampler located inside the building next to the weir (Fig. 3B, 3C). This sampler stored each of the daily samples, and was automated to collect samples throughout 20 days. After this period, the samples were taken to the laboratory.

Water samples were analysed following the analytic methods for water quality parameters established by the Agricultural Laboratory of the Department of Agriculture and Food of the Government of Navarre. The major dissolved compounds were analysed, including nitrate (NO_3^-), phosphate (PO_4^{3-}), and chloride (Cl^-), among others not used herein. The analytic methods employed were ion chromatography for NO_3^- and Cl^- (HPLC; Thermo Fischer Scientific Dionex DX-120, Bremen, Germany) and spectrophotometry (ammonium molybdate) for PO_4^{3-}. In all cases, the detection limit of dissolved compounds was 0.05 mg L^{-1}.

2.3. Data treatment

The study period covered the hydrological years (October to September) 2007-2016, constituting the most complete record in the database. Meteorological and runoff data were processed hourly, daily, and monthly so that different time trends could be analysed.

Daily NO_3^- and PO_4^{3-} concentration values of the database were revised to detect possible errors related to issues with the water sampler. With the aim of understanding the NO_3^- dynamics, the NO_3^-/Cl^- ratio was computed so that different effects produced by events in each watershed could be observed (i.e., concentration increase/dissolution). Cl^- is considered a stable constituent that does not participate in any redox reaction, not used by biological species, and does not participate in the cycles of the most common soil elements, such as nitrogen and phosphorous (Clark and Fritz, 1997).

A local regression method was used to establish a relationship between time and concentrations and detect seasonal patterns. The regression method selected was the locally estimated scatterplot smoothing (LOESS). The LOESS line was obtained with the R statistical software, and the selected span was 0.33, which was the best fit for the available data.

Daily concentration and discharge data (aggregated to daily values) were used to estimate loads of nitrate-nitrogen (NO_3^--N) and phosphate-phosphorous (PO_4^{3-}-P). The load estimation methods employed were numeric integration, regression, and ratio estimator, proposed by the USEPA and described in Meals et al. (2013): a) the numeric integration method is based on the integration of the daily load. In days with an absence of data, the monthly median concentration of the sampled period was employed; b) the regression method fits a rating curve to the observed data, which is used to estimate the load for the selected study period. Daily loads were estimated based on the relationship between observed loads and discharge, time, and season. The LOADEST software developed by the United States Geological Survey was utilized (Runkel et al., 2004); c) the ratio estimator method assumes that the flow weighted concentration in the period with available data is representative of the complete study period. To correct any bias, the ratio between complete flow and sampled flow was used. The use of different methods to obtain load estimations enables the detection of any uncertainties generated in this calculation.

Finally, the load result was transformed into a specific load or yield, dividing the load by the watershed surface. Afterward, the yield was aggregated into monthly, annual, and for the entire study period.

3. RESULTS

3.1. Rainfall and runoff distribution

Annual rainfall average and standard deviation were 793 ± 227 mm at La Tejería and 947 ± 301 mm at Latxaga. The driest and wettest years were 2012 and 2013, respectively, with 531 mm and 511 mm for La Tejería and Latxaga in 2012, and 1,324 mm and 1,665 mm at La Tejería and Latxaga in 2013, respectively (Fig. 4A). The humid season lasted from November to March in both watersheds, with ca. 100 mm per month at La Tejería and 120 mm per month at Latxaga (Fig. 4B).

Regarding runoff, the annual average and standard deviation at La Tejería was 222 ± 126 mm, while at Latxaga it was 249 ± 129 mm. The percentage of rainfall converted into runoff was very similar for both watersheds (31% at La Tejería and 33% at Latxaga). The runoff registered in the hydrological year 2012 was the lowest, with 4 mm at La Tejería and 38 mm at Latxaga. In contrast, the following year (2013) was the year with the highest runoffs, with 415 mm at La Tejería and 513 mm at Latxaga (Fig. 4A). Seasonally, runoff is dependent on rainfall and similar for both watersheds (Fig. 4B). An increase in runoff generally started in November-December, and decreased in May-June-July. Usually, rainfall events in the first part of the hydrological year (October-December) did not generate significant runoff (Fig. 4B). In general, hydrograph recessions presented higher slopes (i.e., were faster) at La Tejería than at Latxaga. The events that occurred during or after summer generated less discharge at both watersheds than those events occurred in spring. The aridity of soil was higher after summer, contrasting with spring, which coincided with the most humid season of the year.

3.2. Nutrient concentration trends at both watersheds.

Considering the entire study period, the nitrate concentration (NO_3^-) measured at La Tejería was nearly four times higher than at Latxaga. Median NO_3^- at La Tejería was 72 mg NO_3^- L^{-1}, which exceeded the 50 mg NO_3^- L^{-1} threshold (e.g., Nitrates Directive). Indeed, 85% of the collected samples were over this value. At Latxaga, median NO_3^- was 21 mg NO_3^- L^{-1}.

Conversely to La Tejería, only 3% of the collected samples at Latxaga were over 50 mg NO_3^- L^{-1} (Table 2).

Differences in NO_3^- between hydrological years were observed at both watersheds. At La Tejería, the highest median was observed in 2007 (87.4 mg NO_3^- L^{-1}) and the lowest in 2013 (47.1 mg NO_3^- L^{-1}). The minimum concentration coincided with the most humid year (Fig. 4A). Oppositely, at Latxaga this pattern was not present, with a maximum median concentration in 2015 (26.0 mg NO_3^- L^{1}) and a minimum in 2012 (11.4 mg NO_3^- L^{-1}), which was the driest year of the study period. In contrast with La Tejería, the average and median concentrations in the humid year at Latxaga (2013) increased considerably compared with the previous year, which coincides with the driest year and also with the minimum median of NO_3^-. This demonstrated the different behaviours of the watersheds (Fig. 4A).

The seasonal distribution within each year was similar for both watersheds. The high NO_3^- period for both watersheds occurred mainly in late autumn and winter months, whereas lower NO_3^- was registered after the harvest, during the summer and the early autumn (Fig. 4B). September and October presented the lowest NO_3^- values. Regarding the NO_3^- trend throughout the year, for both watersheds, the increase in concentration started with the first rainfall events, reaching its maximum peak in December-January and then decreasing during the spring until the summer. After late March, the concentration at Latxaga decreased, approaching 0 mg L^{-1} in the late summer (Fig. 5).

Although the general patterns observed in the seasonal cycle were similar in terms of NO_3^-, some behaviour differed. Whereas Latxaga presented a relatively stable line (Fig. 6), at La Tejería this line presented more ups and downs (see the two local maxima in Fig. 6) probably as a consequence of higher inter- and intra-annual variability in concentration.

Remarkably, the response to specific flow events was different for each watershed (Fig. 7). At La Tejería, a rainfall event caused an increase in the watershed discharge and a decrease in concentration, generating a dilution effect in the stream. Also, from late march and after the harvest, the concentration of NO_3^- remained stable or decreased slightly over time until the sowing period. Conversely, at Latxaga the NO_3^- concentration increased considerably with a rainfall event, along with runoff. Although the response in terms of NO_3^- concentration was different, the NO_3^-/Cl^- ratio demonstrated an important increase in specific flow events at both watersheds (Fig. 7).

Finally, at both watersheds the median phosphate concentration (PO_4^{3-}) was below the detection limit (<0.05 mg PO_4^{3-} L^{-1}) (Table 2). Only 15.4% and 27.2% of the samples were above that threshold at Latxaga and La Tejería, respectively. PO_4^{3-} differed across years, with yearly median values above the detection limit only for a few years (Fig. 8). No clear seasonal patterns were detected for PO_4^{3-}. However, an increment of concentration from spring until the end of summer was observed at La Tejería (Fig. 9).

3.3. Nutrient yields at both watersheds

The estimations obtained by different methods were consistent and showed approximately twice as much NO_3^--N yield at La Tejería (31.8 ± 16.0 kg NO_3^--N ha^{-1} $year^{-1}$) than at Latxaga (17.0 ± 8.6 kg NO_3^--N ha^{-1} $year^{-1}$) (Table 3). Regarding the NO_3^--N yield, a similar pattern was observed at both watersheds, where the NO_3^--N yield was generally controlled by the runoff of each watershed. The highest NO_3^--N yields were observed in the years with the highest runoffs, and vice versa. The year with the lowest NO_3^--N exportation at both watersheds was 2012 (1.1 and 0.6 kg ha^{-1} $year^{-1}$ at Latxaga and La Tejería, respectively). The highest NO_3^--N yield at Latxaga occurred in 2015, and at La Tejería in 2016 (29.8 and 51.8 kg ha^{-1} $year^{-1}$, Fig. 10A).

Seasonal distribution of the NO_3^--N yield was similar at both watersheds, with the winter period (January, February, and March) presenting the higher exports, and summer and early autumn presenting the lower exports. February presented the higher exports at both watersheds, with 8.6 and 4.4 kg ha^{-1} $month^{-1}$ at La Tejería and Latxaga, respectively. At both watersheds, around 51% was exported in winter (January-March) (Fig. 10B), whereas only 0.6% and 1.3% of the annual yield was exported in summer (July-September).

Regarding phosphate, La Tejería exported twice as much PO_4^{3-}-P (71 g ha^{-1} $year^{-1}$, Table 3) than Latxaga (33 g ha^{-1} $year^{-1}$). As shown for NO_3^--N, differences in PO_4^{3-}-P yield across years followed a pattern similar to that of runoff. Throughout the study period, the year with the lowest PO_4^{3-}-P yield was 2012, with 8 g ha^{-1} $year^{-1}$ at Latxaga and 10 g ha^{-1} $year^{-1}$ at La Tejería. In contrast, the year with the highest PO_4^{3-}-P yield was 2013, with 63 and 267 g ha^{-1} $year^{-1}$ at Latxaga and La Tejería, respectively (Fig. 11A). The seasonal distribution of the PO_4^{3-}-P yield was also similar for both watersheds: winter presented the highest exports (40%) and summer presented the lowest (2%). At La Tejería, January was the month with higher exports (22 g ha^{-1} $month^{-1}$) while the month with the highest exports at Latxaga was February (7 g ha^{-1} $month^{-1}$) (Fig. 11B).

4. DISCUSSION

4.1. Hydrology patterns at both watersheds

At Latxaga and La Tejería, low rainfall in the summer as well as higher evapotranspiration requirements led to a lower soil moisture content in these months. Despite the existence of significant rainfall events, these did not generate considerable increases in runoff. At both watersheds, the increase of discharge started in autumn with the humid season. The role of antecedent soil moisture conditions in runoff generation is widely acknowledged. (e.g., Feki et al., 2018; Montaldo et al., 2007; Teegavarapu and Chinatalapudi, 2018; Wang et al., 2018). Higher soil moisture content implies, among other effects, a more significant response of a watershed to an event, generating increased runoff. This has been also reported by previous works carried out at these watersheds (Casalí et al., 2008; Giménez et al., 2012).

In contrast with the seasonal pattern of the runoff observed in Navarre and in other Mediterranean watersheds (Kalogeropoulos and Chalkias, 2013; Tuset et al., 2016), in northern Europe runoff was relatively homogeneous throughout the year (Lagzdins et al., 2012; Lloyd et al., 2016; Ockenden et al., 2016). In these regions, there was no significant difference between the dry period and the wet period as in the Mediterranean watersheds. This fact has enormous implications in the seasonal pattern of nutrient exports, as will be discussed in the following sections.

Hydrograph recessions were faster at La Tejería than at Latxaga, which could be related to the presence of tile drainage in the former (Gramlich et al., 2018). Tile drainage generates an increase in hydraulic conductivity while reducing the water storage capacity of the soil (Blann et al., 2009), leading to a faster recession to baseflow in the hydrographs.

4.2. NO_3^- dynamics in response to storm events

Events with high runoffs produced different responses at both watersheds. At Latxaga, high-flow events generally indicated higher NO_3^- during the event, whereas at La Tejería these events meant lower NO_3^-. These responses suggest a difference in the predominant pathways, with an apparent *piston effect* (mobilization of NO_3^- enriched water previously stored in soils) acting at Latxaga, and a dilution effect occurring at La Tejería, which is consistent with the probable effects of tile-drainage (Keller et al., 2008). Despite the apparent dilution, the increasing NO_3^-/Cl^- ratio indicates that new NO_3^- is being mobilized by high-flow events at both watersheds. In other words, net mobilization of new NO_3^- is occurring at La Tejería despite the significant decrease in concentration. The presence of tile drainage avoids a higher residence time of water and limits soil denitrification, not increasing the NO_3^- concentration of the subsurface water and generating this apparent dilution. However, these events enable the mobilization of NO_3^- from areas where it is not generally supplied, therefore producing this new supply of NO_3^-.

Despite these observations, the response to high-flow events did not influence the long-term behaviour of NO_3^- at the watersheds. There was a contradictory behaviour, in which the watershed experiencing a decrease in NO_3^- concentration (La Tejería) presented higher concentrations and yield throughout the study period. Again, tile drainage at La Tejería could have been a critical factor in explaining this behaviour. The increase in the concentration and export of nutrients due to the presence of tile drainage has been reported by several authors (David et al., 2010; Gramlich et al., 2018; Li et al., 2010; McIsaac and Hu, 2004). This dilution occurs as a consequence of lower residence times, bypass of riparian areas, etc. Besides, in particular cases, dilution could also enhance the hydrological response (higher peak flows, Gramlich et al., 2019), potentially diluting the NO_3^-. That is in fact what we observe at La Tejería, higher concentrations and yields. In contrast, at Latxaga, with the negligible presence of tile drainage, NO_3^- was lower throughout the entire study period, due to a longer residence time of nitrate, which produces higher denitrification. However, NO_3^- increased in high flow periods due to the absence of the dilution effect caused by lower connectivity between soil and stream.

4.3. Seasonal NO_3^- dynamics

Both watersheds followed a similar seasonal pattern, with winter maxima in concentration and loads. NO_3^- concentration started to increase in November following the basal application of fertilizers. Side-dressing application throughout winter and spring maintained NO_3^- relatively high, with a decline in March-May. Later on, after the harvest of winter cereal, minima concentrations and loads were observed. It is interesting to note the different behaviour across watersheds, with Latxaga reaching negligible NO_3^- values probably as a consequence of its wider, more diverse, and denser riparian vegetation (Section 2.1.). Riparian vegetation is considered one of the mains factors limiting nutrient exports from watersheds (Dosskey et al., 2010; Tabacchi et al., 2000). In contrast, La Tejería presented nearly no riparian vegetation (farm plots reach the edge of the stream) and, as a consequence, higher NO_3^- values remained until the stream dried. The NO_3^-/Cl^- ratio provides an additional line of evidence to distinguish between dilution and evapoconcentration effects and NO_3^- sources or sinks. At the end of the crop cycle, the NO_3^-/ Cl^- ratio at La Tejería remained relatively stable, with only a minor decrease, which suggests that no significant NO_3^- sinks were at work. At Latxaga, in contrast, the NO_3^-/ Cl^- ratio decreased down to nearly zero values, clearly indicating a NO_3^- sink.

The seasonal distribution of NO_3^--N yield was heavily conditioned by runoff, with the minor influence of concentration values. Approximately 51 % of the annual yield was generated between January and March, at both watersheds. This observation significantly differs from those obtained under different climatic conditions. For instance, at watersheds located in northern Europe, the yield was usually evenly distributed throughout the year, with no specific season accounting for most of the yield (e.g., Iital et al., 2014). Many authors have manifested the preponderance of discharge over concentration in NO_3^--N export processes (e.g., Darwiche-Criado et al., 2015; Fučík et al., 2015; Sorando et al., 2018).

4.4. Interannual NO_3^- dynamics

According to the NO_3^--N yields, a high runoff generally increases the nutrient yields (Fučík et al., 2017). In the case of Latxaga and La Tejería, years with higher runoffs produced higher NO_3^--N yields. Runoff and NO_3^--N yields followed similar patterns. Differences in NO_3^--N yields could be explained by several factors such as antecedent soil moisture, tile drainage, and possible different fertilization practices in different watershed areas. The increase of the 2013 NO_3^--N yield in comparison with 2012 was considerable. The leaching of NO_3^--N produced in 2013 probably was generated not only by fertilization excess in 2013 but also by nitrogen surplus in 2012, when productivity was probably limited (very dry year), leading to a higher nitrogen surplus in this particular year. In addition, denitrification during 2012 was probably limited due to the low soil moisture and prevailing aerobic conditions in the soils (Skiba, 2008; Martens, 2005).

4.5. PO_4^{3-} concentration dynamics

Although dissolved P is considered the form with less contribution to P losses (Wu et al., 2012; Yaşar Korkanç and Dorum, 2019), it is the form measured at the watersheds assessed herein. The median PO_4^{3-} concentration at both watersheds was lower than the threshold detection limit. Such a low concentration occurred due to the low solubility of the phosphorous form present in soils with high pH (Brady and Weil, 2008; Merrington et al., 2002). Regarding seasonal distribution, an increase of concentration, above the detection limit, was appreciated in the spring and summer (April-August) at the La Tejería watershed. This high concentration appeared when the runoff was lower. The more energetic storm events are concentrated in these periods in Mediterranean catchments (Giménez et al., 2012). Storm events generate an energy-intensive runoff, mobilizing a substantial amount of sediments. Generally, an increase of flow during a storm event supposes an increment of sediments and, as a consequence, of particulate-P transport, as this is the main P-form in soils with high pH (Drewry et al., 2009).

An increase of sediments and particulate-P would facilitate desorption of phosphorous in the stream channel, producing an increase of PO_4^{3-} concentration (Sharpley et al., 1995). Conversely, at Latxaga these patterns were not observed, which could be associated with a more intense presence of riparian vegetation. It was verified that PO_4^{3-} and NO_3^- behave somewhat independently. While PO_4^{3-} concentration tends to increase in high flow events, as aforementioned, the behaviour of NO_3^- presented high variability across watersheds. NO_3^- is highly soluble while PO_4^{3-} was related to sediment concentration.

4.6. PO_4^{3-}-P yield

Both watersheds presented similar PO_4^{3-}-P yield patterns. Although the dynamics of PO_4^{3-}-P are influenced not only by the soluble form of P but also by particulate-P, the runoff is considered a crucial factor in the PO_4^{3-}-P yield (Sharpley, 1995) producing an increment of water discharge and increase of PO_4^{3-}-P yield (Fučík et al., 2017). Consequently, months with higher runoff also presented high PO_4^{3-}-P yield, differing from those with higher concentration, as aforementioned. Similarly, PO_4^{3-}-P yields are higher in years with higher runoff. However, it must be mentioned that the total P yield could be higher than the PO_4^{3-}-P yield reported herein. The phosphorous form considered herein only involved dissolved PO_4^{3-}, which can be 45-90% of total P (Merrington et al., 2002). In contrast with what has been described for concentrations, NO_3^--N and PO_4^{3-}-P yield behaviours followed relatively similar patterns, as their exports were controlled by the available water flow.

4.7. Nutrient export controlling factors

This section enumerates the main factors that could be present at the studied watersheds (Fig. 12), focusing on understanding the differences in nutrient concentrations and yields, according to our observations and the available scientific literature on the topic. Although other factors could be important to other case studies, those included herein were considered to be relevant for La Tejería and Latxaga. It must be highlighted that it is not attempted to infer the controlling factors in agricultural watersheds from the two watersheds studied herein, but rather the other way around, using the available literature to underpin our knowledge of the processes at work.

Soil characteristics and their effects on nutrient dynamics have been assessed previously (Lehmann and Schroth, 2003; Pärn et al., 2018). Empiric studies and simulation models have suggested that differences in organic matter quantity and quality led to differences in organic pools and carbon and nitrogen mineralization. The influence of texture is not sufficiently clear, although it is known that clay soils retain more organic matter than sandy ones when the same organic inputs are applied (Matus and Mairie, 2000). Denitrification regarding soil characteristics and texture has been also widely studied (Cambardella et al., 1999; Mastrocicco et al., 2019, 2011). Although some studies evidence a strong influence of texture on denitrification processes, with higher rates observed in soils with high content of clay and lower rates in soils with a high content of sand (D´Haene et al., 2003), other studies reported no significant differences regarding texture (Hofstra et al.,2005). Besides, a high preferential flow suggests higher nutrient transports to the subsoil (Brady and Weil, 2008) and lower residence time of nitrates in the soil, which could hinder denitrification processes. Despite the diversities between watersheds regarding soil organic matter content, depth, and texture, the differences were not sufficient to draw conclusions. Subtle differences in preferential flow (vertic conditions through the soil profile in ca. 40% of La Tejería's surface), however, could have contributed to nitrate leaching.

Every agrosystem encompasses a share of land that is not cultivated (i.e., unproductive areas). In general, these areas present limitations for cultivation – e.g., excessive slope or shallow soils. Casal et al. (2019) verified that non-cultivated areas retained an important fraction of nitrogen, leading to a decrease in the active fertilized area and consequently reducing nitrogen exports at a French catchment. Herein the share of unproductive areas at Latxaga (10.6 %) was almost five times higher than at La Tejería (2.3 %), and was, in general, closer to the stream. These unproductive areas did not receive any fertilization and could act as sinks of the nutrients originating from the upper parts of each watershed, affecting the total yield of nutrients.

Even if the riparian vegetation occupies a reduced area of the total watershed, its location near the water bodies enables it to act as a filter and/or sink of sediments and nutrients (Chase et al., 2016; Dosskey et al., 2010; Janssen et al., 2018; Neilen et al., 2017; Tabacchi et al., 2000). The width, density, and diversity of riparian vegetation have been reported to affect nutrient transports to streams (Broadmeadow and Nisbet, 2004; de Souza et al., 2013). For instance, herbaceous vegetation improves water infiltration and protects from runoff and erosion while woody vegetation protects streambanks from mass failure, and, in the case of senescent species, the leaves increase the soil roughness, reducing the runoff (Dosskey et al., 2010). Moreover, the content of biomass is the primary indicator of nutrient uptake (Dosskey et al., 2010). As exposed in Section 2.1., there are essential differences in the riparian vegetation of the two watersheds: at Latxaga there is wider, denser, higher, and more diverse and developed riparian vegetation near the stream. At La Tejería, croplands reach the edge of the channel in many cases, with negligible riparian vegetation. According to scientific literature, when other conditions are similar, lower nutrient exports would be expected at Latxaga rather than at La Tejería.

The stream sinuosity index (ratio between the real length of a stream and the shortest straight line) is a parameter related to riparian vegetation, and its value at Latxaga was 1.13 m m^{-1} while La Tejería presented 1.04 m m^{-1}. Higher sinuosity causes a higher interaction of the water with the hyporheic zone of the bed (Peterson and Benning, 2013), increasing the potential of denitrification and nitrogen uptake in riparian areas. Although differences in sinuosity values could seem trivial, Lassaletta (2007) reported changes in average sinuosity, from 1.14 to 1.07 after land consolidation works, which could have induced changes in riparian vegetation and nutrient exports. Thus, the differences verified at Latxaga and La Tejería could be sufficient to produce higher interaction of water with the hyporheic zone and, as a consequence, decrease NO_3^- in stream water.

Although the natural characteristics of each watershed play essential roles regarding NO_3^- dynamics, management practices are also relevant. The impact of N fertilization on NO_3^--N exports depends on different factors such as N fertilization rate, time and type of application, type of fertilizer, soil condition before the application, and crop phenology and characteristics. A linear relationship has been established between N application rates and the total nitrate leaching from soils - meaning that, under similar circumstances, an increase in N fertilizer rates produces an increase in mean leaching losses of NO_3^--N (Liang et al., 2011; Muschietti-Piana et al., 2017). Consequently, it is imperative to control N fertilization rates, as N surplus (the N supplied in excess to the crop necessities) is considered the primary driver of N losses in croplands (Thorburn and Wilkinson, 2013). According to the recommended fertilization rates and average productivities, the N surplus at La Tejería (46.7 kg N ha^{-1} $year^{-1}$) was 11 % higher than at Latxaga (41.9 kg N ha^{-1} $year^{-1}$). Interestingly, a higher surplus was estimated for La Tejería (which received a lower amount of N) due to the higher productivities obtained at Latxaga. The nitrate yield from watersheds depends mainly on N surplus. Although this relationship is not linear, it requires a threshold value below which N yield is negligible (Fenn et al., 2006; Ventura et al., 2008). At La Tejería, the N surplus 11 % higher supposed a NO_3^--N yield 87 % higher. Besides, this threshold over which significant amounts of NO_3^- are leached depends on the available N retention capacity of the watershed. By comparing N yields and surplus N in the Navarrese watersheds, these thresholds can be estimated as approximately 15 and 25 kg N ha^{-1} $year^{-1}$ for La Tejería and Latxaga, respectively, which are consistent with the differences previously discussed in riparian vegetation and other factors.

The presence of tile drainage at one of the watersheds is a relevant management practice that influences N exports (Arenas Amado et al., 2017). Tile drainage is typically employed in productive agricultural areas where natural drainage is poor (Randall and Goss, 2008; Gramlich et al., 2018). Several studies have remarked that tile drainage causes a considerable increase in the NO_3^--N yield (Gentry et al., 1998; McIsaac and Hu, 2004; Woodley et al., 2018). Tile drainage acts as a bypass and decreases residence time and thus the interaction with soils and riparian vegetation, limiting in this way denitrification and nutrient uptake (McIsaac and Hu, 2004). For instance, in two wide regions in which the main differences were related to the intensity of drainage, McIsaac and Hu (2004) reported a N yield almost four times higher at an extensively drained area (21 m ha^{-1}) than at a relatively undrained area (0.7 m ha^{-1}). Tile drainage was present at La Tejería, and its density was estimated as approximately 25 m ha^{-1}. At Latxaga, no tile drains were observed nor reported by farmers. Given the importance of tile drainage in N exports, its presence/absence could be sufficient to explain the differences verified in the NO_3^--N yield values of Latxaga and La Tejería.

Finally, explicitly focusing on PO_4^{3-} exports, several studies reported that sediments and phosphorous dynamics share an important connection (Drewry et al., 2009; Kotti et al., 2000; Odhiambo, 2018; Shore et al., 2016). A fraction of particulate-P can be desorbed from sediments when the latter is mobilized under high-flow conditions and transformed into a bioavailable form, generally PO_4^{3-} (Sharpley et al., 1995). Previous works carried out at the Navarrese watersheds reported that the median suspended sediment concentration was approximately five times higher and sediment yield was three times higher at La Tejería than at Latxaga (Merchán et al., 2019). This was mainly explained by the different characteristics in morphology and topography of each watershed (Casalí et al., 2008). Thus, the observed differences in PO_4^{3-}-P exports could be justified by these differences in sediment dynamics.

So far, the feasible influence of these controlling factors, according to our observations and available literature on the topic, has been examined separately, i.e., without considering possible interactions. The quantification of the effect of each factor and any possible synergies or counter effects deserve additional analyses such as statistical assessments and process modelling, which are outside the scope of the present study.

4.8. Comparison with other studies

The observations made at the Navarrese watersheds, regarding NO_3^--N yields, were in agreement with those reported for arable watersheds all across Europe. In the United Kingdom, three catchments comparable to the Navarrese ones exported ca. 7-19 kg NO_3^--N ha^{-1} $year^{-1}$, with an average nitrate concentration of ca. 6.5-35 mg NO_3^- L^{-1}(Lloyd et al., 2016). In agricultural watersheds of the Baltic countries, Deelstra et al. (2014) reported nitrate yields of ca. 5-47 kg NO_3^--N ha^{-1} $year^{-1}$. Other studies have confirmed the range of NO_3^--N yield values: in Latvia (Lagzdins et al., 2012), Sweden (Kyllmar et al., 2014), Estonia (Iital et al., 2014) and Lithuania (Povilaitis et al., 2014) . In Central Europe, a range of 10-50 kg NO_3^--N ha^{-1} $year^{-1}$ was reported at different areas of a small catchment in the Czech Republic (Fučík et al., 2017). Regarding agricultural catchments in the Mediterranean region, the highest export of NO_3^--N occurred in the December-March period (De Girolamo et al., 2017b). To the best of the authors' knowledge, there is scarce data regarding NO_3^--N exports at small scale watersheds in Mediterranean regions. Larger watersheds in the Iberian Peninsula export 5-21.5 kg NO_3^--N ha^{-1} $year^{-1}$, according to Romero et al. (2016). The results obtained for the Navarrese watersheds were of the same order of magnitude than those reported above.

Concerning water quality, the most critical P form is considered to be PO_4^{3-} due to its biological availability. However, phosphate usually does not represent an essential fraction of the total phosphorus load. Consequently, the PO_4^{3-}-P yield estimated at the Navarrese watersheds is only a fraction of the total P yield. Indeed, studies developed in northern Europe reported P loads that were two and three orders of magnitude higher than those observed at La Tejeria and Latxaga (Kyllmar et al., 2006; Pengerud et al., 2015).

5. CONCLUSIONS

Two experimental watersheds with similar climatic characteristics and management practices, and cultivated with rainfed cereals, have been assessed throughout ten years. Differences regarding water quality, mainly nitrate and phosphate concentrations and exports, have been observed.

Differences in nutrient concentration and yield obtained at these watersheds have demonstrated the relevance of the intrinsic characteristics of each watershed. Vegetation, tile drainage, and stream channel sinuosity were crucial factors affecting nutrient exports at the studied watersheds. Besides, riparian vegetation was considered to be a buffering factor in nutrient concentration, smoothing the nutrient concentration peak in specific periods.

An increase of vegetative elements in specific locations, better drainage management, and sufficient width of the riparian forest (which enables the stream to develop a specific sinuosity) would not only improve the water quality of streams in agricultural watersheds but would also produce more significant carbon sequestration, improvement in soil structure and soil fauna, decrease in erosion, and increase in the presence of aquatic organisms. These facts, combined with correct management choices, would contribute to the progress towards sustainable agriculture.

Although long-term water quality monitoring implemented in these watersheds and the suitable traceability of management practices within the watershed - which includes the influence of tile drainage, the evolution of riparian vegetation, development of non-cultivated areas, and land use - will help quantify the effect of each factor on the exports of nutrient pollution, a thorough analysis of the obtained data would be necessary. In this context, a non-linear time series analysis would be particularly suitable. These nature analyses would permit to obtain a causal interaction network among nutrient export controlling factors, thereby enabling the quantification of retention/export of nutrients by herein described controlling factors in the watershed. The knowledge of the interactions of factors would permit a better understanding of nutrient transport. In addition, the observations made in these watersheds, the in-depth analysis of controlling factors for nutrient export carried out in this study, and the time series analysis that is expected to be carried out, will allow an adequate evaluation of agricultural watershed management tools to assess consequences in different scenarios regarding land use and management.

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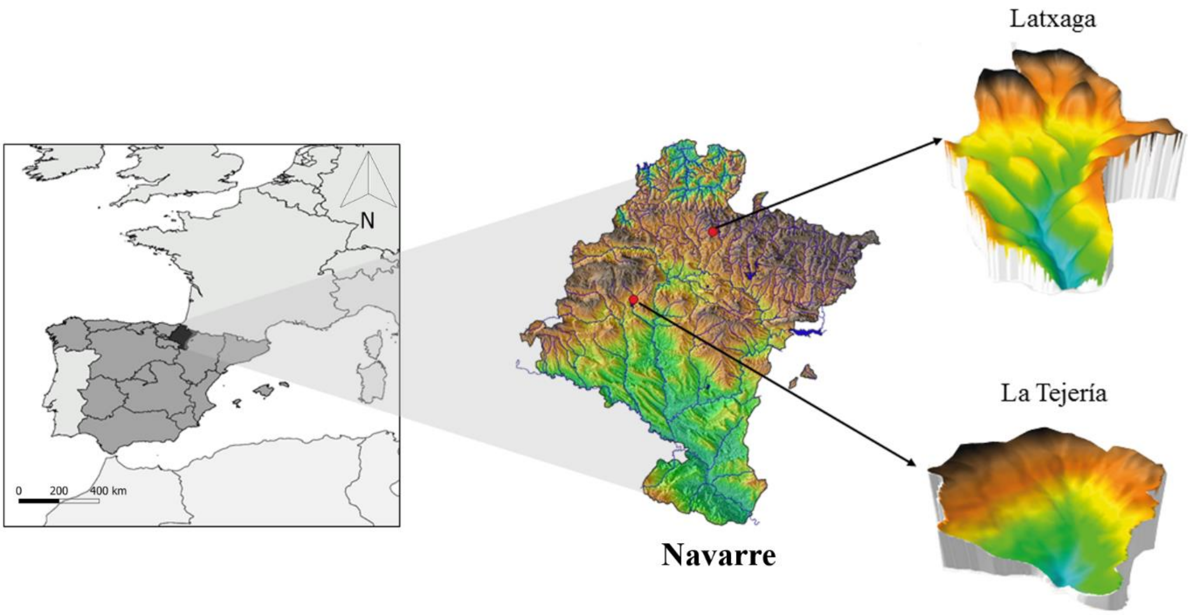

Figure 1. Location of the Latxaga and La Tejería watersheds, two experimental agricultural watersheds of the Government of Navarre. (Source: IDENA, 2010)

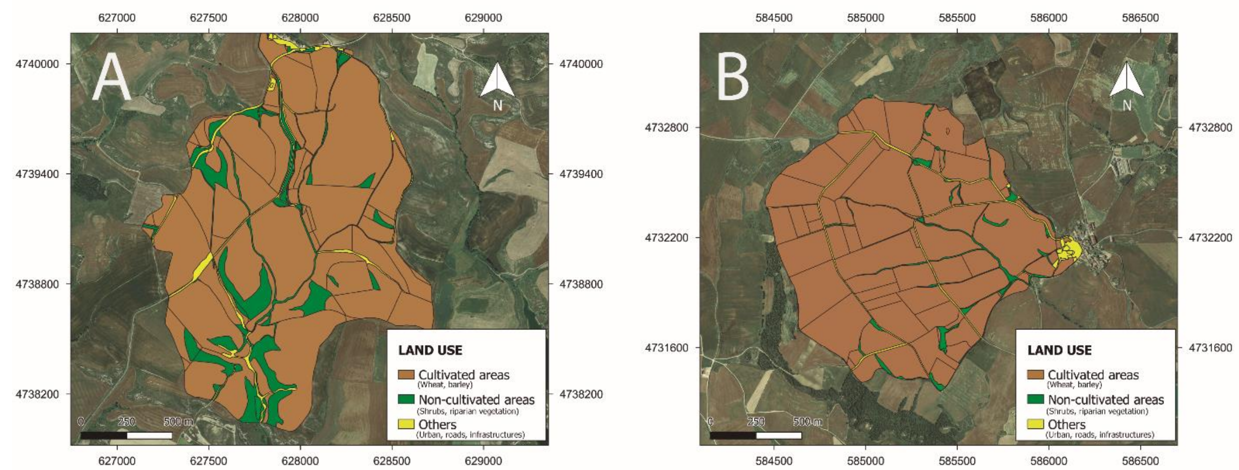

Figure 2. Land use distribution at (A) Latxaga and (B) La Tejería. (Source: IDENA, 2017)

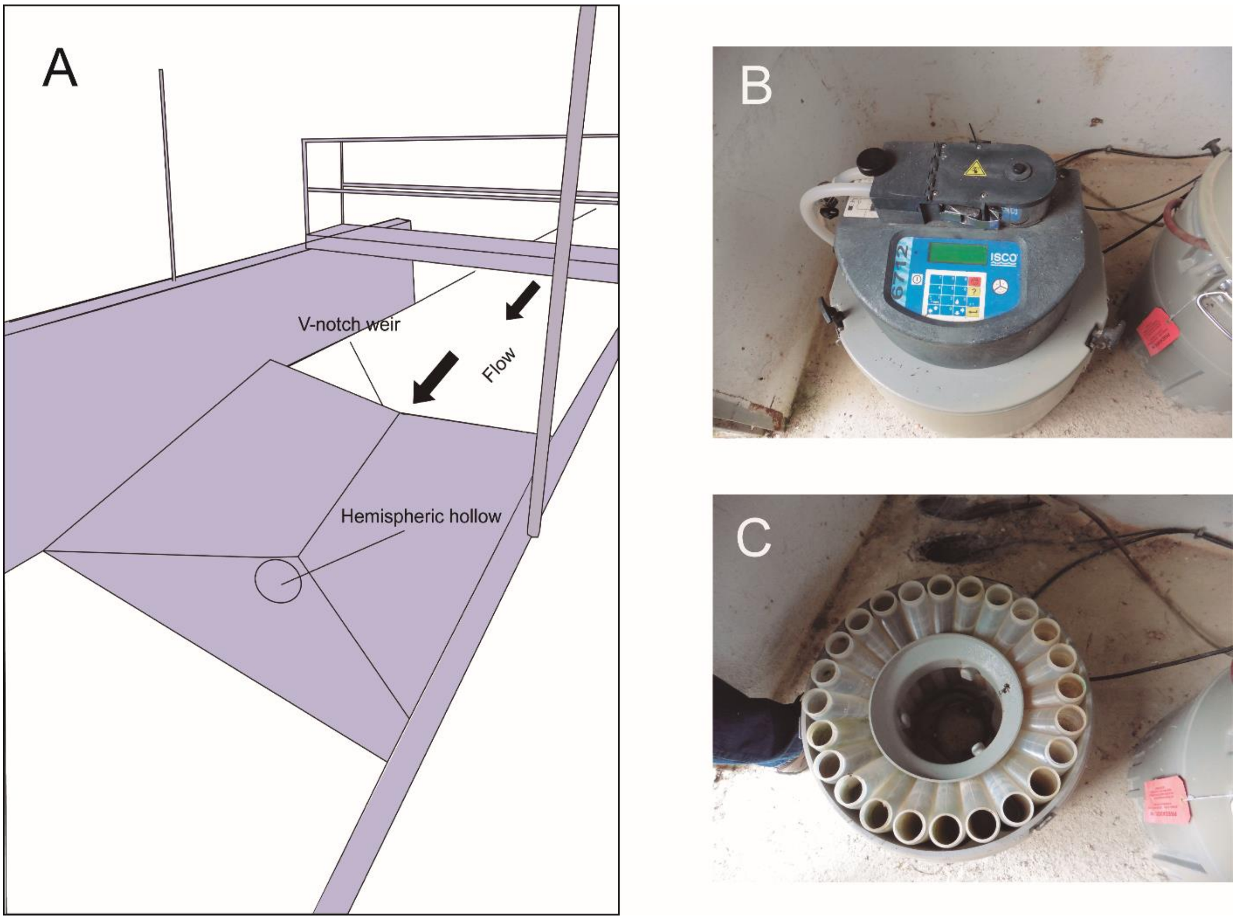

Figure 3. (A) Hydrological station at the watershed outlet and hemispheric hollow, and (B, C) the automatic sampler.

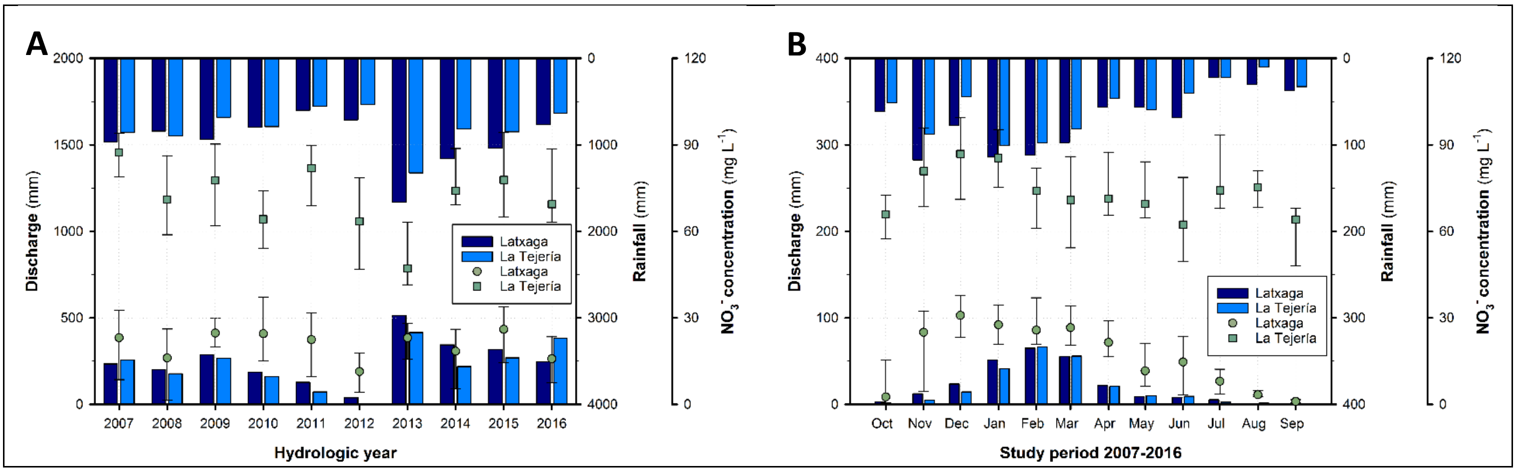

Figure 4. Annual (A) and monthly (B) distribution of rainfall, runoff, and median nitrate concentration with 25th and 75th percentiles at Latxaga and La Tejería.¶

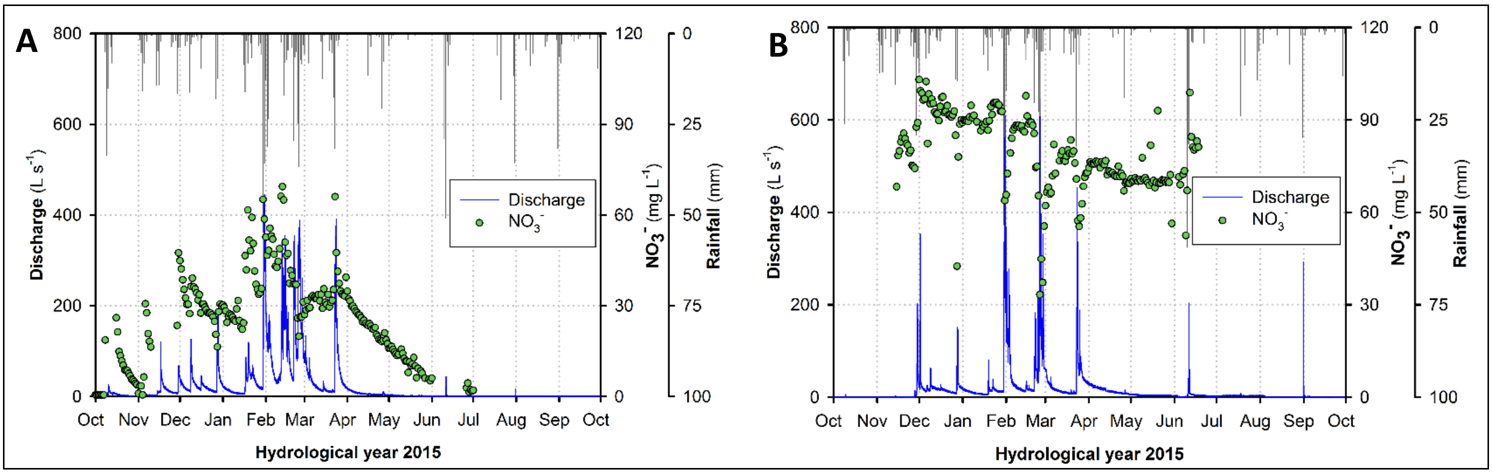

Figure 5. Rainfall, discharge, and nitrate concentration distribution in a typical hydrological year (2015) at Latxaga (A) and La Tejería (B)

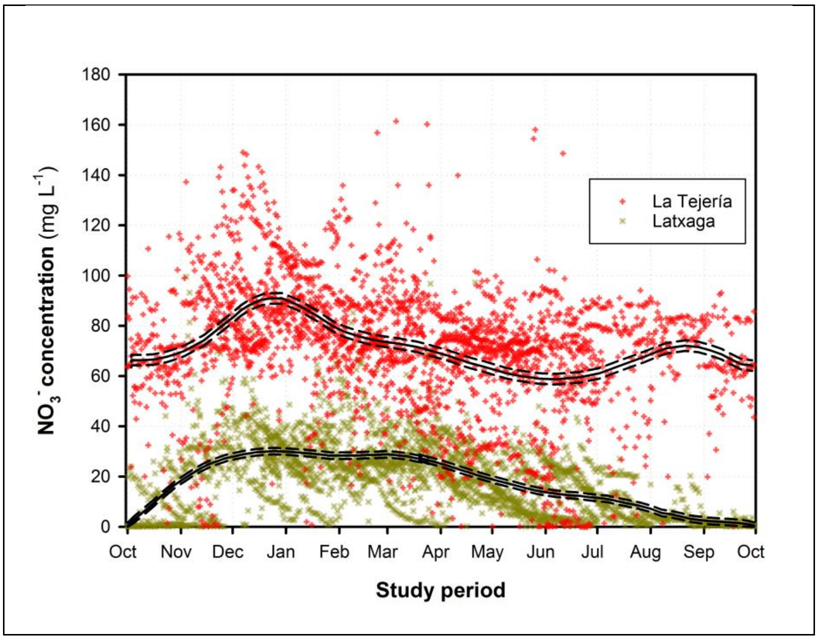

Figure 6. LOESS smoothing method nitrate results for the Latxaga and La Tejería watersheds

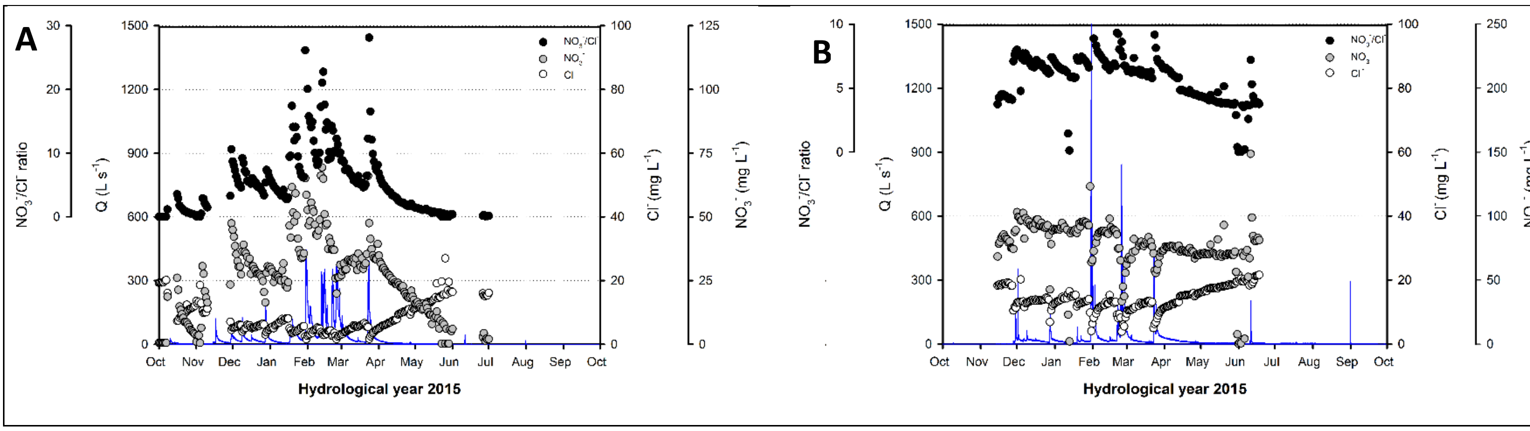

Figure 7. Nitrate concentration, chloride concentration, and nitrate/chloride ratio at the Latxaga (A) and La Tejería (B) watersheds.

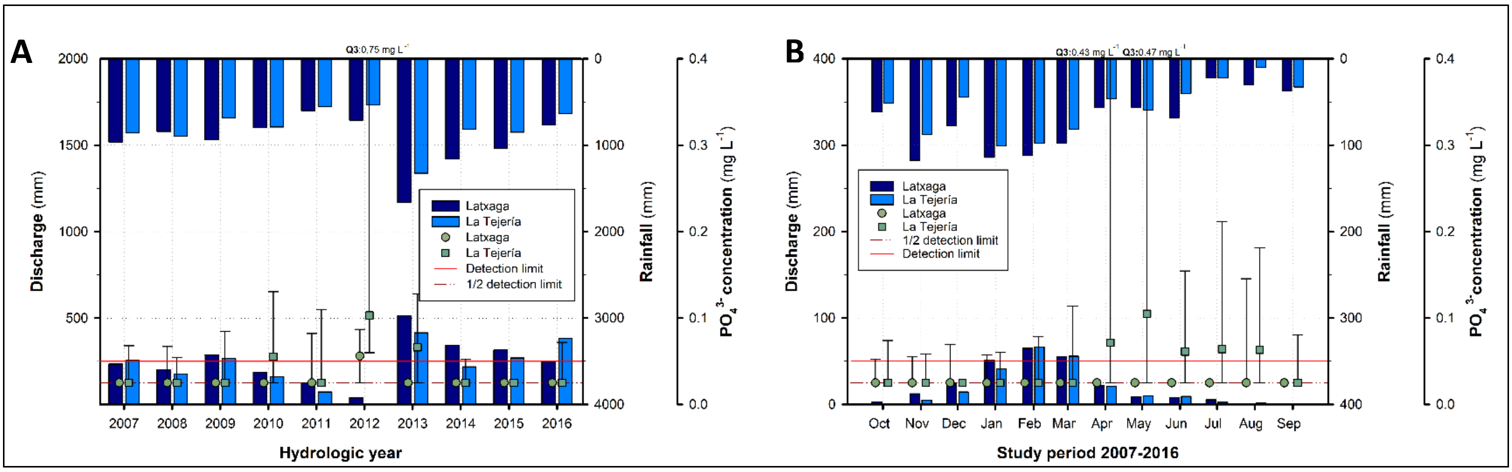

Figure 8. Annual (A) and monthly (B) distribution of rainfall, discharge, and median phosphate concentration with 25th and 75th percentiles at Latxaga and La Tejería.

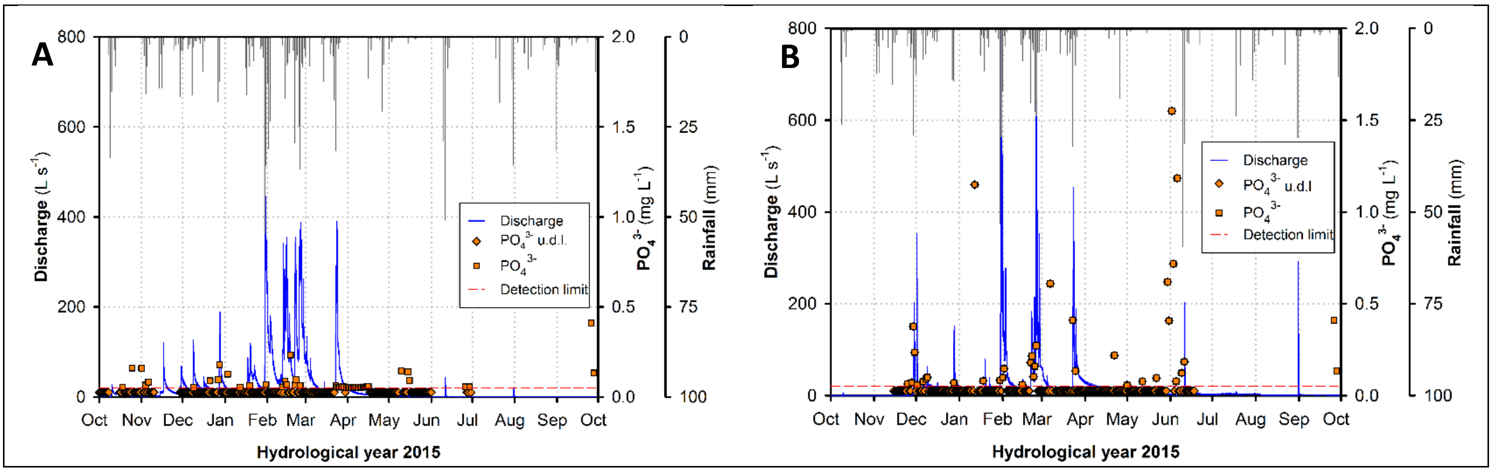

Figure 9. Rainfall, discharge, and phosphate concentration distribution in a typical hydrological year (2015) at Latxaga (A) and La Tejería (B)

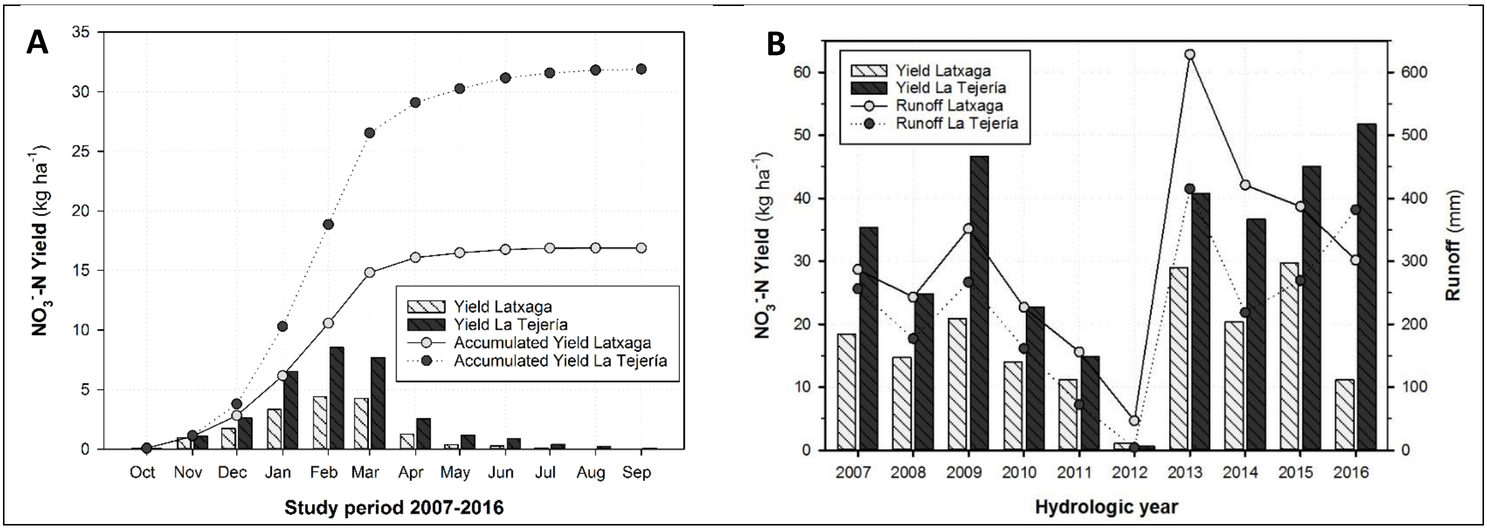

Figure 10. Monthly and monthly accumulated nitrate- N yield (A) and annual nitrate-N yield and runoff (B) at the Latxaga and La Tejería watersheds.

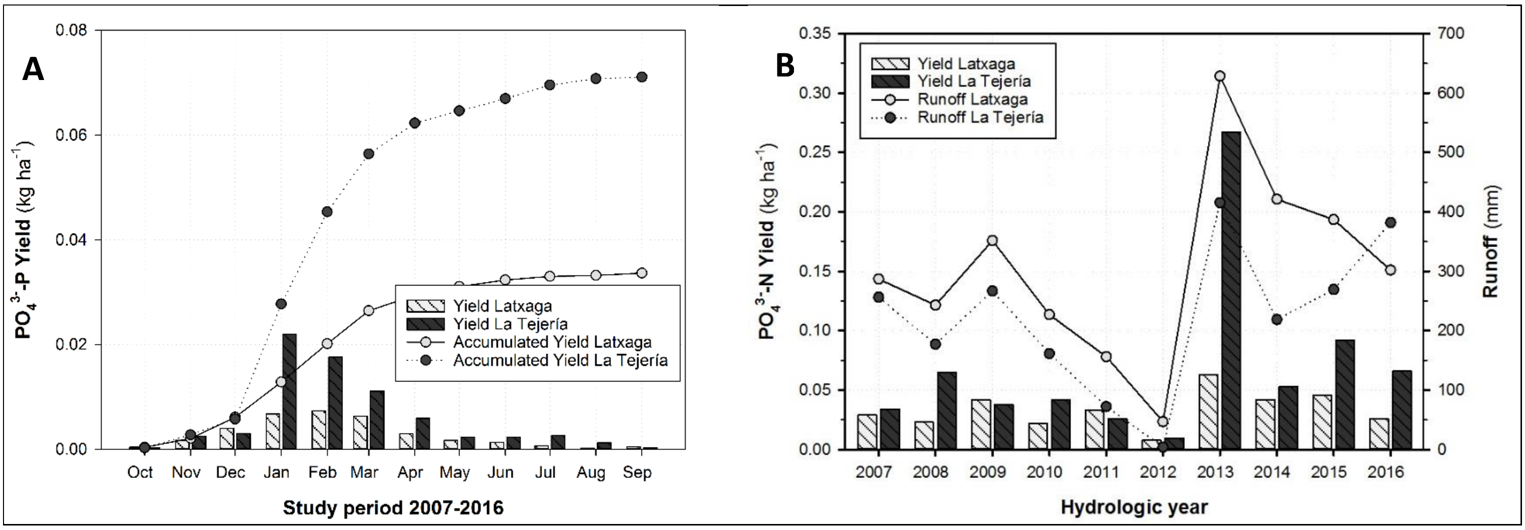

Figure 11. Monthly and monthly accumulated phosphate-P yield (A), and annual phosphate-P yield and runoff (B) at the Latxaga and La Tejería watersheds.

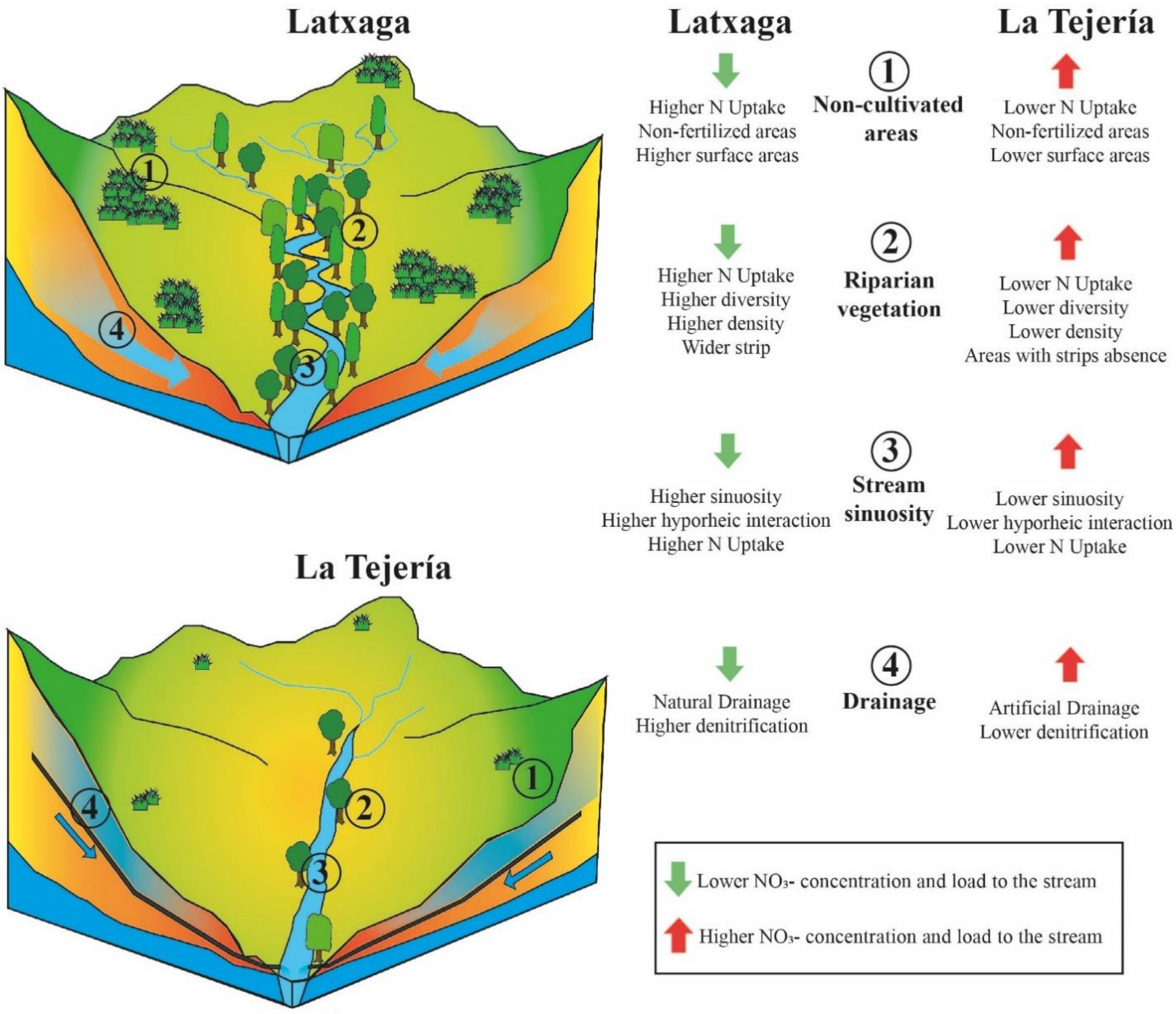

Figure 12. Schematics of the main controlling factors of nitrate dynamics

Table 1. Main characteristics of the Latxaga and La Tejería watersheds.

	Latxaga	**La Tejería**
Area (ha)	207	169
Average Temperature (ºC)	11.8	12.3
Average Precipitation (mm)	850	750
Average Slope (%)	17	15.5
Land Use (ha)		
Cultivated area (Wheat, barley)	178 (85%)	157 (93%)
Non-cultivated vegetated area (Shrubs, riparian vegetation)	21 (11%)	4 (2%)
Others (Roads, infrastructures)	8 (4%)	8 (5%)
Fertilization (kg ha^{-1})	190	170
Productivity (Mg ha^{-1})	4,9	4,3
Stream sinuosity index (m m^{-1})	1.13	1.04
Tile drainage density (m ha^{-1})	0	25

Table 2. Parametric and non-parametric statistics of nitrate and phosphate concentration at the Latxaga and La Tejería watersheds in the 2007-2016 period.

Conc. (mg L^{-1})	NO_3^-		PO_4^{3-}	
	Latxaga	La Tejería	Latxaga	La Tejería
p10	2.09	37.34	0.025	0.025
p25	8.07	62.02	0.025	0.025
p50	20.99	73.49	0.025	0.025
p75	29.76	86.08	0.025	0.089
p90	38.79	98.11	0.083	0.365
Average	20.78	71.81	0.060	0.201
S.D.	14.84	24.62	0.376	0.723

Conc.: Concentration

S.D.: Standard deviation.

Table 3. Yield estimations of nitrate-N and phosphate-P at Latxaga and La Tejería, with the methods described in Meals et al., 2013

Yield estimations (kg ha^{-1} year^{-1})	Nitrate-N		Phosphate-P	
	Latxaga	La Tejería	Latxaga	La Tejería
Ratio estimator*	17.04	31.81	0.033	0.071
Regression**	20.11	37.84	0.033	0.068
Numeric integration	16.61	32.19	0.032	0.066

*The ratio estimator method employed was the Beale Ratio (Meals et al., 2013).

**The LOADEST software, developed by the US Geological Survey, was utilized for the Regression (Runkel et al., 2004).