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Understanding nutrient (nitrate and phosphate) exportation processes in two agrarian watershed in Navarre

Presented by/ Presentadopor:

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AGRI-FOOD AND RURAL ENVIRONMENT ENGINEERING DEGREE
GRADO EN INGENIERÍA AGROALIMENTARIA Y DEL MEDIO RURAL

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ABSTRACT

Rainfed land covers most of Navarre arable land surface, contributing with over 60% of the crop production. In this study, the discharge and water quality data collected during October 2006-September 2016 by the Government of Navarre in two watersheds with rather similar climate and agricultural management representing typical rainfed conditions in the middle Navarre (La Tejería, 169 ha, and Latxaga, 207 ha) were analyzed to understand significant differences in nutrient dynamics previously reported for these watersheds. Annual discharge was higher in Latxaga watershed (≈250 mm/year) than in La Tejería (≈222 mm/year). Median nitrate concentration (≈70 mg/L) and nitrate export (≈32 kg N/ha/year) in La Tejería were higher than those recorded in Latxaga (≈20 mg/L and 17 kg N/ha/year, respectively). Similarly, phosphate concentration (≈0.12 mg/L) and export (≈0.05 kg P/ha/year) were higher in La Tejería than in Latxaga (≈0.07 mg/L and 0.03 kg P/ha/year). The influence in the nitrate and phosphate dynamics of different factors such as climate, soils, fertilization, shape of the watersheds, riparian vegetation, distribution of unproductive areas and subsurface drainage were assessed through a literature review. The factors that most likely play the main role in the higher nitrate export in La Tejería are the presence of tile drainage, the minor potential of riparian areas to decrease nitrate load and the proportion and location of unproductive areas. Phosphate dynamics in these watersheds are probably controlled by sediment dynamics and the differences in sediment exports between La Tejería and Latxaga suffices to explain the differences in phosphate exports.

Key words: environmental impact; rainfed agriculture; dissolved nutrients dynamics; land use.

RESUMEN

El cultivo de secano cubre la mayor superficie arable de Navarra, contribuyendo en más del 60% en la producción de cultivos. En este estudio se analizan los datos (de octubre de 2006 a septiembre de 2016) de caudal y de calidad de agua en dos cuencas agrarias similares en cuanto a clima y manejo agrícola del Gobierno de Navarra que representan las condiciones de cultivos secanos de la zona media de Navarra (La Tejería, 169 ha, y Latxaga, 207 ha), con el fin de entender las diferencias en la dinámica de nutrientes citadas en estudios anteriores. El caudal anual en la cuenca de Latxaga (≈250 mm/año) fue mayor que en La Tejería (≈222 mm/año). Las concentraciones (≈70 mg/L) y las exportaciones de nitrato (32 kg N/ha/año) fueron mayores en La Tejería en comparación con las obtenidas en Latxaga (≈20 mg/L y 17 kg N/ha/año respectivamente). De manera similar, las concentraciones (0.12 mg/L) y exportaciones (0.05 kg P/ha/año) de fosfato fueron mayores en La Tejería (0.07 mg/L y 0.03 kg P/ha/año en Latxaga). Mediante revisiones bibliográficas, se evaluó la influencia de diferentes factores (condiciones climáticas, los suelos, la fertilización, la forma de las cuencas, la vegetación riparia, la distribución de zonas improductivas y el drenaje subsuperficial) en las dinámicas del nitrato y el fosfato, siendo los últimos tres factores citados los que desempeñan probablemente el papel más importante en la exportación de nitratos. Las diferentes exportaciones de sedimentos entre las dos cuencas probablemente explican las diferentes exportaciones de fosfato obtenidas.

Palabras clave: impacto medioambiental, agricultura de secano; dinámicas de los nutrientes disueltos; uso del terreno.

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1. INTRODUCTION AND OBJECTIVE

1.1. Background

Global land area covers more than13 billion ha, of which about 37% corresponds to agricultural area. Cultivated land has grown significantly in recent decades, while rainfed land has slightly decreased. Rainfed agriculture plays an important role in food production, as about an 80% of agriculture is rainfed, contributing nearly 58% of the global food production (World Bank, 2014). In accordance with FAO (2011), this type of agriculture's production depends on rainfall, and therefore, soil quality plays an important role on the lands potential. Nutrient availability and nutrient retention capacity of the soil are one of the most limiting factors, followed by soil depth, drainage characteristics, soil structure, cultivation practices and land slope. Due to the reduced soil nutrient availability in many lands and other degradation factors such as sloping terrain or rainfall and runoff contributions to erosion, rainfed systems have high soil degradation risks (FAO, 2011).

Agricultural land contributes in an important way to water pollution. The intensification of several practices has created big impacts on water quality, such as the increase in the use of mineral fertilizers, which has incremented ten times since 1960 (FAO, 1996). Water pollution due to fertilizing practices affects both surface and groundwater quality, leading to environmental problems such as eutrophication, as a result of nutrients runoff (phosphorous particularly), or nitrate leaching. Cultivation is included in the group of agricultural activities leading to surface and groundwater pollution, along with other practices such as irrigation, pastures and aquaculture (FAO, 1996).

1.1.1. Nitrogen

Nitrogen (N), along with phosphorous (P) and potassium (K), are considered the major plant nutrients (FAO, 2006). It is one of the most limitating element on crop production, and its overfertilization causes high agronomic, environmental and health problems. Nitrogen on the soil can be found in its organic form, which is present on the organic matter, humus and living organisms. Inorganic nitrogen (around 2% of the soil total N) can be found as nitrate (NO_3^-), ammonia (NH_4^+) or nitrite (NO_2^-) form. Nevertheless, plants can only absorb and use the simple ionic forms of N: ammonia (NH_4^+) and nitrate (NO_3^-). Unlike P and K, which dynamics are regulated by a chemical equilibrium, N cycle is mainly controlled by biological processes, derived from soil microbial activities, which affect most the mineral forms and organic reserve forms of N (Perdomo, 2003).

The total N content in the soil is affected by many different factors such as climate and vegetation, which is directly correlated to microorganisms activity; local effects, including topography, slope orientation and the type of soil; source material (clay content) and the management of the soil (tillage or non-tillage, for example) (Perdomo, 2003).

The soil nitrogen cycle pathways complete a complex network of physical, biological and chemical processes, through which N enter the soil N cycle in a numerous different forms and ways(Merrington et al., 2002). This complexity leads to the difficulty of measuring the mineral N quantity in the soil and its availability for the plant, as it is continuously interacting with each other and with the environment. There are three main ways in which nitrogen is imported from the outside to the soil: atmospheric deposition, biological N_2 fixation and fertilizers. As most atmospheric N compounds are soluble in water, atmospheric deposition normally occurs through wet processes, such as rainfall, even if it may occur a dry deposition of gaseous and particulate material. A study made in south and eastern England (and the same part of Germany) estimated that there was an atmospheric deposition of 30-50 kg N/ha, of which 30% was immobilized, 12% denitrified 5% leached and the remaining was for the crop uptake (Goulding et al., 1998).

The bacteria *Rhizobia* is one of the most important agricultural example that explains the biological fixation. It consists on a close symbiotic relationship between the bacteria with leguminous crops, at the nodules of the roots of the legume, which reduces the atmospheric N to NH_3. This biological fixation by leguminous can be used by the crops following it and it can get to fix around 10 - 100 kg N/ha for arable legumes and 100 to 250 kg N/ha for forage legumes.

Fertilizers are also other important source of N input for the soil, which are normally applied when the soil is not capable enough to provide the entire N that the crop requires. They are both mineral and organic fertilizers, and the first one directly supplies mineral N to the soil in the form of NH_4^+ and NO_3^-, which is directly available for crop uptake. Animal manure usually excreted as dung and urine, is directly spilled to the soil surface when the livestock is grazing or applied by farmers. It provides inorganic N (mostly NH_4^+), which is easily available for the plant, and organic N (Merrington et al., 2002).

Moreover, there are some chemical and biological transformations within the soil nitrogen cycle, which lead to variations on the amount of mineral N on the soil (available for crop uptake) and the amount of N in risk of being lost into the environment by processes such as lixiviation. The two most important transformation processes that involve the transition between inorganic and organic forms of nitrogen in the soil are nitrogen mineralization and immobilization (Merrington et al., 2002). Nitrogen mineralization is the transformation of organic N to inorganic N, in the form of NH_4^+or NO_3^-, while nitrogen immobilization is the opposite process of mineralization. It is the transformation of soil inorganic N (NH_4^+, NO_3^- or NO_2^-) into organic N, carried out by microorganisms when they absorb mineral N and transform it into the constituent nitrogen of their cells and tissues (Perdomo, 2003).

1.1.2. Phosphorous

Phosphorous, along with water, N and K, is consideredone of the most yield-limiting factors of agricultural production, even if its presence in plants is much lower than those of N. Unlike N, P has not gaseous phase, and it is mainly derived from weathering of geological materials. It is characterized by its very low solution concentrations due to its strong adsorption to soil particle surfaces. Like nitrogen, phosphorous in soil is present in both inorganic and organic forms, although its forms are different from nitrogen ones. It is categorized in five nutrient pools: non-liable inorganic phosphorous, liable P absorbed to soil particles, biomass P associated with living organisms, organic P associated with non-living soil organic matter and dissolved P in both inorganic and organic forms. As P is closely related to organic matter, most organic P is located in the topsoil, while its presence decrease with depth. P is taken up by plants as $H_2PO_4^-$ or HPO_4^{2-} depending upon the soil pH (Merrington et al., 2002).

Phosphorous transformations in soil depend on different factors such as soil, organic substrate, climate and season(Merrington et al., 2002). It involves both mineralization and immobilization processes, carried out by microorganisms activity, which occur simultaneously. The loss of phosphorous from agricultural systems may appear to be low compared with the amount of nitrogen loss. However, low P concentrations cause serious environmental problems in water. Phosphorous is transported from soils by runoff, soil erosion, leaching and subsurface flow, being surface runoff the main mechanisms producing P losses from agricultural systems. It is mainly influenced by fertililiser application (rate, timing, form and method), rainfall and farm type. P is principally transported in its particulate form. During storm events, when suspended sediments concentration in the stream water is higher, the major particulate P loss occur. In contrast with N, leaching of P is not common, as its solution concentration in soils is quite low. Soil type, pH, weather conditions and fertilizer usage are some factors affecting P leaching from agriculture. Furthermore, subsurface drains and macropores also influence P transport, promoting P leaching (Merrington et al., 2002).

According to FAO (2018), the amount of phosphorous nutrient (as P_2O_5) used as fertilizer in agriculture worldwide has increased from 34.55 to 47.96 million tons in the period 2002-2016. As mentioned before, the fertilizer application is closely related to P loss, so it is essential to control those applications, in order to avoid environmental problems such as eutrophication.

1.1.3. Nutrient use evolution as fertilizers

Nitrogen used as fertilizer is worldwide the most demanded nutrient (115,100 thousand tons) followed by phosphate (P_2O_5) (43,803 thousand tons) and potash (K_2O) (31,829 thousand tons) (FAO, 2015).

Due to the growth in the demand of agricultural products for the last decades, fertilizer consumption has also increased in the last years. According to last data FAO (2018), in 2015 the total fertilizer nutrient worldwide ($N+P_2O_5+K_2O$) used in agriculture was 195.73 million of tons. In Europe, as reported by FAO (2016), it is forecasted a compound annual growth rate from 2015 to 2019 on the demand of N of the 0.43%, of the 1.58% for P_2O_5 and of the 1.90% for K_2O. Nitrogen is worldwide the most demanded fertilizer, followed by phosphorous (as P_2O_5) and potash (K_2O), and it is predicted to continue that way. According to the International Fertilizer Association(IFA, 2018), urea (46% N), diammonium phosphate (DAP) (18% N, 46% P_2O_5) and potassium chloride (60% K_2O) are worldwide the most consumed N, P and K fertilizer products respectively. Due to its composition and its reactions within the soil, when urea is applied to the soil, it should be buried, with a thin soil layer covering the fertilizer, in order to avoid N losses by volatilization. Usually urea is rapidly transformed to NH_4^+ and retained by soil colloids. Because of its mobility through the soil, it is recommended to be applied fractionally, when the crop uptake is greater.Unlike urea, DAP contains both nitrogen and phosphate. It has a synergizing effect, as the presence of ammonium promotes the exploitation of P. High NH_4^+ amounts reduces P binding reactions, making it more available for the plant (DELCROP S.A., 2013).

1.2. Rainfed agriculture in Navarre

Rainfed agriculture plays an important role in Navarre, as it covers most of Navarre arable land surface(Government of Navarre, 2004; Government of Navarre, 2018a). About the 60% of the terrain is under forested area, while unproductive areas cover less than a 4%.According to current data obtained from the agrarian observatory of the Government of Navarre (Government of Navarre, 2018a), rainfed areas are mostly distributed in the central and south part of Navarre, producing over the 60% of the total crop production. Regarding land use, herbaceous crops clearly predominate over other land uses, representing a 25% of the total surface. Winter grains covered about the 78% of the total rainfed land, producing about the 38% of the total rainfed production (Government of Navarre, 2018a).

As mentioned before, some environmental impacts such as soil erosion processes and water pollution are produced by agrarian activities, so the concern about environmental problems caused by agriculture is also present in Navarre. For that purpose, since 1993, the Agriculture, Livestock and Food Department of the Govern of Navarre developed a network of experimental watersheds, representative of the different agrarian and natural conditions of Navarre. The network consist on four experimental watershed. In 1994 La Tejería (Villanueva de Yierri) and

Latxaga (Beortegui and Urroz-Villa) watersheds were first stablished, representing the rainfed land conditions of the middle area of Navarre. The third watershed was Oskotz-Muskitz (Valle de Imotz), which exemplify an intensive livestock area. Landazuria was the last one, representing the currently implemented irrigated areas. Each watershed have one hydrology station, one automatic meteorology station and some rainfall gauges distributed, so in the end, discharge, turbidity and water quality parameters are measured, except for Oskotz watershed, which has two hydrology station: one measuring the parameters for the whole watershed (forests and grasslands) and the other one, located at the end of the watershed, measures just the parameters for the forest (Casalí et al., 2006; Donézar and del Valle de Lersundi, 2001).

The impacts of agriculture on nitrate exportation on waters in Navarre have been reported several times. For instance, the LIFE-Nitrates (2018) project consisted an exhaustive study of nitrate contamination in the Ebro Valley. The main objective of this project was to obtain a better knowledge of the impact of agrarian activities on nitrate water pollution, beyond defining and promoting good practices and tools to contribute the prevention and reduction of this type of contamination. In addition to this project, there are some other studies, such as Casalí et al. (2008), analyzing agricultural impacts on water quality, hydrology and erosion in central Navarre. This study showed that, despite having similar management, land use, climate and soil conditions, nitrate concentration and exportation in La Tejería and Latxaga watersheds was quite different between both watersheds. They concluded that some differences in watershed morphology and topography, and vegetation on stream channels could affect to the unexpected results obtained, in addition of the need of further investigation in this issue.

1.3. Objective

The objective of the present study were (a) to assess the dynamics of nitrate and phosphate concentrations in two small watersheds under rainfed agriculture, (b) to estimate the amount of nitrate-N and phosphate-P exported, and (c) to understand the processes influencing the differences between both watersheds. For that, the discharge and water quality data collected in La Tejería and Latxaga watersheds by the Government of Navarre during October 2006-September 2016 were analyzed and then compared and contrasted with the scientific literature.

2. MATERIALS AND METHODS

2.1. Description of experimental watersheds

Both watersheds described below (La Tejería and Latxaga) represent the cultivation conditions of the dry-land cereal crops of the middle zone of Navarre. These watersheds were chosen because of their representativeness of the area, and its uniform and impermeable geological material.

2.1.1. La Tejería watershed

La Tejería watershed (Villanueva de Yerri) covers an area of 169 ha and is located in the central-west part of Navarre, at an altitude between 496 and 649 meters (Figure 1). The geographical coordinates of the gauging station (watershed outlet) are 42º44’10.6’’N and 1º56’57.2’’W. It presents a moderate relief, with an average slope of 12%.

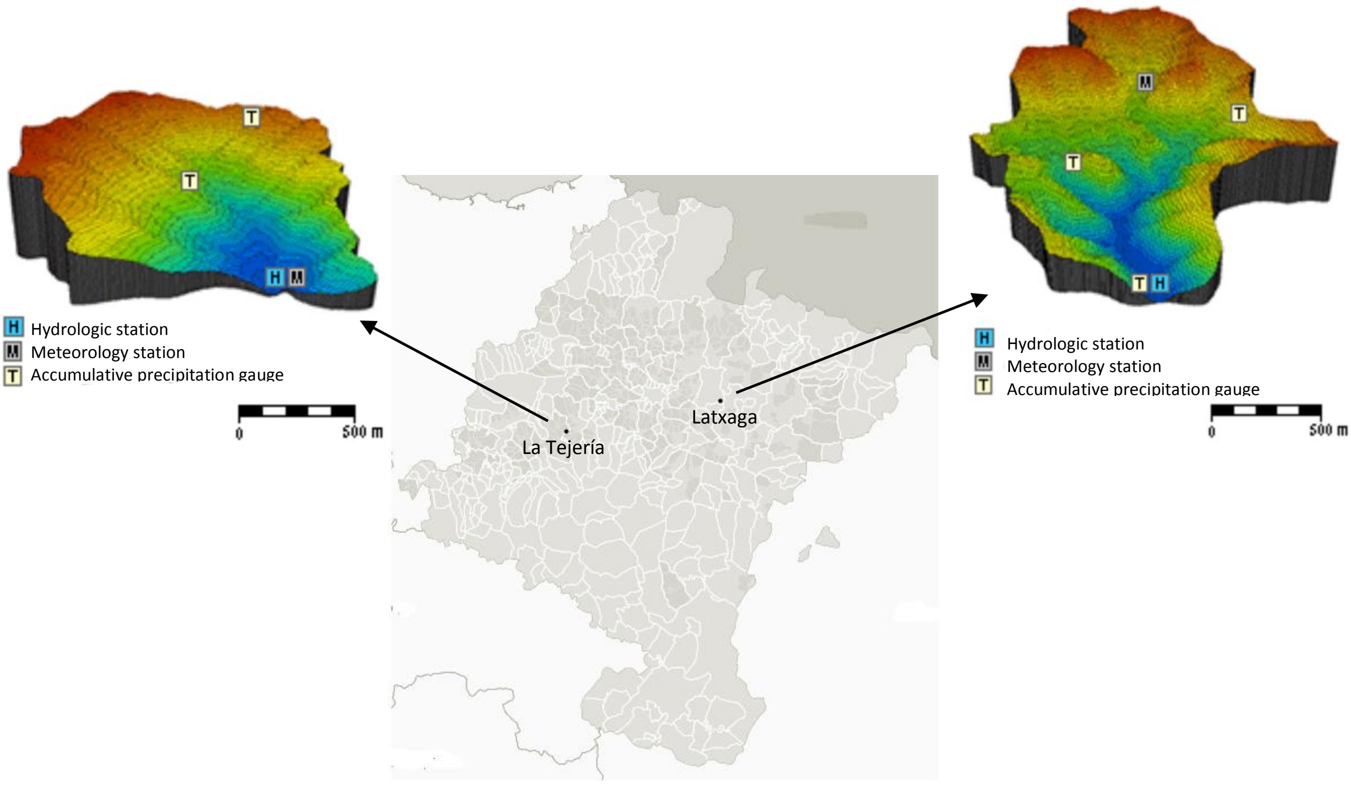

Figure 1. Location of La Tejería and Latxaga watersheds. *Source: DEM images reproduced from Government of Navarre (2018b).*

According to Köppen climatic classification, its climate was classified asMediterranean with fresh summers, which consists on cold or temperate winters and dry and fresh summers, being the Mediterranean forest its natural vegetation (Government of Navarre, 2018b). The average annual temperature is 12ºC, reaching values of 42.3ºC in summer and -10.7ºC in winter, for the period 1997-2016 (meteorological station in Villanueva de Yerri GN) (Figure 2). Annual precipitation is 700-755 mm, being 80 mm the maximum precipitation in 24 hours (return period, T = 10 years). January, February, March and November are the months with higher precipitation values, while July, August and September present the lowest ones. The annual potential evapotranspiration is 1,100 mm (Blaney & Criddle method).

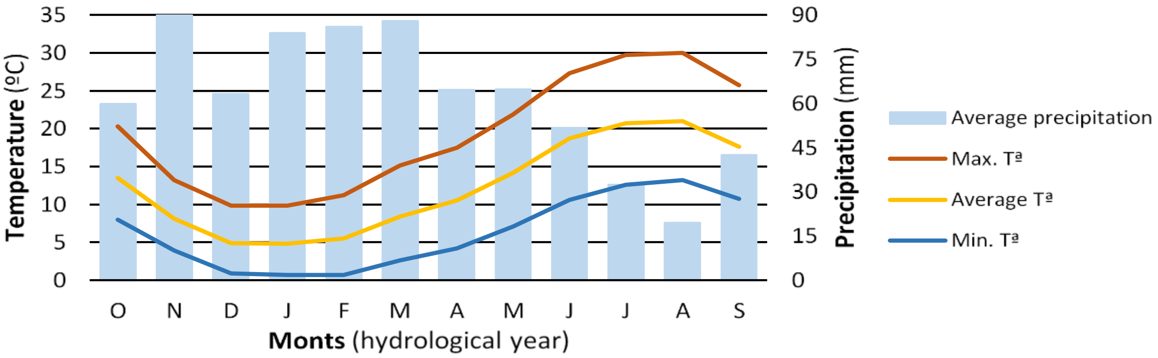

Figure 2. Ombrothermal diagram of Villanueva de Yerri automatic station (1997-2017). *Source: made from Government of Navarre (2018c)*

According to the geological information (Government of Navarre, 1996a), most abundant geological materials underlining the watershed are ocher-yellowish shales and sandstones (Continental Tertiary). Predominant materials are marls and sandstones of continental facies. Gravels, sands and clays of alluvial deposits underline watershed bottom (Quaternary).

The soil map of the La Tejería watershed (Government of Navarre, n.d.*a*) reflected that shallow erosion hillslopes cover around 128 ha, deep accumulation hillslopes 25 ha and deep swales 6 ha. The soil has silty clay and silty clay loam texture, between 1-2% of organic matter and more than a 40% of carbonates. According to the USDA Soil Taxonomy classification (Soil Survey Staff, 2014), the soil class *Vertic Haploxerept* (Figure 3) is the one covering most of the surface of the watershed (41%), located on erosion hillslopes (laminar water erosion) in the center of the watershed on marls with sandstone paleochannels. These soils are shallow (0.5-1 m depth) and have an irregular organic matter distribution through the soil, with values around 1% at 1m depth. Moreover, they are free of salinity and alkalinity. The textural family in the control section is fine clay, with clay amounts between 30 and 45%; and their mineralogical family is limestone with a carbonate percentage around 36%. The surface horizon is of massive structure, of clay loam texture. They are in heavily wavy reliefs, with maximum slopes between 8 and 16%.

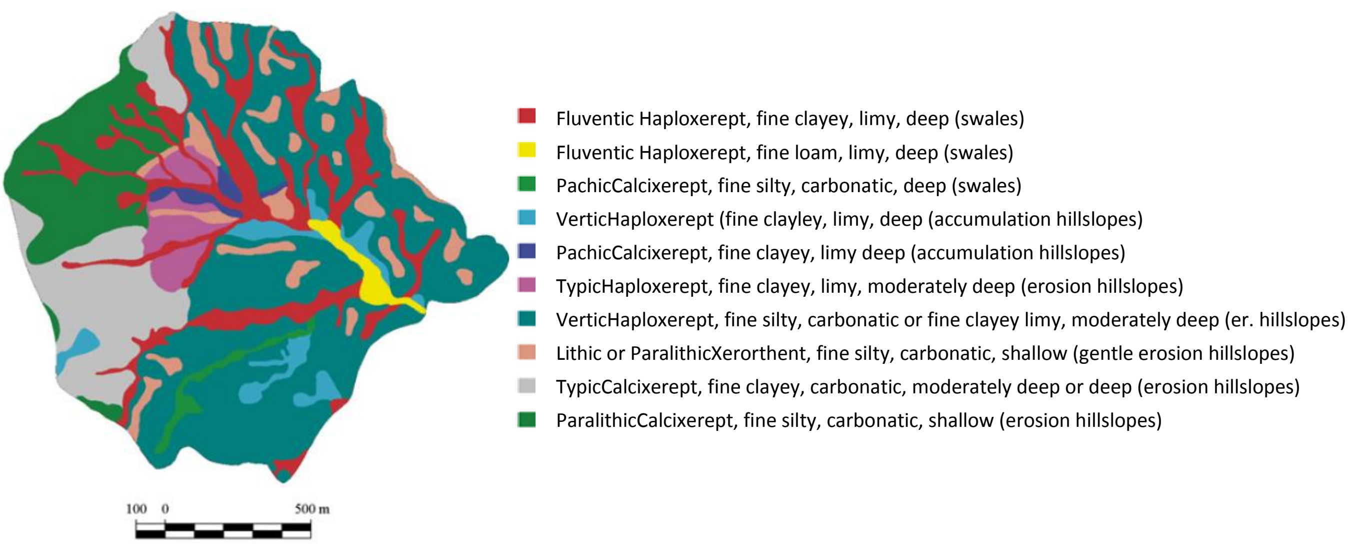

Figure 3. Soil map of La Tejería watershed. *Source: reproduced from Casalí et al. (2008)*

Currently, more than 90% of the watershed area is dedicated to rainfed cereals, cultivated with annual crops, mostly wheat, barley and oat. The annual average production varies depending on the area of cultivation. On hillslopes, average annual yields vary from 3,500 to 4,000 kg/ha while on swales, average yields reach above 5,500 kg/ha. According with governmental estimates in the agrarian region in which La Tejería is located (Government of Navarre, 2018a), wheat and barley average annual production was about 4,487 and 4,018 kg/ha respectively, even if wheat just covered the 40% of the total arable land.

Nitrogen annual application rates averagedbetween160 and 180 kg N/ha, usually in form of urea, although sometimes urea with ammonium sulfate is applied in order to meet the sulfur needs. Another fertilizer used in this area is super phosphate 45% or diammonium phosphate (DAP: 18-46-0). Fertilizer application is usually made twice: the first one is applied at the tillering initiation stage and the second one at the end of the tillering stage (nearly mid-January and -March respectively). In addition to nitrogen fertilization, there is also an extra phosphorus application every 3 years at the sowing stage in order to restore the soil from crop extractions (about 50-60 kg P_2O_5/ha). There has not been a remarkable change on the type of fertilizer used during last decades, although application rates had been better adjusted to the needs of the crops [Luis Orcaray (INTIA), personal communication].

Harvest residues were not incorporated to the soil. It was forbidden to burn the residues unless there existed a previous authorization(Government of Navarre, n.d.*a*).

As mentioned above, almost the total surface of La Tejería (more than 90%) was under cultivation, being the rest of the area covered by natural vegetation. Brachipodium is the vegetation occupying most spaces between plots slopes and some small gall oak forests. Riparian vegetation consists on white willow (*Salix alba*) and black poplar (*Populus nigra*) (Government of Navarre, n.d.*a*).

2.1.2. Latxaga watershed

Latxaga watershed (Beortegi and Urroz-Villa) covers an area of 207 ha and is located in the central-east part of Navarre, at an altitude between 504 and 639 meters (Figure 1). The geographical coordinates of the gauging station (watershed outlet) are 42º47’7.5’’N and 1º26’11.4’’W. It presents a rougher relief compared to La Tejería watershed, with slopes varying between 7% on the valley bottom, to 30% on hillslopes.

Its climate wasclassified as oceanic or west costal maritime (two dry months). It consist on a temperate climate with fresh summers and abundant rainfall. Natural vegetation of this type of climate are oaks forests. Its average annual temperature was of 12ºC, reaching values of 39.9ºC in summer and -12.4ºC in winter (data collected for the period 1998-2016 from the meteorological station in Beortegui GN, Figure 4). Annual precipitation is 800-850 mm, and months with maximum and minimum precipitation, maximum precipitation in 24 hours and annual evapotranspiration values are the same to the ones reported for La Tejería watershed.

The geologic map of Aoiz and the Navarre geologic cartography memory (Government of Navarre, 1996b) reflected that most common geological materials underlying Latxaga are marls, limonites, calcarenites and some sandstone layers. It is characterized by its low sandy level. Other geological materials present are gravels, sands and clays of the valley bottoms.

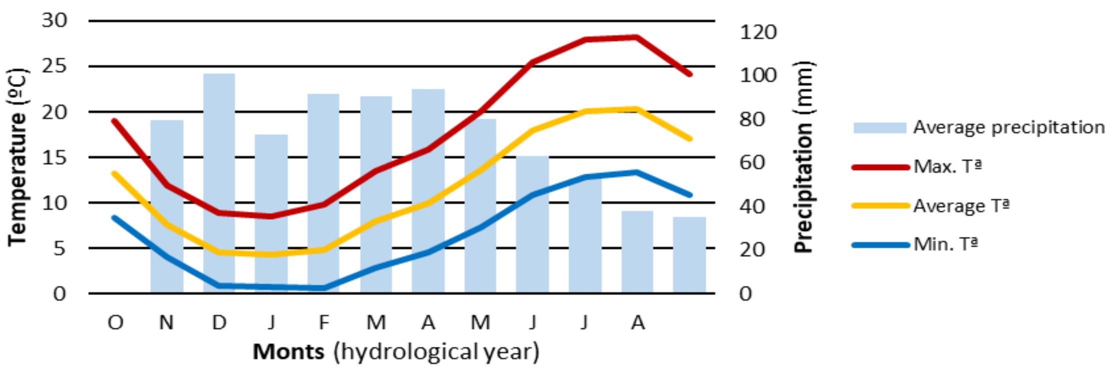

Figure 4. Ombrothermal diagram of Beortegui automatic station (1997-2017). *Source: made from Government of Navarre (2018c)*

According to the soil map of the Latxaga watershed (Government of Navarre, n.d.*b*), shallow erosion hillslopes also cover the most part of the watershed (169 ha) and, unlike La Tejería watershed, deep swales cover greater area (36 ha). The soil has a silty clay loam texture, an organic matter content between 1.8-2.5% and more than a 40% of carbonates. According to the USDA Soil Taxonomy classification (Soil Survey Staff, 2014), the soil class *Paralitic Xerorthent* covers most of the surface of the watershed (89 ha) (Figure 5), located on erosion hillslopes (moderate water laminar erosion) under marly flysch. The soil profile presents just a surface horizon, lying directly on rock. In some cases, due to the high slope of the terrain and its facility to erosion, that surface horizon disappear generating rocky outcrops. This type of soils are shallow (<0.5 m depth) and have a 1.1% of organic matter content.

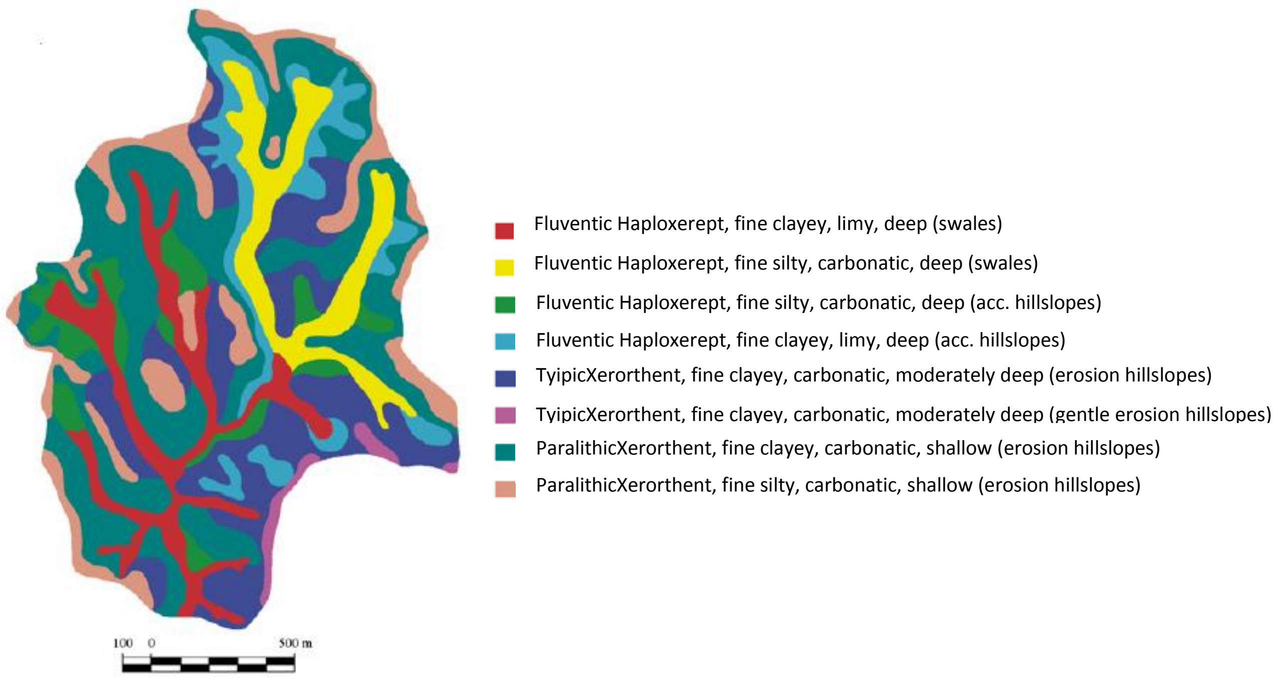

Figure 5. Soil map of Latxaga watershed. *Source: reproduced from Casali et al. (2008)*

Latxaga watershed is less covered by cultivated land than La Tejería (about 80 % or 90 % of the total area of Latxaga, depending on the year). It is mostly cultivated with winter grain, covered with wheat and barley. The average yields in the swales takes values higher than 5,500 kg/ha while on the hillslopes, vary from 3,500 to 4,000 kg/ha. According with governmental estimates in the agrarian region in which the watershed is located (Navarre Government, 2018a), wheat occupy an average of 66% of the total arable land of Latxaga, obtaining a 5,021 kg/ha average annual production. The rest of the surface was covered by barley, and the average annual production obtained was of 4,773 kg/ha.

Fertilization managements were close to those of La Tejería watershed. The application was also made twice, at the initiation and the end of the tillering state, but the annual nitrogen dose applied was higher than in the previous watershed, according with a higher expected production. Annual fertilization rate varied between 180 and 200. Phosphate 45% or DAP were also applied, in the following the same management as in La Tejería watershed. There had not been either remarkable changes on the type of fertilizer used during last decades, and harvest residues were managed in the same way as in the former watershed.

Unlike La Tejería, natural vegetation presence in Latxaga watershed was greater. Potential vegetation corresponded to white oak, meaning a forest of white oaks, in which other trees appear in isolation, such as common-pine (*Pinus sylvestris)* and Italian maples (*Acer opalus)*. After residues burning and overgrazing, the terrain suffered some intense erosion processes (Government of Navarre, n.d.*b*). Therefore, surface stayed almost covered by boxwood bushes. Riparian vegetation consisted on white willow (*Salix alba*), narrow leaf ash (*Fraxinus angustifolia*) and black poplar (*Populus nigra*) (Government of Navarre, n.d.*b*).

2.2. Data collection

2.2.1. Measurement devices

According to Donézar and del Valle de Lersundi (2001), in each watershed an automatic meteorology station with a wind monitor, a relative moisture and air temperature probe, a global solar radiation sensor, a soil temperature sensor, and a tilting cups pluviometer with heating incorporated was installed. Temperature, relative moisture, rainfall, wind velocity and direction, solar radiation, besides other meteorological parameters are daily measured, and additionally, all former parameters but rainfall are recorded every 10 minutes.

Besides, a hydrological stationwas installed in each watershed. It consists of a discharge measurement device, which comprises a triangular profile flat-V weir of concrete and three sensors: a digital limnigraph, a programmable automatic sampler and a turbidimeter (Figure 6). Additionally, there was a spherical hollow made in the downstream face of the weir where water samples are taken from every 6 hours (normally at 3, 9, 15 and 21 hours, solar time), in order to obtain a representative daily sample. Daily water samples were automatically collected on 24 bottles of 500 ml, unless the discharge values were low, when sampling was interrupted. The samples were analyzed at the Agrarian Laboratory of the Agriculture, Livestock and Food Department of the Government of Navarre, determining values of the following variables: nitrate and phosphate concentrations (mg/L), as well as other major dissolved constituents (potassium, carbonate, bicarbonate, calcium, magnesium, chlorides, sulfates and sodium concentrations) and sediment concentration (g/L). In particular, NO_3^- concentration was determined by ionic chromatography technique whereas PO_4^{3-} concentration was determined by spectrophotometry. As mentioned before, whenever the discharge was close to zero, the sampler was switched off to avoid equipment malfunction.

(a)
(b)

Figure 6. Pictures of the hydrological station from Latxaga watershed, exemplifying (a) the triangular profile flat-V weir and (b) the spherical hollow that takes the samples.

2.2.2. Available data

All the data for the study was provided by the Government of Navarre, which can be consulted, at least partially(Government of Navarre, 2018*b*).Even if La Tejería's and Latxaga's meteorological stations provide data since 1995, the study period was reducedto those months having at least 50% of the days with data. A 10 years study period was established, covering hydrological years (October 2006 – September 2016), as more than the 69% and 64% of the months have more than 50% of daily data, at La Tejería and Latxaga respectively. Meteorological and discharge data recorded every 10-min was then processed to daily data.

2.3. Data treatment

To obtain a reliable representation of the data, it was considered that these type of data (discharge and N and P concentrations) usually have some extreme values, so the median was the statistical parameter that reflect better these data, as it is not strongly influenced by extreme values (Helsel and Hirsch, 2002). Therefore, for both La Tejería and Latxaga watersheds the median and the inter-quartile range (IQR) were calculated for nitrate and phosphate concentrations, and for the discharge.

Problems such as mechanical failures of the stations orsummer low flow produced lack of data in the study period. In this case, for the total study period (3653 days), there were just 2533 and 2425 daily water samples collected for La Tejería and Latxaga watershed, respectively. To estimate both concentrations, the criteria of just estimate the median of those months in which more than 50% of days collected water samples was stablished. For La Tejería, 71% of the months of the study period fulfill stablished criteria while 67% of the months fulfilled them for Latxaga.

To assess the difference between median values, a non-parametrical method of common use was applied. The method used was the *Test of the median of K independent samples*, which determines if k independent groups (not necessarily of equal size) have been taken from the same sample or from samples with equal medians (Badii et al., 2012).

To calculate daily loads of nitrate as nitrogen (nitrate-N) and phosphate as phosphorous (phosphate-P), daily concentration and discharge data was used. The estimation for the study period (hydrological years 2007-2016) requires some assumptions regarding non-sampled days. In this study, three different methods were assessedfor load estimation: numeric integration, regression and the Beale Ratio Estimator. According to Meals et al. (2013), numeric integration is the simplest approach to yield estimation. It is based in the integration of the daily load. Its use is adequate when sampling frequency is high (100 samples per year or more) and when they are well distributed so they capture most of the events. It is a cost-effective method for yield estimation. Regression method is commonly used when there is a strong relationship between flow and concentration. It consisted on fitting a seven parameters rating curve to the observed data and then estimate the load for the selected study period. For the study, US Geological Survey software LOADEST (Runkel et al., 2004) was used to perform this method. Ratio estimators are powerful statistical methods for the estimation of pollutants when flow data is continuous but concentration data is intermittent. In the present study case, Beale Ratio Estimator method was used to correct the observed load. Once load was computed, yields were obtained by dividing the loads by the watershed surface.

2.4. Analysis of thedifferences

As reported by Casalí et al. (2008), despite the similarity of both watersheds, further studies are needed to explain the differences in nitrate yields between both watersheds. This study showed that in both watersheds nitrate concentrations followed a seasonal pattern (highest concentrations during the winter and early spring months), having great differences in the average exported nitrate yields: La Tejería's yield doubles Latxaga's one. Moreover, they estimated an average loss of 22% (maximum of 34%) and 8% (maximum of 12%) of the total fertilizer amount applied, for La Tejería and Latxaga respectively. They observed an important inter-annual variability of nitrate and phosphate yields, which have sense with the current climatic characteristics, besides the intra-watershed spatial variability. Apart from this report, other researches (Giménez et al., 2012; Jégo et al., 2008; Sánchez Pérez et al., 2003) analyzing similar situations claimed that further analysis were needed due to the high variability of the phenomena involved. Casalí et al. (2006 and 2008) suggested that some factors such as morphology, topography, stream channels vegetation, climate, agricultural management, soil condition, etc. highly influence on nitrate and phosphate yield export.

Therefore, some hypothesis were proposed for this study in order to explain the differences in nutrient dynamics and exports between the two watersheds: which factors control most nitrate and phosphate exported yields and analyze how each one affects, in order to try to understand the obtained results. In accordance with reviewed literature, factors proposed in this study that controlled nitrate and phosphate dynamics were riparian vegetation (Dosskey et al., 2010), climate (Stuart et al., 2011), soils (Honisch et al., 2002), shape of the watershed (Angier et al., 2005), proportion and distribution of unproductive area (Labriére et al., 2018) and different agricultural managements (Basso et al., 2010; McIsaac and Hu, 2004).

- For climate, not only temperatures and rainfall were taken into account but also its inter- and intra-annual distribution. This was primarily because of the seasonal pattern followed by nitrate and phosphate average export yield.

- Different soils characteristics such as type of soil, texture, organic matter content and depth were also considered to analyze differences between both watersheds.
- The shape of the watersheds was also contemplated: their orientation, sinuosity and the hillslope's convexity.
- Agricultural practices such as fertilization (does and type), plough and waste management were also considered.
- To evaluate riparian vegetation's effect, different aspects such as type of riparian vegetation, its density and distribution, previous vegetation, etc. were assessed.
- The analysis of terrain fragmentation was focused on evaluating the proportion of arable terrain, unproductive lands and their distribution through the watersheds.
- For drainage, apart from the density, the distribution of tile drainage through the soil analyzed too. Other agricultural practices such as fertilization (doses and type), plough and waste management were also considered.

It is important to note that, this study was not based on the experimentation of the different factors mentioned above, but on an analysis of the results, while they were compared and contrasted with the reviewed scientific literature.

3. RESULTS

The following sections presents the discharge, nitrate and phosphate concentrations and nitrate-N and phosphate-P yields obtained during the study period (October 2006- September 2017) in La Tejería and Latxaga watersheds.

3.1. Discharge

It was assumed that everydaily discharge value equal or lesser than 0.3 L/s in La Tejería adopted the same value (<0.3 L/s), and in Latxaga, where rainfall was greater, discharge values equal or lesser than 0.6 L/s, adopted a discharge <0.6 L/s. In La Tejería, median daily discharge values during the study period (hydrological years 2007-2016) ranged from <0.3 L/s (2012) to 4.6 L/s (2013), being 1.6 L/s (inter-quartile range: 0.7-3.7 L/s) the value for the whole study period. Table 1 shows median and inter-quartile range (IQR) annual discharge values for the whole study period, for both La Tejería and Latxaga watersheds, besides accumulated rainfall of each year.

Table 1. Median and IQR* discharge (L/s), and rainfallvalues for both La Tejería and Latxaga watersheds during the study period (2007-2016).

	Discharge (L/s)					
Hydro. year	La Tejería			Latxaga		
(Oct-Sept)	**Median**	**IQR***	***Rainfall (mm)***	**Median**	**IQR***	***Rainfall (mm)***
2007	2.5	0.4-14.5	*857*	2.1	<0.6-4.9	*977*
2008	1.8	0.9-9.9	*893*	1.6	<0.6-21.7	*837*
2009	0.5	<0.3-17.9	*667*	3.5	<0.6-10.4	*938*
2010	1.1	<0.3-14.8	*786*	0.8	<0.6-21.9	*793*
2011	0.6	<0.3-9.1	*548*	0.9	<0.6-6.5	*709*
2012	<0.3	<0.3-<0.3	*531*	<0.6	<0.6-<0.6	*596*
2013	4.6	0.4-11.7	*1329*	8.6	1.4-35.3	*1661*
2014	4.4	1.6-11.9	*819*	6.1	0.8-14.4	*1156*
2015	4.1	2.4-32.7	*851*	2.3	<0.6-24.4	*1033*
2016	1.4	0.3-15.5	*638*	0.6	<0.6-8.6	*761*
Average	**1.6**	**0.7-3.7**	***792***	**2.2**	**0.9-3.1**	***946***

*IQR: Inter-quartile Range

During the study periodthe pattern obtained for each year was: higher discharge values all along winter and early-spring months and lower values the rest of the year (Table 2). For La Tejería watershed, maximum median daily discharge per month observed was 22 L/s (February) while 0 L/s (negligible flow) was the minimum median daily discharge obtained (October, August and September).

Table 2. Median and IQR daily discharge (L/s) per month of La Tejería watershed during the study period (2007-2016) (hydrological year).

Months (hydro. year)	**Oct.**	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**
Median	0	0	4	11	22	19	8	3	0	0	0	0
IQR*	0	2	12	26	40	26	12	5	3	3	1	0
Q1**	0	0	1	3	5	8	3	1	0	0	0	0
Q3***	0	2	13	29	45	34	15	6	3	3	1	0

*IQR: Inter-quartile range; **Q1: First quartile; ***Q3: Third quartile.

In Latxaga watershed, the pattern followed during the study period was similar to the one of La Tejería. The discharge was 2.2 L/s (IQR: 0.9-3.1 L/s). Minimum annual discharge obtained was negligible (2012), while the highest daily median discharge was 8.6 L/s (2013). As represented in Table 1, months with high rainfall values obtained greater discharge.

Same patterns of La Tejería were observed in Latxaga watershed in relation with high and low discharge values according to the year months. Maximum median daily discharge per month obtained at Latxaga was 22 L/s (February) while 1 L/s was the minimum median daily discharge obtained (from June to October). Table 3 showed more detailed information about median and IQR daily discharge (L/s) values of Latxaga watershed during the study period.

Table 3. Median and IQR daily discharge (L/s) per month of Latxaga watershed during the study period (2007-2016) (hydrological year).

Months (hydro. year)	**Oct.**	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**
Median	1	3	8	13	22	17	7	2	1	1	1	1
IQR*	0	10	20	37	53	46	13	4	2	0	0	0
Q1**	1	1	3	6	4	7	3	2	0	1	1	1
Q3***	1	11	23	43	57	53	16	5	2	1	1	1

*IQR: Interquartile Range; **Q1: First quartile; ***Q3: Third quartile.

Months with higher discharge values coincide with greatest rainfall events and vice versa: 2012 was the driest year of the study period, with the lowest discharge values, while the following year (2013) was the wettest one, which gave the greatest discharge results. It was also observed that discharge distribution during the year did not follow a common pattern through different years, as it was strongly dependent on rainfall (not just quantity but distribution too), but after large discharge peaks, there was usually an immediate decline.

3.2. Nitrate and phosphate concentrations

During the study period (hydrological years 2007-2016), nitrate median annual concentrations obtained at La Tejería watershed ranged from 58.4 mg/L (IQR: 52.1-66.0 mg/L) in 2016 to 95.4 mg/L (IQR: 86.6-110.5 mg/L) in 2007, being 71.5 mg/L (IQR: 64.5-76.6 mg/L) the nitrate median annual concentration for the whole study period (Table 4). Phosphate concentrations obtained were much lower than nitrate ones, being in some cases 100 times lower. Phosphate median daily concentrations vary from 0.06 mg/L (IQR: 0.05-0.15 mg/L) in 2008 to 0.46 mg/L (IQR: 0.09-0.78 mg/L) in 2012, being 0.12 mg/L (IQR: 0.09-0.23 mg/L) the phosphate median annual concentration for the study period.

Regarding rainfall, nitrate highest concentration year (2007) did not coincide with highest rainfall year (2013), and either the phosphate did. Moreover, second highest nitrate concentration value was obtained the driest year of the study period (2012). The lowest nitrate concentration was obtained when rainfall was slightly higher than the average rainfall of the study period (725 mm), happening the same with lowest phosphate concentration value. Table 4 showed more detailed results obtained about nitrate and phosphate median annual concentrations in La Tejería watershed. The year with highest discharge value (2013) did not either coincide with the year with highest nitrate concentration value (2007), nor did the year with the lowest discharge (2009) with the lowest concentration of nitrate (2016).

Table 4. Monthly median and IQR for nitrates and phosphate concentrations, rainfall (mm) and discharge (L/s) obtained during the study period in La Tejería watershed.

Hydro. year	**Nitrates (mg/L)**		**Phosphates (mg/L)**		*Rainfall*	*Discharge*
(Oct-Sept)	Median	IQR*	Median	IQR*	*(mm)*	*(L/s)*
2007	95.4	86.6 - 110.5	0.08	0.06 - 0.11	*857*	***2.5***
2008	72.1	64.3 - 83.4	0.06	0.05 - 0.15	*893*	***1.8***
2009	77.7	73.8 - 84.2	0.08	0.07 - 0.33	*667*	***0.5***
2010	64.6	52.8 - 67.7	0.32	0.21 - 0.89	*786*	***1.1***
2011	88.0	84.3 - 94.6	0.26	0.17 - 0.28	*549*	***0.6***
2012	64.5	49.3 - 85.2	0.46	0.09 - 0.78	*531*	***<0.3***
2013	60.8	29.7 - 105.6	0.14	0.11 - 0.17	*1329*	***4.6***
2014	73.5	56.1 - 77.2	0.15	0.11 - 0.77	*820*	***4.4***
2015	70.9	63.9 - 81.8	0.10	0.08 - 2.03	*851*	***4.1***
2016	58.4	52.1 – 66.0	0.11	0.09 - 0.41	*638*	***1.4***
Average	71.5	64.5-76.6	0.12	0.09-0.23	*792*	***1.6***

*IQR: inter-quartile range

Figure 7 represents nitrate concentration dynamic through a close-to-average year (regarding to rainfall). 2007 was the year chosen, as it was the most completed one whose rainfall was close to the average of the study period. Nitrate concentrations through this year vary from 0.3 mg/L to 149.1 mg/L, being 95.4 mg/L (IQR: 86.6 - 110.5) the daily median. Results obtained in Figure 7 reflect an increase on nitrate concentration just after each increase peak of discharge. It was also observed that nitrate increases were higher when previous discharge values were low for a while. Another pattern observed was that, when there was a period of continuous high discharge values (from the 31st of January to 2nd of May), nitrate concentration followed the pattern observed before, but being the highest value observed each peak lower than the previous one. These patterns were followed during the whole study period (see *ANNEX I.Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during each hydrological year of the study period*).

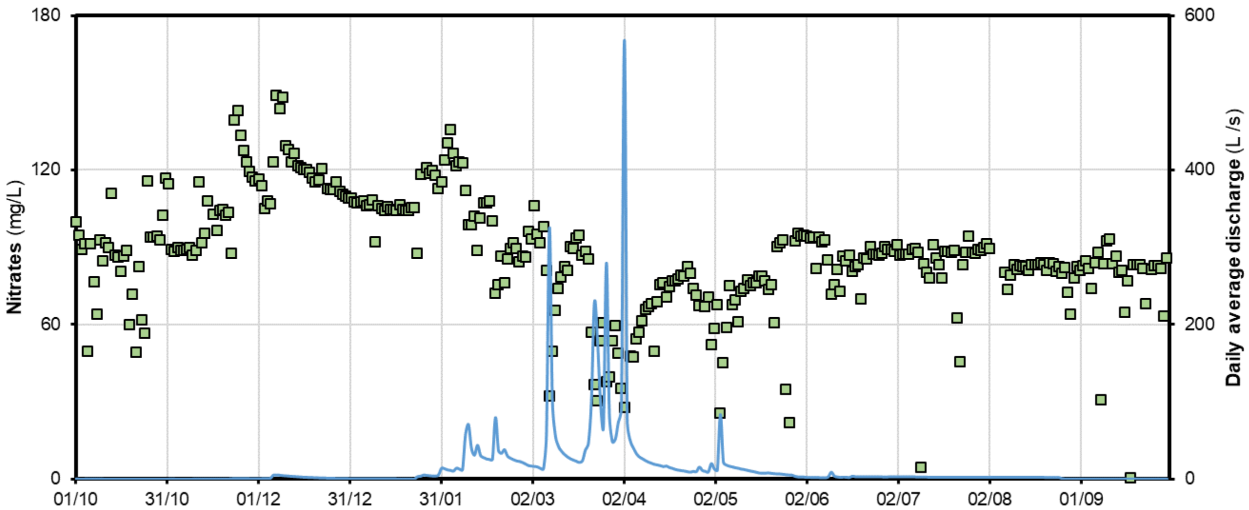

Figure 7. Nitrate concentration and daily average discharge of La Tejería watershed in a normal year (data from hydrological year 2007, which exemplified a normal year regarding the discharge)

Results obtained in the extreme years were slightly different. 2012 was chosen as the year representing dry conditions (Figure 8). Nitrate concentrations in the driest year of the study period varied from 0.0 to 112.8 mg/L, being the daily mean nitrate concentration of 64.5 mg/L (IQR: 49.3 - 85.2 mg/L). In contrast, nitrate concentrations of the wettest year (represented by year 2013, Figure 9) ranged from 0.5 to 143.4mg/L, with a daily median of 60.8 mg/L (IQR: 29.7 - 105.6 mg/L). It was more complicate to contemplate that pattern in Figure 8 as discharge values were quite low (almost equal to cero), but they could be predicted in Figure 9 as well as they were shown in Figure 7.

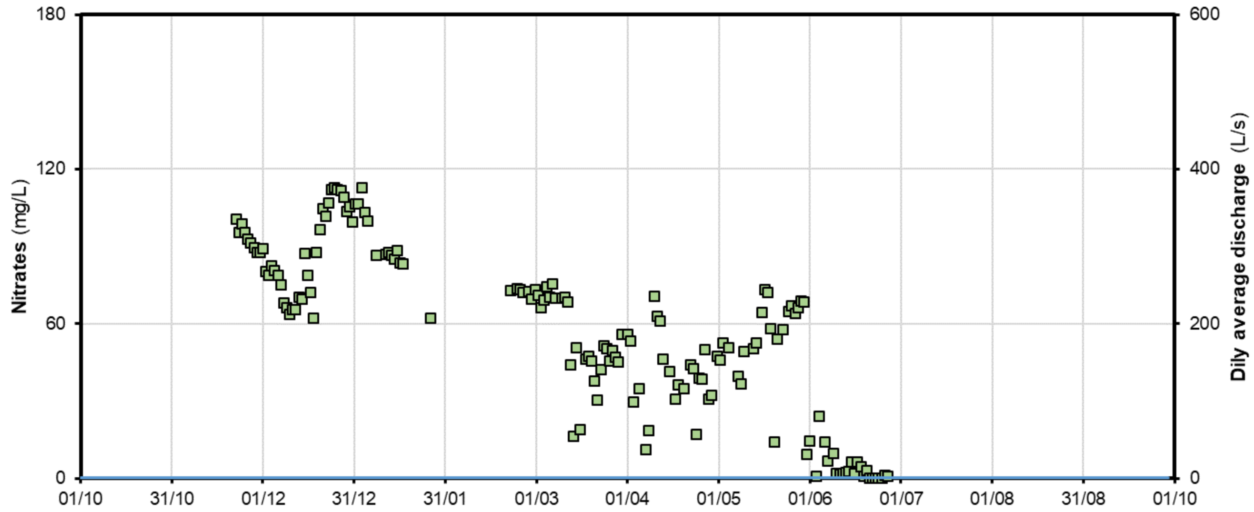

Figure 8. Nitrate concentration and daily average discharge of La Tejería watershed in a dry year (data from 2012, which represented a dry year).

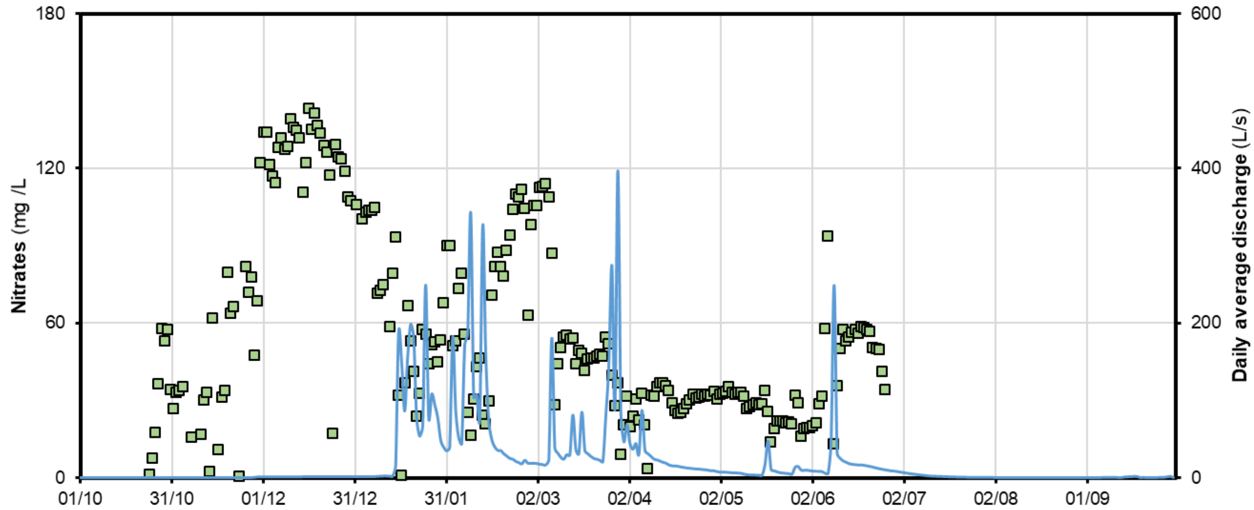

Figure 9. Nitrate concentration and daily average discharge of La Tejería watershed in a wet year (data from 2013, representing year of wet conditions).

According to the *Test of the median of K independent samples*, daily mean nitrate concentrations obtained in 2007 were not significantly higher than in 2012 (just three months showed notable higher median values while the other nine resulted similar). The same happened when nitrate concentration medians between 2007 and 2013 were compared: just one month presented remarkable differences. Nevertheless, when comparing 2012 with 2013, two months of the driest year presented significant higher mean concentration values than the wettest one, while other two months of the wettest year also obtained higher concentrations than 2012.

Phosphate concentrations patterns were more difficult to predict. Figure 10 reflectsmonthlymean phosphate concentration and daily average discharge during the whole study period. Phosphate concentrations did not follow same patterns as nitrate concentration did among discharge (see *ANNEX III. Monthly mean phosphate concentrations (mg/L) in La Tejería during each hydrological year of the study period*).

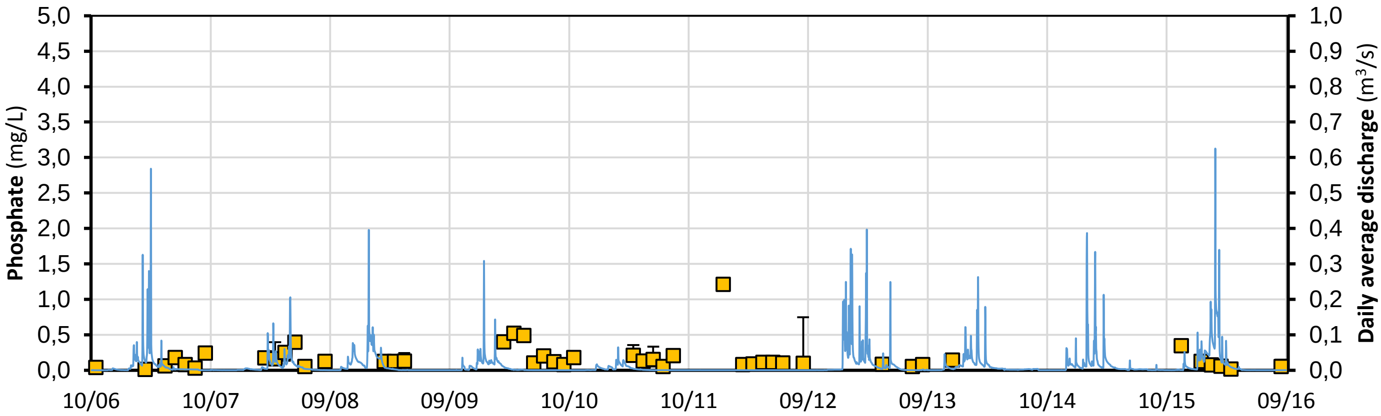

Figure 10. Monthly median phosphate concentrations and daily average discharge of La Tejería watershed during the whole study period.

Similar pattern occur in Latxaga watershed. Nitrate median annual concentrations obtained ranged from 8.9 mg/L (IQR: 7.5-9.2 mg/L) in 2012 to 26.8 mg/L (IQR: 17.0-31.3 mg/L) in 2011, being 20.5 mg/L (IQR: 17.2-24.2 mg/L) the median nitrate concentration for the whole study period (Table 5). Phosphate concentrations obtained were also much lesser than nitrates ones. Phosphate median annual concentrations vary from 0.06 mg/L (IQR: 0.00 and 0.05) in 2014 and 2015 to 0.11 mg/L (IQR: 0.09-0.13 mg/L) in 2008, being 0.07 mg/L (IQR: 0.06-0.10 mg/L) the phosphate median annual concentration for the study period.

Table 5. Monthly median and IQR for nitrates and phosphate concentrations, rainfall (mm) and discharge (L/s) obtained during the study period in Latxaga watershed.

Hydro. year	**Nitrates (mg/L)**		**Phosphates (mg/L)**		*Rainfall*	*Discharge*
(Oct-Sept)	Median	IQR*	Median	IQR*	*(mm)*	*(L/s)*
2007	19.6	8.9 - 28.0	0.07	0.07 - 0.07	*977*	2.1
2008	9.7	2.9 - 29.4	0.11	0.09 - 0.13	*837*	1.6
2009	23.0	11.3 - 25.6	-	-	*938*	3.5
2010	24.6	20.8 - 38.7	-	-	*793*	0.8
2011	26.8	17.0 - 31.3	0.09	0.08 - 0.11	*709*	0.9
2012	8.9	7.5 - 9.2	0.10	0.08 - 0.29	*596*	<0.6
2013	25.8	20.8 – 28.0	0.07	0.07 - 0.07	*1661*	8.6
2014	18.6	3.7 - 27.7	0.06	0.06 - 0.06	*1157*	6.1
2015	21.5	3.0 - 33.7	0.06	0.06 - 0.11	*1033*	2.3
2016	16.7	8.4 - 22.7	-	-	*762*	0.6
Average	**20.5**	**17.2-24.2**	**0.07**	**0.06-0.10**	***946***	**2.2**

*IQR: inter-quartile range; (-): not available data

In relation with rainfall, nitrate highest concentration (2011) year did not either coincide with highest rainfall year (2013), and either the phosphate did. In this watershed, the lowest nitrate concentration value was obtained in the driest year (2012). Besides, this year, the second highest phosphate concentration value was recovered. Lowest phosphate concentrations were captured in 2014 and 2015, when rainfall was quite over the annual average (1157 and 1033 mm respectively). Table 5 showed more detailed results obtained about nitrate and phosphate median annual concentrations in Latxaga watershed. Comparing with discharge values, the year with the highest nitrate concentration (2011) value did not coincide with the higher discharge value (2013), but did coincide the lowest nitrate concentration year with the lowest discharge one (2012). The same happened with phosphate concentrations.

In Figures 11, 12 and 13 all patterns mentioned above could be more clearly observed. In Figure 11, the period from approximately the 20th October to the 20th of January clearly reflected the increase of nitrate concentration just after an increase of the discharge. Nitrate concentration peak from the November 24th, which followed a period of low discharge values, was higher than the next nitrate concentration increase of the 6th of December, even if the discharge obtained was lower.

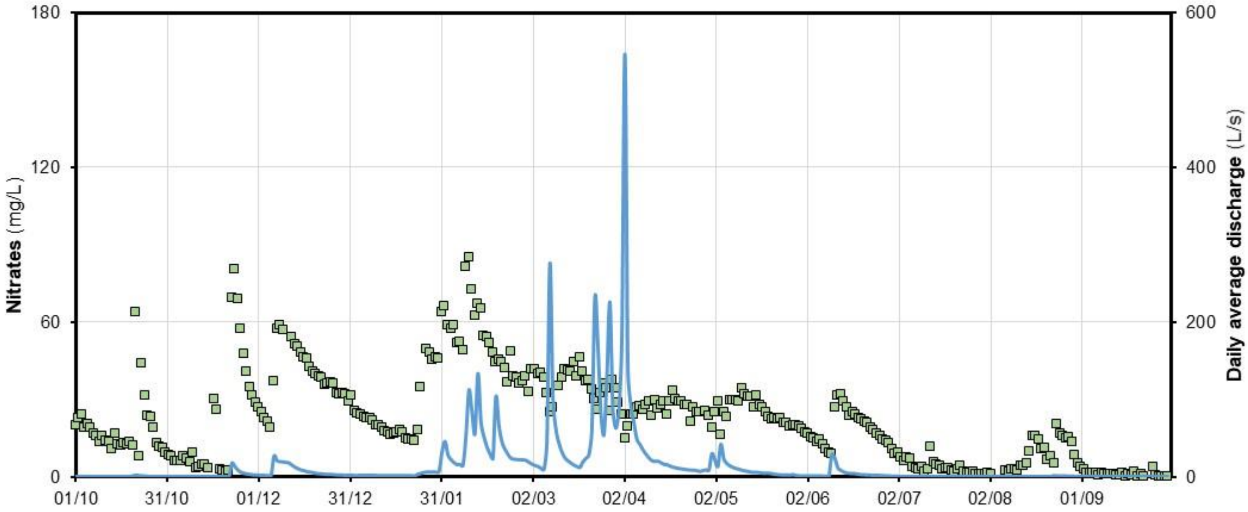

Figure 11. Nitrate concentration and daily average discharge of Latxaga watershed in a normal year (data from year 2007, which exemplified a normal year regarding the discharge)

Nitrate concentrations of the driest year of the study period (2012) varied from 0.1 to 37.4 mg/L, being the daily mean nitrate concentration of 8.9 mg/L (IQR: 7.5-9.2 mg/L), while nitrate concentrations of the wettest year (2013) ranged from 0.5 to 96.8 mg/L, with a daily median of 25.8 mg/L (IQR: 20.8-28.0 mg/L). Figure 12 presented in a better way than Figure 8 the tendency of the nitrate concentration in a dry year. Even if discharge values were much lower, nitrate concentrations kept on increasing whenever an increase on discharge occurred (see ANNEX II. *Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during each hydrological year of the study period*).

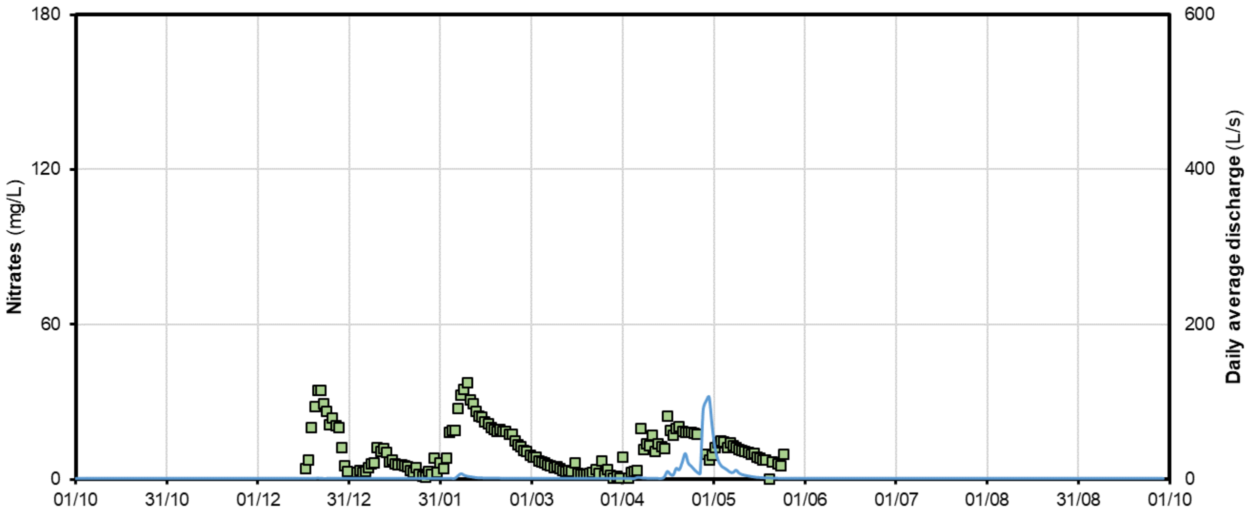

Figure 12. Nitrate concentration and daily average discharge of Latxaga watershed in a dry year (data from hydrological year 2012, which represented a dry year)

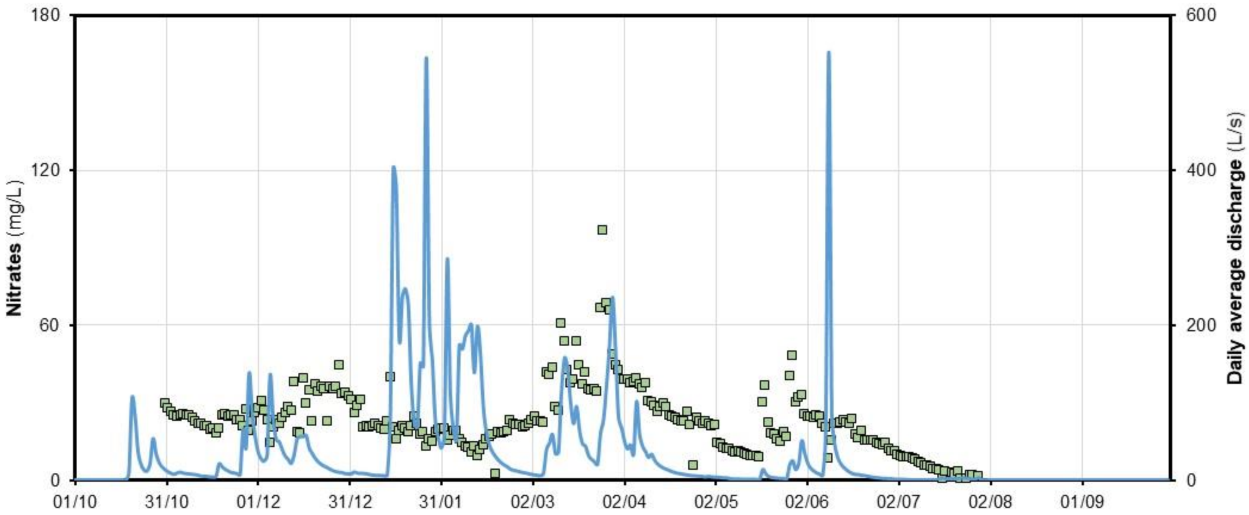

Figure 13. Nitrate concentration and daily average discharge of Latxaga watershed in a wet year (data from hydrological year 2013, representing year of wet conditions)

Results obtained after comparing medians with the *Test of the median of K independent samples*were slightly different from the ones obtained in La Tejería. The mean discharge of three months of 2012 were higher than the ones of 2007, whereas the mean discharge of two months of 2007 appeared to be higher than 2012's. When comparing 2012 and 2013, the same result was achieved, while there was not any remarkable differences between 2007 and 2013 discharge medians.

The same happened in Latxaga (Figure 14) regarding to phosphate concentration as did in La Tejería. Moreover, due to the short data quantity available about phosphate concentration in this watershed, it was harder to find a pattern in phosphate dynamics during the whole study period (see *ANNEX III. Monthly mean phosphate concentrations (mg/L) in Latxaga during each hydrological year of the study period*).

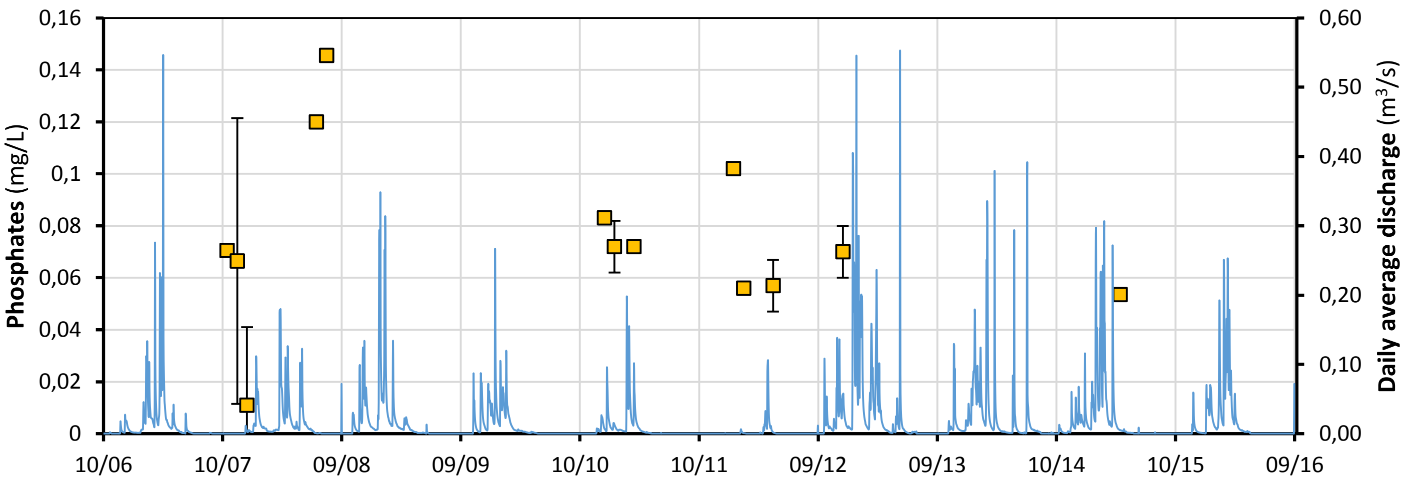

Figure 14. Monthly median phosphate concentrations and daily average discharge of Latxaga watershed during the whole study period.

3.3. Nitrate-N and phosphate-P yields

Three different methods for load estimation were used, obtaining subsequently nitrate-N yields values. Table 6 reflects nitrate-N yields obtained during the study period in La Tejería watershed, which resulted to be quite similar between the three methods, even if LOADEST method (regression) overestimate load values with respect to the other methods. The results obtained all along the study had a great variability. Annual yields obtained with the Beale Rate Estimator ranged from 0.5 kg/ha in 2012 to 51.8 kg/ha in 2016, with an average of 31.9 kg/ha for the whole study period. Results calculated with the Regression method (with LOADEST software) vary from 0.5 kg/ha (2012) to 61.5 kg/ha (2016), obtaining an average of 37.8 kg/ha.Numeric integration method presented the highest average nitrate-N yield (32.2 kg/ha), with values ranging from 0.5 kg/ha in 2012 to 52.5 kg/ha in 2016. Lowest nitrate-N yield was obtained during the driest year of the study period, being significantly smaller than the other yields presented. Regarding obtained results, three methods showed similar values, although regression significantly overestimates in relation with the others. Therefore, any of them could be used, presenting reliable results. For the present study, the results obtained with Beale Ratio Estimator were used for the analysis, since it is normally the most unbiased estimator (Meals et al., 2013).

Table 6. Annual nitrate-N yields obtained in La Tejería watershed during the study period with three load estimation methods.

	Nitrate-N yield (kg/ha/year)										
METHOD	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**Average**
Beale Ratio Estimator	35.4	24.8	46.7	22.7	14.9	0.6	40.8	36.7	45.0	51.8	31.9
Regression (LOADEST)	51.9	30.7	53.8	32.1	13.8	0.5	54.8	36.5	42.8	61.5	37.8
Numeric integration	35.6	24.8	46.8	22.7	14.7	0.5	41.2	37.7	45.3	52.5	32.2

These values were close to the ones obtained in Casalí et al. (2008). Measured nitrate-N yields during their study period (1997-2005) were slightly higher (an annual average of 37.0 kg nitrate-N /ha), with values ranging from 1.6 kg nitrate-N /ha/year to 47.4 kg nitrate-N /ha/year.

Figure 15 shows the intra-annual variability of nitrate-N in La Tejería watershed. January (6.5 kg/ha with Beale Ratio estimator method, 6.2 kg/ha with regression and 6.5 kg/ha with numeric integration), February (8.6 kg/ha, 8.5 kg/ha 8.6 kg/ha) and March (7.7 kg/ha, 7.3 kg/ha and 7.9 kg/ha) were by far months with highest nitrate-N yield values, representing 71% (Beale Ratio estimator) of the total nitrate-N yield exported in a year. In contrast, September and October were months with the lowest nitrate-N yields, with values varying between 0.0 kg/ha to 0.1 kg/ha. The pattern observed was an increase in nitrate-N yield during winter and early-spring months, followed by an important decrease the following months.

As was expected, obtained phosphate-P yields were pretty much lower than nitrate-N ones, being 100 times lower than nitrate-N yields. Table 7 shows phosphate-P yields for the study period obtained with the three load estimation methods. Comparing with nitrate-N yields, obtained phosphate-P yields variability during the study period was remarkably lower. Average phosphate-P yields for the study period obtained with Beale Ratio Estimator as 0.05 kg/ha/year, with values ranging from 0.01 kg/ha/year (2012) to 0.17 kg/ha/year (2013). Regression method presented an average phosphate-P yield of 0.07 kg/ha, with values varying from 0.00 kg/ha/year to 0.18 kg/ha/year. 0.07 kg/ha was the annual phosphate-P yield obtained with numeric integration method, obtaining the lowest value in 2012 (0.01 kg/ha) and the highest one in 2013 (0.26 kg/ha). As happened with nitrate-N yield, the lowest yield for the three methods was obtained in the driest year (2012). Furthermore, phosphate-P highest yield was recorded the wettest year (2013), being considerably higher than values obtained other years. In this case, as the former one, the three methods presented really closed results, so the three of them could be used to estimate phosphate-P load, and so the yield.

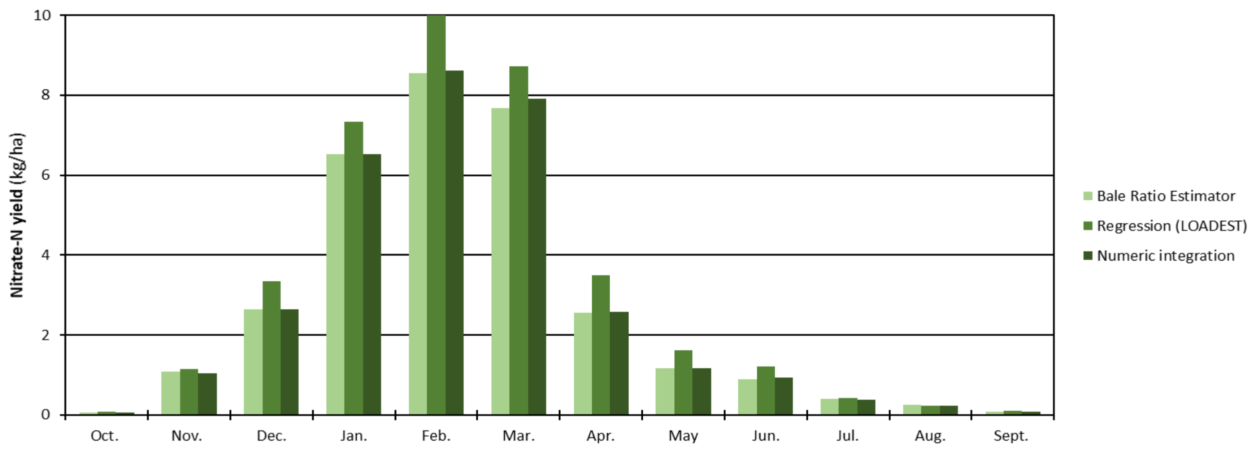

Figure 15. Intra-annual variability of nitrate-N yield in La Tejería watershed during the study period (hydrologic years 2007-2016) obtained with three load estimation methods.

In accordance with (Casalí et al. 2008) results, the average phosphate-P yield obtained during

Table 7. Annual phosphate-P yields obtained in La Tejería watershed during the study period with three load estimation methods.

	Phosphate-P yield (kg/ha/year)										
METHOD	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**Average**
Beale Ratio Estimator	-	0.04	0.02	0.03	0.02	0.01	0.17	0.03	0.06	0.04	0.05
Regression (LOADEST)	0.05	0.05	0.07	0.05	0.02	0.00	0.18	0.07	0.09	0.10	0.07
Numeric integration	0.03	0.06	0.03	0.04	0.02	0.01	0.26	0.05	0.09	0.07	0.07

(-): not available data.

1997-2005 time period was similar but quite smaller, 0.00 kg/ha/year, unlike happened with phosphate-P yield. Yields from that period of time ranged from 0.00 kg/ha in 2000 to 0.10 kg/ha in 2003.

The intra-annual variability of phosphate-P in La Tejería watershed is represented in Figure 16. The same pattern followed with nitrate-N was obeyed: winter and early-spring months presented the highest phosphate-P yields, while summer and early-autumn months showed significantly lower values. In this case, January, February and March presented the highest phosphate-P yields (from 0.01 to 0.22 kg/ha/month), representing again 71% of the total phosphate-P yield exported in a year. September and October presented the lowest phosphate-P yields (0.00 kg/ha/month).

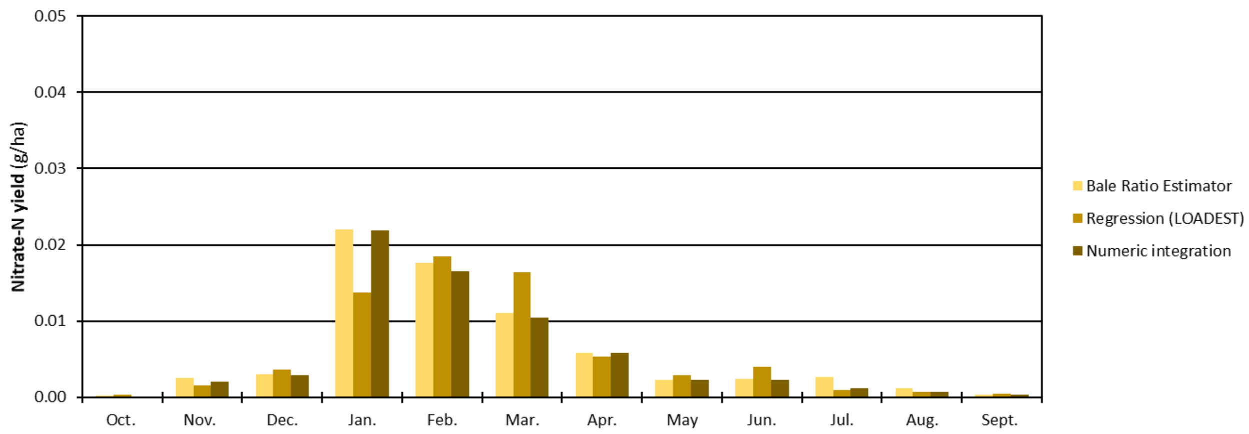

Figure 16. Intra-annual variability of phosphate-P yield in La Tejería watershed during the study period (hydrological years 2007-2016) obtained with three load estimation methods.

Similar patterns were observed at Latxaga watershed. Even if nitrate-N yields obtained in Latxaga were lower than ones obtained in La Tejería, yields dynamics followed the same guide. At Table 8 are represented the annual nitrate-N yields obtained in Latxaga watershed during the study period with the three load estimation methods. Average nitrate-N yield obtained with Beale Ratio Estimator method was 17.7 kg/ha, with values ranging from 1.1 in 2012 to 29.8 kg/ha in 2015. Regression method gave an average value of 20.1 kg/ha, with a minimum yield of 2.5 kg/ha obtained in 2012 and a maximum value of 35.6 kg/ha in 2013. Values obtained with numeric integration method were similar, obtaining an average yield of 16.6 kg/ha, being 1.2 kg/ha (2012) the lowest and 29.2 kg/ha (2013) the highest yields presented. Lowest yields obtained coincide again with the driest year of the study period (2012), while highest yields corresponded to the wettest year in the case of Regression and numeric integration methods.

Table 8. Annual nitrate-N yields obtained in Latxaga watershed during the study period with three load estimation methods.

	Nitrate-N yield (kg/ha/year)										
METHOD	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**Average**
Beale Ratio Estimator	18.4	14.7	20.9	14.0	11.1	1.1	29.0	20.4	29.8	11.1	17.1
Regression (LOADEST)	23.5	19.3	26.0	18.0	11.7	2.5	35.6	23.6	22.8	18.2	20.1
Numeric integration	18.4	14.7	18.5	13.8	10.9	1.2	29.2	19.9	28.8	10.8	16.6

These values were similar to the ones obtained by Casali et al. (2008) for the period 1997-2005. They estimated an average nitrate-N yield of 16.5 kg/ha/year, with values varying from 0.7 kg/ha in 2002 to 27.8 kg/ha in 2004.

The intra-annual variability of the study period in Latxaga is shown in Figure 17. Nitrate-N yield dynamic followed the same pattern that has been seen so far. There was a notorious increase on the yield in winter and early-spring months, reaching values up to 4.4 kg/ha in February with the three methods. After March, nitrate-N yields tended to decrease until yields of 0.0 kg/ha obtained in September. As happened in La Tejería watershed, January, February and March were months with highest yields, meaning again a 71% of the total nitrate-N yield exported during a year, while August, September and October were again months with lowest values.

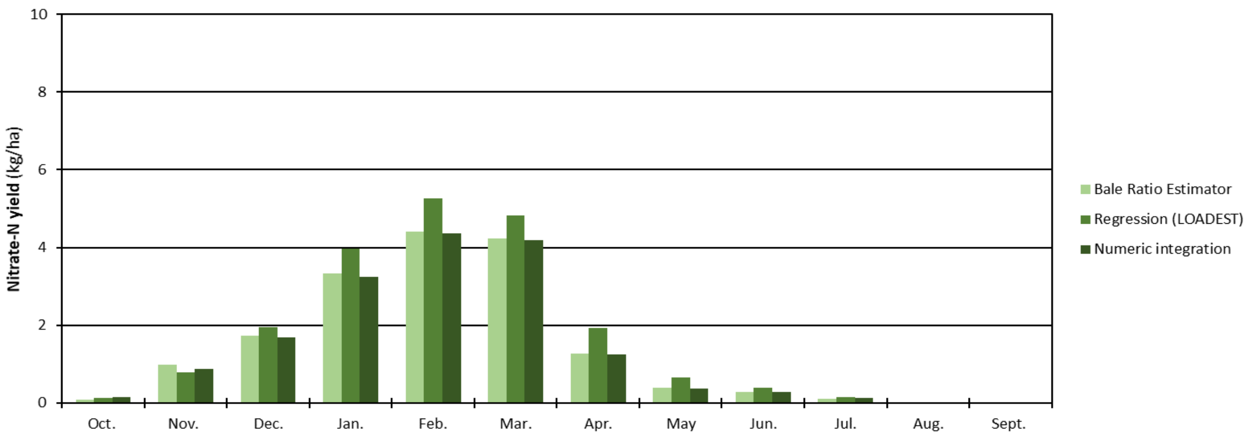

Figure 17. Intra-annual variability of nitrate-N yield in Latxaga watershed during the study period (2007-2016) obtained with three load estimation methods.

Phosphate-P yields in Latxaga watersheds presented values even lower than La Tejería's one. Intra-annual variability of the whole study period was very short, with values ranging from 0.00

kg/ha/year to 0.01 kg/ha/year, being 0.03 kg/ha the average phosphate-P yield for the entire study period. As represented in Table 9, in this particular case, the three load estimation methods gave the same results. Highest yields were obtained in 2010, 2011 and 2012, while the rest of the study period obtained values of 0.00 kg/ha.

Table 9. Annual phosphate-P yields obtained in Latxaga watershed during the study period with three load estimation methods.

	Phosphate-P yield (kg/ha/year)										
METHOD	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**Average**
Beale Ratio Estimator	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.03
Regression (LOADEST)	0.03	0.03	0.04	0.03	0.02	0.01	0.08	0.05	0.04	0.03	0.03
Numeric integration	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.03

Obtained yields were again very similar to the ones presented by Casali et al. (2008). They obtained an average phosphate-P yield of 0.00 kg/ha for the whole study period, with recorded values varying from 0.02 kg/ha in 2005 to 0.28 kg/ha in 2004.

Figure 18 shows the intra-annual variability of phosphate-P yield in Latxaga during the study period, which follows once again the pattern seen up to now. January, February and March were newly months with highest yields (0.01 kg/ha with the three methods), meaning a 61% of the total phosphate-P yield exported in a year, followed by a tendency of decrease in the following months until reaching yields of 0.00 kg/ha.

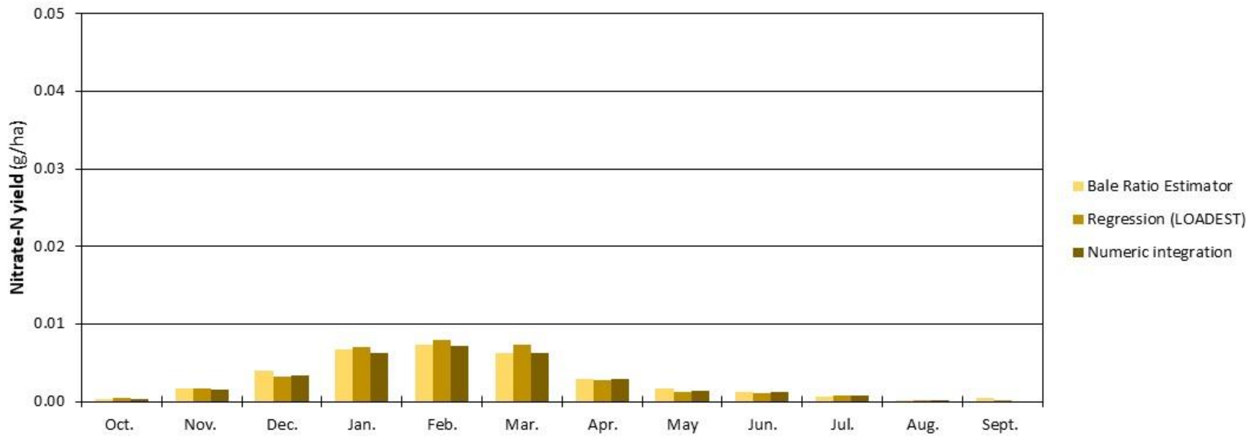

Figure 18. Intra-annual variability of phosphate-P yield in Latxaga watershed during the study period (2007-2016) obtained with three load estimation methods.

3.4. Differences between watersheds

This section compares the results that have been seen so far in order to summarize them and contrast both watersheds.

Figure 19 represents monthly discharge and nitrate concentration values obtained in La Tejería (T) and Latxaga (L) watershed during the study period. Specific discharge was greater in Latxaga during the entire study period, while nitrate concentrations were notably lower. Nitrate concentrations of La Tejería watershed exceeded the critical threshold of 50 mg/L (Merrington et al., 2002) every month of the study period whereas nitrate concentrations presented in Latxaga were, in general, below the threshold. The median nitrate concentration in La Tejería watershed (71.5 mg/L) was more than three times greater than Latxaga's concentrations (20.5

mg/L), while the annual specific discharge of La Tejería (222 mm)was lower compared to Latxaga's discharge (250 mm).

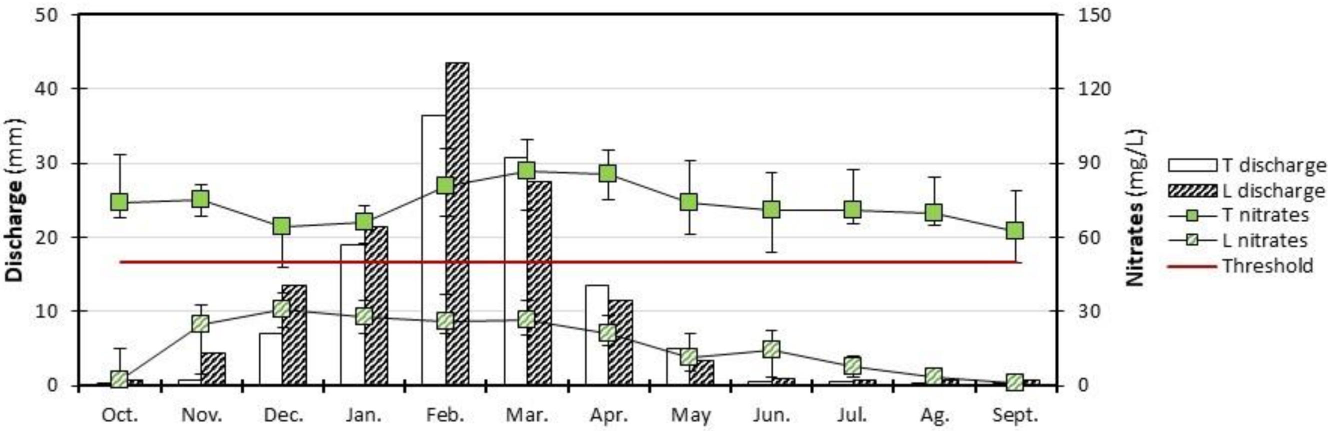

Figure 19. Discharges and nitrate concentrations for both La Tejería and Latxaga watersheds for the study period. *(T: La Tejería; L: Latxaga; Threshold: >50 mg/L)* (Vertical lines represent inter-quartile ranges).

Differences in nitrate-N yields results between La Tejería and Latxaga watersheds are shown in Figure 20. Results presented are the ones obtained by the Bale Ratio Estimator method, as it is reported as the one with a lower bias (Meals et al., 2013). La Tejería watershed clearly showed higher nitrate-N yields during the entire study period, being more remarkable during winter and early-spring months. This watershed presented an annual average nitrate-N yield that almost doubled Latxaga's values (31.9 kg/ha vs.17.1 kg/ha).

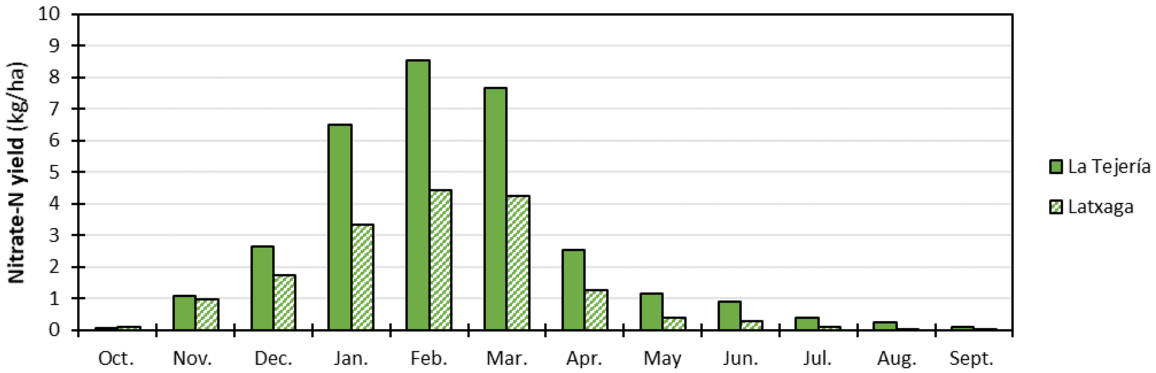

Figure 20. Nitrate-N yields (kg/ha) obtained in La Tejería and Latxaga watersheds during the study period**.**

Unlike happened with nitrate, phosphate concentrations (Figure 21) did not reveal a significant difference between both watersheds, although median phosphate concentration in La Tejería was almost again doubling Latxaga's phosphate concentrations (0.12 mg/L vs. 0.07 mg/L). Phosphate concentrations at Latxaga stayed almost constant through the year (0.03 mg/L), while at La Tejería watershed there was a remarkable increase in summer months, reaching values of 0.11 mg/L. Nevertheless, it is important to remark that phosphate concentration variability was significantly higher than nitrate's one in both watersheds (Figure 19 and Figure 21).

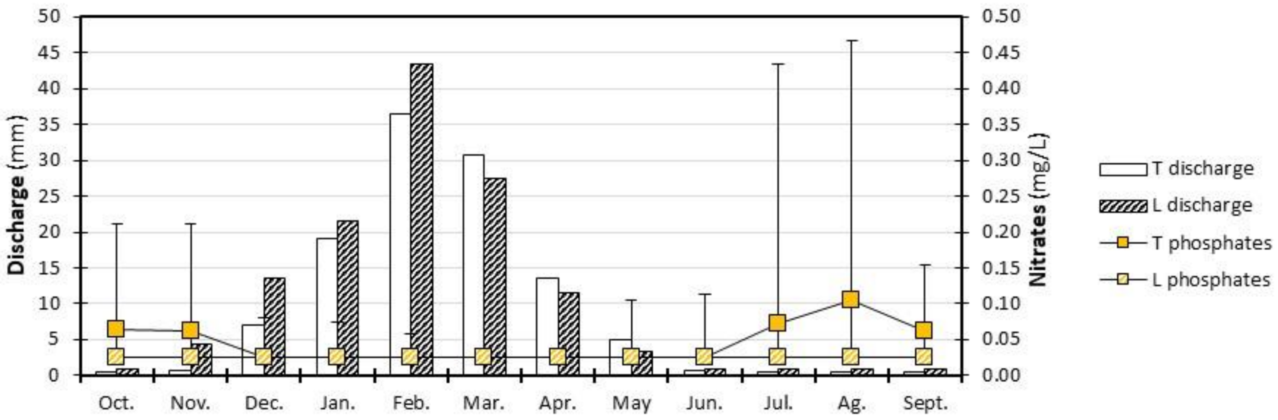

Figure 21. Discharges and phosphate concentrations for both La Tejería and Latxaga watersheds for the study period. *(T: La Tejería; L: Latxaga)* (Vertical lines represent inter-quartile ranges).

Regarding phosphate-P yields, Figure 22 presents obtained yields in both watersheds. Phosphate-P yields were higher again in La Tejería watershed, although in December, yield presented at Latxaga was greater. Average annual yields were 0.03 kg/ha for Latxaga and 0.05 kg/ha for La Tejería (1000 times lower than nitrates concentrations comparing both watersheds).

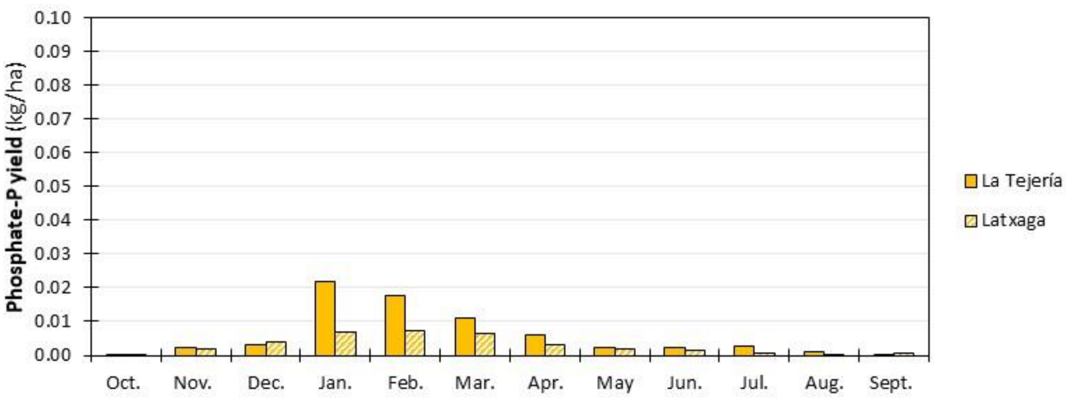

Figure 22. Phosphate-P yields (kg/ha) obtained in La Tejería and Latxaga watersheds during the study period.

3. RESULTS

4. DISCUSSION

In this section, the results obtained are discussed and analyzed in accordance with the hypothesis previously mentioned and the literature reviewed. Riparian vegetation, climate, soils, shape of the watershed, unproductive areas and different agricultural managements were proposed as main factors determining nitrate and phosphate exportation dynamics in the presented case. Table 10 summarizes the most important values obtained so far in both watersheds during the study period.

Table 10. Rainfall (mm), discharge (L/s), nitrate and phosphate concentrations (mg/L), and nitrate-N and phosphate-P yields (kg/ha) obtained in La Tejería and Latxaga watersheds during the study period. Results showed in parenthesis correspond to inter-quartile range values.

Watersheds	Rainfall (mm)	Discharge (L/s)	**Concentrations** (mg/L)		**Yield** (kg/ha/year)	
			Nitrates	Phosphates	Nitrate-N	Phosphate-P
La Tejería	729	1.6 (3.0)	71.5 (12.1)	0.12 (0.14)	31.9	0.05
Latxaga	946	2.2 (2.3)	20.5 (7.0)	0.07 (0.04)	17.1	0.03

Nitrate-N: nitrate as nitrogen; Phosphate-P: phosphate as phosphorous.

Nitrate is the prevailing nitrogen form in aerated waters, representing up to 90% of the total nitrogen (Durand et al., 2011), whereas phosphate proportion out of total phosphorous can be from 40 to 90% depending on the particular study case (Merrington et al., 2002). That wide range in which phosphate represents the total phosphorous in water does not give certain and representative results as nitrate does. Moreover, phosphorous losses originated from agricultural systems are considered relatively low compared with agronomic phosphorous requirements, even if small quantities (20 µg P/L) can cause important environmental problems in water.

4.1. Climate

Climate implications on the rate of nitrate leaching are clear, but it is difficult to understand the influence of its variations, even if predictions insinuate that most changes in climate produce an increase in nitrogen leaching (Stuart et al., 2011). The general pattern is the following: an increase in precipitation leads to an increase in runoff, evapotranspiration and groundwater recharge, while a precipitation decreaseimplies a decrease in recharge and falling water levels. N leaching is more affected by temperature than is affected by precipitation changes. This was largely due to the reduction in crop yield, N uptake and soil mineral nitrogen, which cause an increase of N losses (Børgesen and Olesen, 2011; Jabloun et al., 2015). Jabloun et al. (2015) also described that the impact of climate variations on nitrogen leaching and concentration was driven by seasonal changes in precipitation and temperatures. They reported that spring, summer and autumn precipitations enhanced nitrogen leaching, whilst winter precipitation did not have as much effect on nitrogen loss.

For the case presented, average temperature and its intra-annual variability was rather similar between both watersheds. Therefore, temperature would not be a determinant factor when analyzing differences in nitrate and phosphate exportation in this particular case. Regarding precipitation, average rainfall in Latxaga (946 mm) was higher than La Tejería (792 mm), which should suggest a higher potential of nitrogen exportation for the first watershed. However, results obtained showed higher nitrogen losses in La Tejería watershed. The reason for that would be that, although rainfall plays an important role controlling nitrogen leaching, other factors affect that loss in a more important way. Consequently, precipitation was either not considered a determining factor in this study, as differences between both watersheds regarding rainfall were not enough for it.

4.2. Soils

Soil characteristics and its effects on nutrient dynamics have been assessed in various studies (Giménez et al., 2012; Honisch et al., 2002; Pärn et al., 2018) and some others suggested its importance on the explanation of nitrate and phosphate dynamics(Casali et al., 1999; Donézar and del Valle de Lersundi, 2001). Some empiric studies and simulation models suggested that differences in organic matter quantity and quality made the difference on organic pools and carbon and nitrogen mineralization, while the influence of soil texture is not enough clear yet. Although it is known that clay soils retain more organic matter than sandy ones when the same organic inputs are applied (Matus and Maire, 2000).

Soil texture of La Tejería was silty clay and silty clay loam, with an organic matter content between 1 and 2%, and deep (>1 m). *Vertic Haploxerept* was the predominant soil class, covering almost the 41% of the watershed, located on erosion hillslopes in the center of the watershed. It is characterized by the presence of cracks in some periods. Moreover, its textural family of the control section is fine clayey, with a clay content between 40 and 50%. Another distinction of this type of soil is its low carbonate content in comparison with surrounding soils. Latxags's soils texture was silty clay loam, with an organic matter content higher than the previous watershed (1.8-2.5%). The soil class *Paralitic Xerorthent* covered the most part of the watershed (43%), located on erosion hillslopes too. It is a shallower soil compared with *Vertic Haploxerept* class. Moreover, due to its high slopes and ease to erode, the surface horizon tends to disappear. Notwithstanding there existed some differences regarding to the soil organic matter content, depth and/or texture between both watersheds regarding soil characteristics, there were not enough to draw any clear conclusion, as further investigations and more detailed studies are needed for a better understanding of the influence of soil characteristics on nutrient dynamics in these watersheds. Consequently, the soil was not contemplated as one of the most determinant factor explaining the differences in nutrient exports in these watersheds. .

4.3. Shape of the watershed

La Tejería presented a circular shape with a smoother topography (Figure 22a) than Latxaga (Figure 22b) and higher slope gradient on the stream channels. Moreover, important soil losses were registered associated to ephemeral gullies and furrows, being the erosion rates in some cases superior to the maximum tolerance values (Casalí et al., 2008). In contrast, Latxaga presented a more complex topography, with steeply slope cultivated areas but lower slope gradient on stream channels, besides being covered by more riparian vegetation (see section *4.5. Riparian vegetation*). Erosion rates tolerance values at Latxaga were hardly exceeded, and soil losses related to ephemeral gullies and furrows were negligible.

Knowing that sediment transported under high run-off is the major pathway of phosphorous loss in agricultural systems (about 90% of the phosphorous transported from arable land)(Angier et al., 2005; Merrington et al. 2002). Previous studies reported sediment export rates in La Tejería as two to three times higher than Latxaga (Casalí et al., 2008, Merchan et al., under review). Through an erosion simulation model, Casalí et al. (2008) suggested that La Tejería shapewas the main factor explaining the higher sediment loss observed in this watershed. Consequently, watershed's shape is expected to have an important role in the phosphorous exportation in these watersheds. The higher export of phosphate-P in La Tejería (0.05 kg/ha/year) in relation to Latxaga (0.03 kg/ha/year) is within this range of values and therefore the differences in sediment export are enough to explain the differences in phosphate-P exports. Particulate nitrate should also be considered as another pathway of nitrogen loss, although this nitrogen form was not assessed in this study and its influence is minor in watershed balances (Durand et al., 2011).

(a) (b)

Figure 22. Representation of (a) La Tejería and (b) Latxaga shapes.

4.4. Fertilization

The impact of N fertilization on nitrate-N exportation depends on some different factors like N fertilization rate, time and type of application, type of fertilizer, soil condition before the application and crop phenology and characteristics (Basso et al., 2010; Liang et al., 2011; Muschietti-Piana et al., 2018).Crop N uptake is variable both temporally and spatially, thus, there is a trend of increasing N application rates over the recommended doses, as it is complicated to predict crop yields. Different studies (Muschietti-Piana et al., 2018; Liang et al., 2011) showed a linear correlation between N application rates and the total nitrate leaching, meaning that, under similar circumstances, an increase in N fertilizer rate implies an increase in mean leaching losses of nitrate-N. Consequently, it is very important to control N fertilization rates, as N surplus (the N supplied over the crop necessities) is considered the primary driver of N loss from croplands (Thorburn et al., 2013).N cycling in soil vary according to the type of fertilizer used: nitrate-N concentration residue in soil is greater when urea N is applied, compared with organic N or unfertilized treatments. Urea N applications have higher nitrate-N leaching losses (five times greater than organic N or unfertilized treatments), while organic N applications are more related to gaseous losses by denitrification (Shelton et al., 2018). Furthermore, more N leaching is produced below the root-zone than in runoff in the cropping system (Thorburn et al., 2013); therefore, crop phenological state and cover crop strongly affect the efficiency of N fertilizers. Liang et al. (2011) reported that fluxes of nitrate leaching were higher at tillering stage, followed by harvesting stage, booting stage and seeding stage. These results were obtained because of the need of N uptake of the plant at different phenological stages, in addition to other factors such as rainfall, N application time and air temperature.

In this particular case, nitrogen applications were made similarly, as in both watersheds the fertilizer used was usually urea, and the application timing was almost the same. The most remarkable difference between both watersheds regarding fertilization would be application rate, as they were higher in Latxaga (180-200 kg N/ha) than in La Tejería (160-180 kg/ha). However, a simplified mass balance assuming average productions of the area and nitrogen percentage present in cropsand its residues suggest, that the average annual crop uptake for La Tejería watershed was of 122.6 kg/ha, while in Latxaga it was expected a higher nitrogen uptake (148.5 kg N/ha). Thus, according to the presented data, there was estimated an annual average surplus of 47 kg N/ha at La Tejería, a 9% more of N surplus than that generated in Latxaga (41.5 kg N/ha).

Therefore, even if fertilization should be considered as a determinant factor deciding the differences in nitrate and phosphate exportation between both watersheds, theavailable data was not reliable for the study, as application rates were completely dependent of each farmer decision, which was not regular through years not even through adjacent plots. Moreover, due to the uncertainty of the estimated plant uptake and surplus, there was not possible to obtain any clear conclusion of the influence of fertilization in this specific case. It is recommended a thoughtful monitoring of fertilizer application and obtained productions in these watersheds in order to fulfil this knowledge gap.

4.5. Riparian vegetation

Even if riparian zones occupy a little area of the landscape, they are a very important controlling factor of water and chemical transferences between stream systems and terrestrial lands.Vegetation filters surface runoff and encourage water infiltration, reducing runoff and its physical capacity for carrying sediments (Chase et al., 2016; Dosskey et al., 2010). Both phosphorous and nitrogen leaching loss are strongly affected by vegetation type. In the case of P, leaching losses are higher in grass than in woody vegetation, being independent of rainfall scale. In contrast, N leaching loss depend upon rainfall. When rainfall is high, N leaching losses are higher in woody vegetation, as grasses are more effective for N removal. In contrast, when lower rainfall events occur, vegetation type have not as much influence on N leaching losses, but soil microbial processes do (Neilen et al., 2017). Overall, herbaceous vegetation protect and stabilize surface soils from runoff and erosion, while woody vegetation stabilize high steep streambanks from mass failure (Dosskey et al., 2010). As important as riparian vegetation type is the riparian forest structure (density, height, stem diameter, etc.). As de Souza et al. (2013) reported, high densities of small trees are as beneficial as higher trees. Site-specific conditions such as climate (rainfall) also influence riparian vegetation efficiency.

Regarding both vegetation and riparian vegetation, La Tejería watershed was not as densely vegetated as Latxaga (Figure 23), beyond having less vegetation diversity. Woody and herbaceous species were abundant in Latxaga watershed (Figure 23b,d), being the white oak (*Quercus pubescens*), the common-pine (*Pinus sylvestirs*) and Italian maple (*Acer opalus*) the potential vegetation. Shrubs and some lianes covered the forests underground vegetation. Small soil eroded areas were covered by boxwood shrubs. Riparian vegetation of main stream channel was mainly composed of white oaks (*Salix alba*), narrow leaf ash (*Fraxinus angustifolia*) and black poplar (*Populus nigra*). Meanwhile, La Tejería vegetation low density is reflected in Figure 23a,c. Brachipodiumis the vegetation occupying most spaces between plots slopes and some small gall oak forests, while riparian vegetation consists on white willow (*Salix alba*) and black poplar (*Populus nigra*).

Therefore, higher riparian vegetation diversity and density in Latxaga clearly contributed to the lower nitrate-N and phosphate-P yields obtained during the study period. However, quantification of this effect is hard without specific studies.

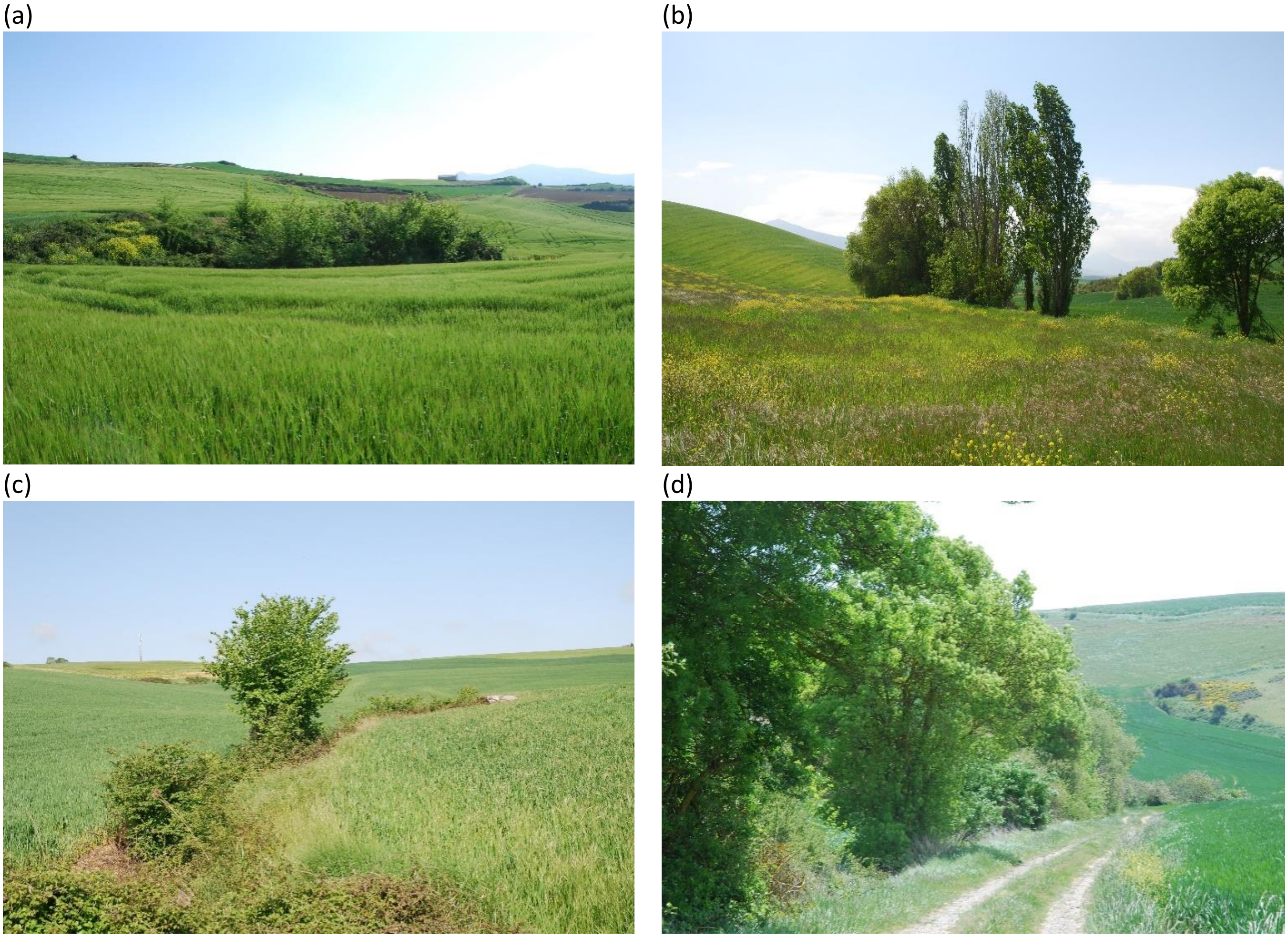

Figure 23. Representations of (a,c) La Tejeria and (b,d) Latxaga riparian vegetation.

4.6. Proportion and location of unproductive areas

Agricultural lands are progressively increasing while natural land covers (wetland, forest, grassland) are declining as an attempt to increase worldwide food security, even if natural land cover usually retains more sediments and nutrients than agricultural lands (Uwimana et al., 2018), reducing therefore nutrient and sediment losses. Furthermore, beyond the difference of nutrient and sediment catchment depending on land use, land management also differ between different land uses, such as fertilizer applications and plough. These farming practices, in general, make the soil more susceptible to erosion (Labrière et al., 2015).

Even though land uses in both watersheds were similar, the proportion of arable land between them was quite different, besides its distinct distribution through the watersheds. In La Tejería watershed, the 93% of the total land was arable, while about a 2% was covered by forest and grassland and the other 5% was dedicated to other land uses (Figure 24a). In contrast, in Latxaga watershed, about the 85% of the land was arable, the 11% was forest and grassland, and the other 4% of the terrain was occupied by other land uses (Figure 24b). Moreover, the 22 ha of grasslands and forests in Latxaga were bigger areas (Figure 22a and 22b), more distributed through the watershed than in La Tejería, being closer and more interspersed within plots. This suggested that sediments and nitrates are trapped by grasslands and riparian forests in Latxaga watershed much more likely than in La Tejería. Furthermore, as depicted in Figure 23b, most grasslands and forests were near stream channels, while at La Tejería (Figure 23a), they were not as close to stream channels. Therefore, runoff coming from upstream the grasslands and forests was diminished, reducing sediment (phosphate) and nitrate inputs to water. In addition, 93% of the total land in La Tejería watershed received fertilizer applications, whereas in Latxaga, just a 85% of the total area received fertilization applications, even if application rates in La Tejería were lower, what clearly modifies the specific inputs (ca. 158 and 162 kg N/ha for La Tejería and Latxaga, respectively).

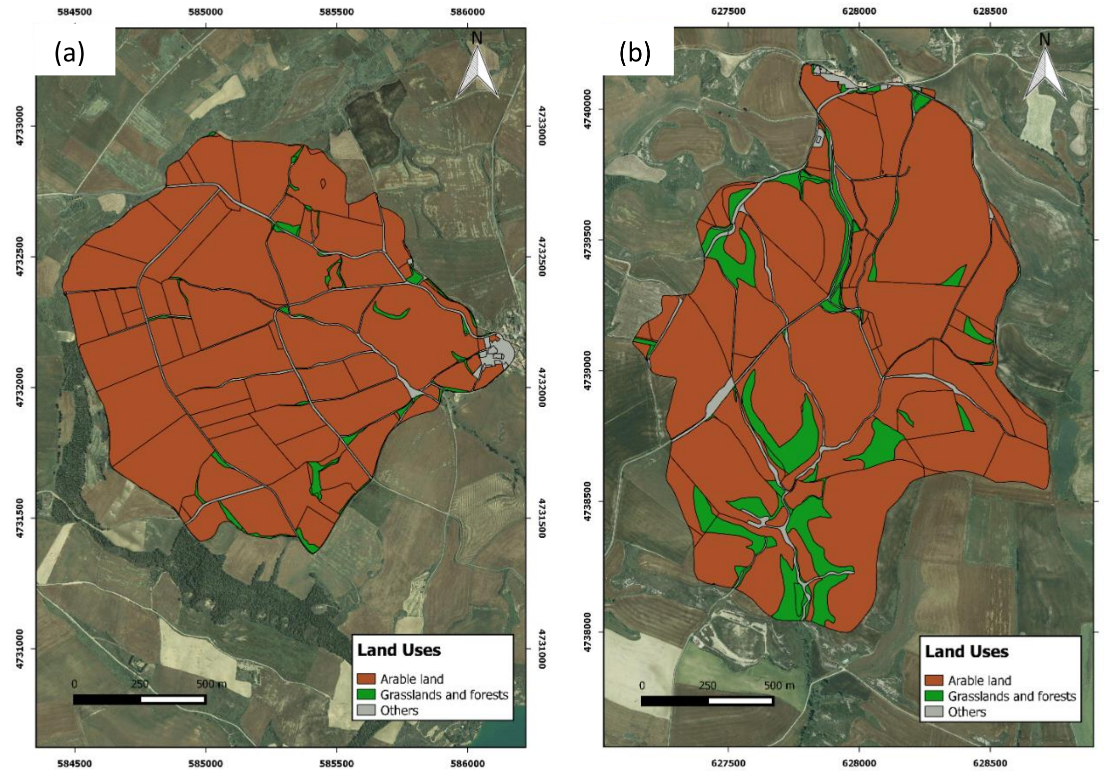

Figure 24. Map of land uses in La Tejería (a) and Latxaga (b) watersheds. *Source: orthophoto and agricultural plots from IDENA (2018).*

Consequently, land uses of the studied terrain and their distribution through the watersheds were considered one of the most determining factors explaining the differences in nitrate and phosphate exportations between both watersheds.

4.7. Subsurface drainage

Many different studies have shown that subsurface tile drainage is considered one of the most important agricultural management practice affecting the increase of nitrogen load into surface and groundwater (Randall and Goss, 2008). In many cases, it is the principal factor controlling watershed discharge and nitrogen export, being responsible of the 50-59% watershed nitrogen load, supplying the 44-82% to the nitrate-N export (Arenas Amado et al., 2017; Williams et al., 2015). Nitrate-N is the major form of nitrogen exported, being tile drainage its principal loss pathway from agricultural fields. Furthermore, differences among tile-drained watersheds and non-tile drained ones have been clearly shown in different studies. For instance, nitrate-N yield in tile-drained countries in Illinois was twice as much as in non-drained countries with similar crops, fertilization rates, etc. (McIsaac and Hu, 2004). Subsurface drainage reduces the time of soil water saturation by decreasing water table level, and therefore, diminishing in-field denitrification. Spacing between draining lines showed also an effect on nitrate losses, being the losses greater with lower drainage spacing (Randall and Goss, 2008).

There was not clear data about drainage density of both watersheds. However, in accordance with personal communication from farmers, personnel of the Department of Rural Development and Local Administration (Government of Navarre) and some field monitoring, the drainage density at La Tejería watershed was higher than in Latxaga. Figure 25 represents the drainage types presented in the watersheds: active and inactive agrarian drains, tile drains and concrete drains. As a result, there was a greater water yield generated in La Tejería watershed, which promoted higher riverine N losses (McIsaac and Hu, 2004). This drainage density explained the different nitrate-N yields obtained in the study, as higher yields were obtained in La Tejería watershed (31.9 kg/ha/year) compared to the ones obtained in Latxaga (17.1 kg/ha/year).

Regarding phosphate-P yields, there was not a found clear relationship between phosphate-P yields and subsurface drainage, as phosphate losses are more related with sediment exportation. Therefore, subsurface drainage was considered one of the most deciding factor explaining the differences obtained in nitrate-N yield results in the study.

(a) (b)

Figure 25. Examples of different drainage types present in La Tejería watershed: (a) active agricultural drain, (b) inactive agricultural drain, (c) tile drain and (d) concrete drain

4. DISCUSSION

5. CONCLUSIONS

The present study consisted on an examination and analysis of meteorological and hydrological data from two watersheds that represent the cultivation conditions of the rainfed cereal crops of the middle area of Navarra, in order to understand the patterns followed by nitrate and phosphate concentrations and yields under the specific conditions presented in La Tejería and Latxaga watersheds.

For that purpose, daily discharge, and nitrate and phosphate concentration and yield data of the watersheds wasanalyzed and then compared, followed by an assessment of some factors that influence the nitrate and phosphate dynamics and behavior. Specifically, climate, soils, shape of the watershed, fertilization, riparian vegetation, proportion and location of unproductive areas, and subsurface drainage were the factors evaluated through a literature review.

Both nitrate and phosphate exportation in La Tejería (31.9 kg nitrate-N/ha/year and 0.05 kg phosphate-P/ha/year) watershed were higher than in Latxaga (17.1 kg nitrate-N/ha/year and 0.03 kg phosphate-P/ha/year) during almost the entire study period, even if the management of the watersheds was rather similar in both cases. Furthermore, small particularities of each watershed were reflected in high differences in the nitrates and phosphates exportation, despite being clear the similarities in climate, soil and most of the agricultural management. Indeed, La Tejería watershed showed greater nitrate and phosphate concentration values during most of the study period, and so did the nitrate-N and phosphate-P yields. Both nitrate concentrations and yields followed a seasonal pattern, obtaining higher exportations in late autumn and winter months. However, there was not a clear pattern followed by phosphate concentrations nor yields.

After comparing and contrasting the results with the reviewed scientific literature, the following was concluded:

- Even if the effect of climate was reflected in the results obtained in each watershed, it was not considered one of the most determinant factor describing nitrate and phosphate exportations differences between the watersheds, as besides climate similarities between the watersheds, other factors affect in a more important way.
- There were not enough differences in soil characteristics to draw any clear conclusion. Further investigations and more detailed studiesare needed for a better understanding of its influence on nutrient dynamics in these watersheds. Therefore, soils were not either considered as one of the most determinant factors explaining the differences in nutrient exportations between the watersheds.
- Results showed that the shape of the watershed was expected to have an important role in the phosphorous exportation, as phosphorous losses are closely related to sediment transport. It may also affect particulate nitrate exportation, although this form of nitrogen was not assessed in the study.
- Despite fertilization playing a paramount role in nutrient dynamics, it was not possible to obtain any clear conclusion of its influence in this specific case due to the uncertainty of the irregular fertilization rates through the study period and among different farmers, estimated productions and plant uptake, proportion of the watershed cultivated, etc.
- Higher riparian vegetation density and diversity contributed to lower nitrate-N and phosphate-P yields, although quantifying its effect is hard.

- The proportion and location of unproductive areas through the watershed also were considered as one of the most determining factors explaining the differences in nitrate and phosphate exportations between both watersheds.
- Subsurface drainage was considered as other determining factor defining the differences in nitrate-N exportation between both watersheds, while there was not any clear relation with phosphate-P exportation.

In conclusion, the results obtained during the study period were coherent with those obtained in former studies in these watersheds and the reviewed literature. However, there is a clear need of further investigations in this scope due to the great relevance of nitrate and phosphate loss, given their impact in both economic (fertilizer use) and environmental impacts. To this end, extensive monitoring of fertilization rates, crop distribution and productions in these watersheds, along with some specific studies on riparian vegetation or drainage impacts on nutrient dynamics are required.

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ANNEX I. Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during each hydrological year of the study period.

ANNEX I. Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during each hydrological year of the study period.

The following graphs represent daily average concentrations (mg/L) and daily average discharge (L/s) for La Tejería watershed during each hydrological year (October – September) of the study period.

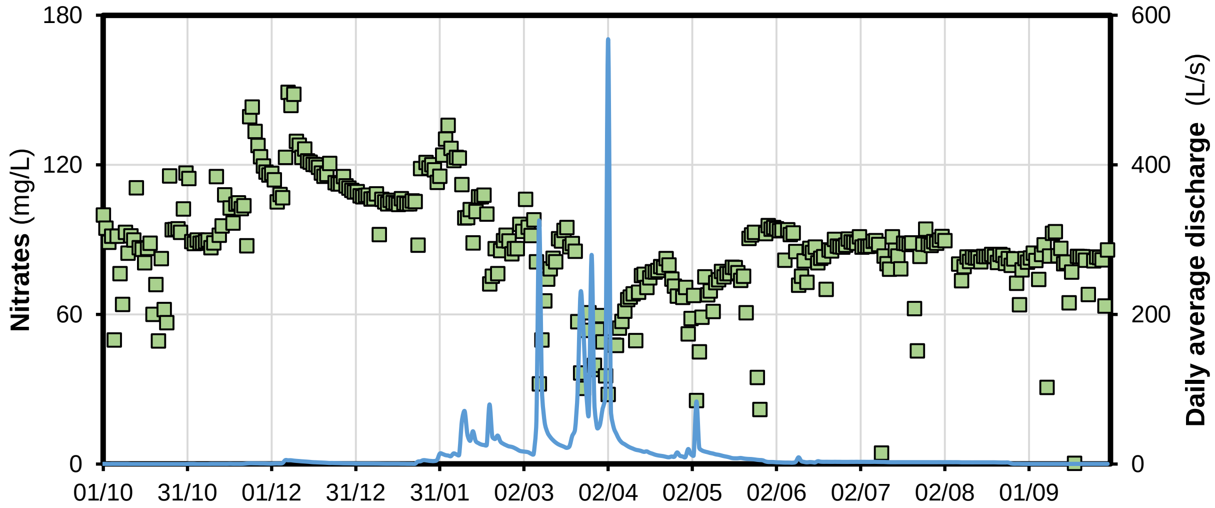

Figure 26. Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during the hydrological year 2007.

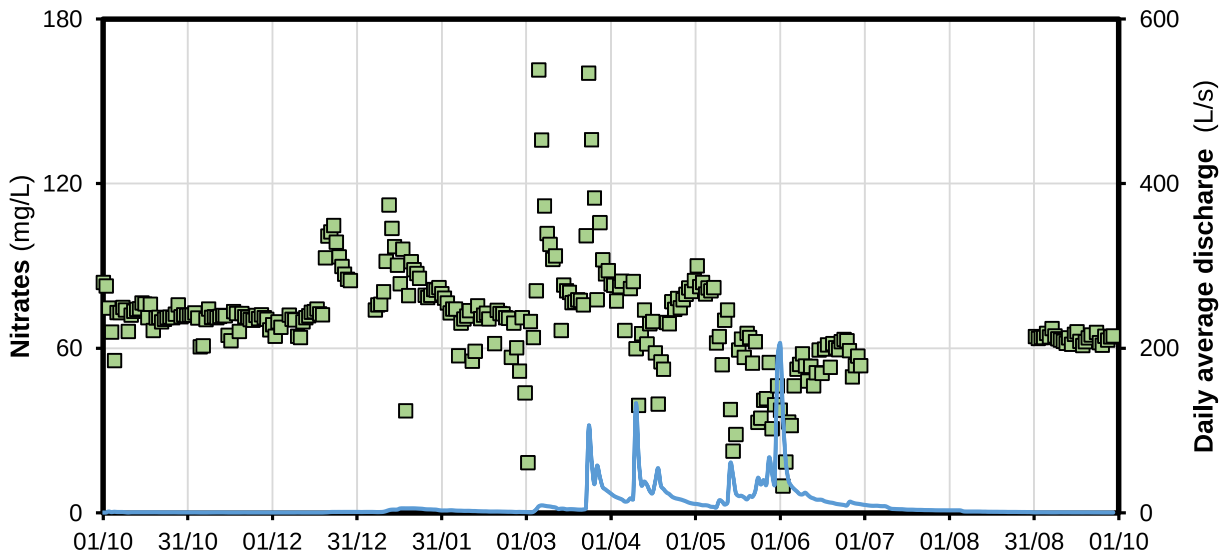

Figure 27. Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during the hydrological year 2008.

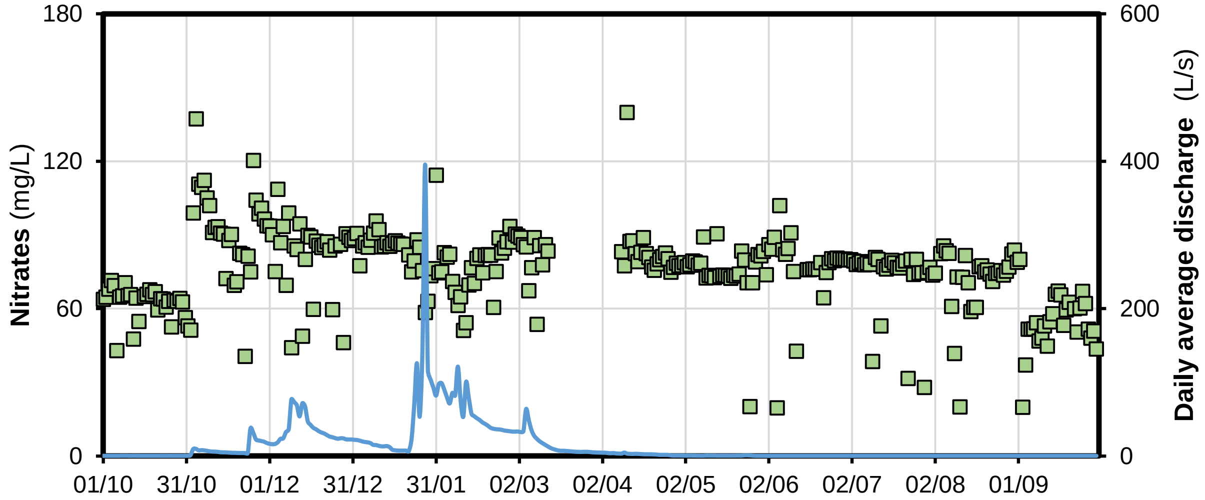

Figure 28. Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during the hydrological year 2009.

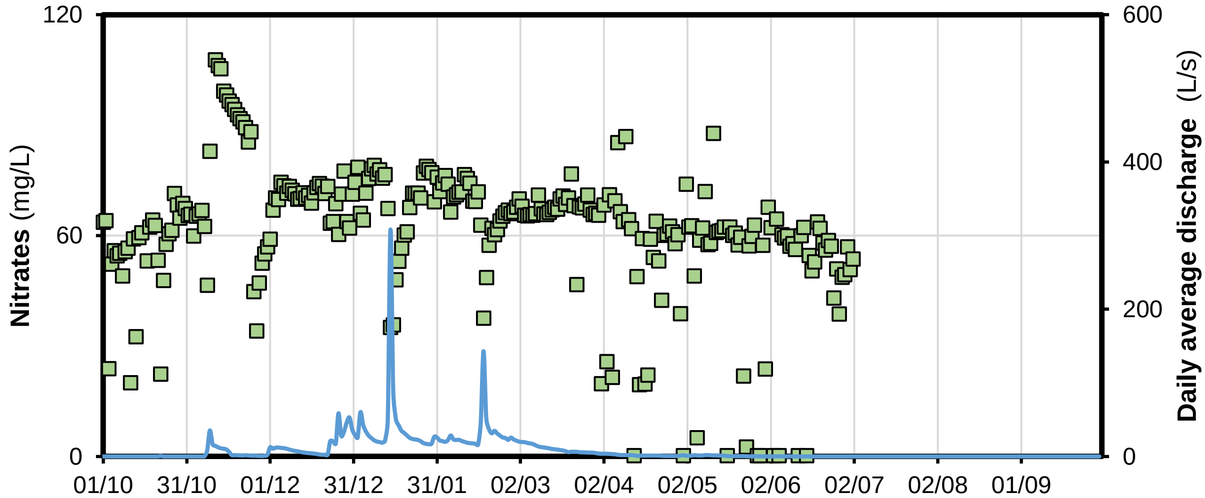

Figure 29. Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during the hydrological year 2010.

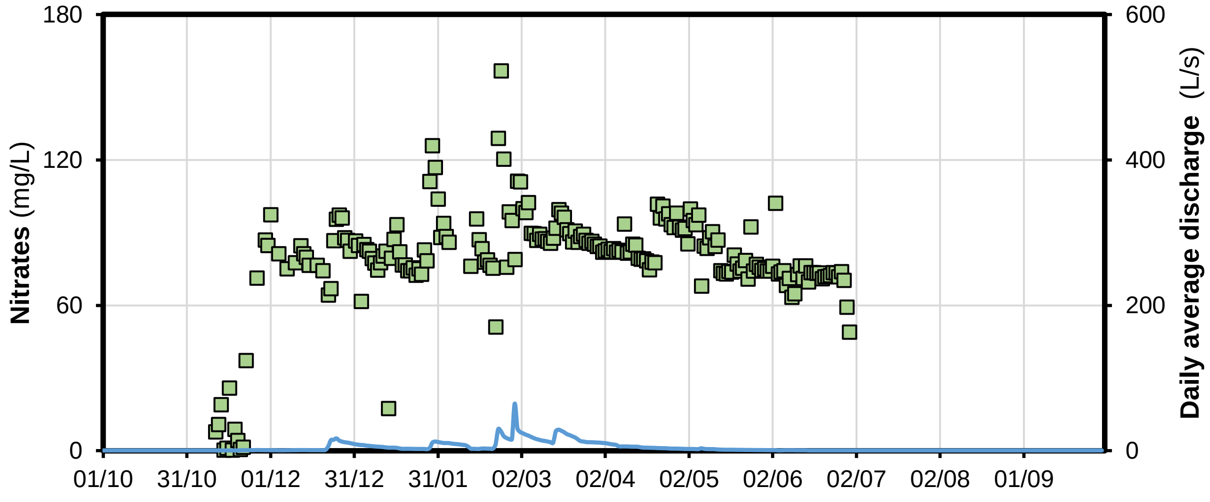

Figure 30. Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during the hydrological year 2011.

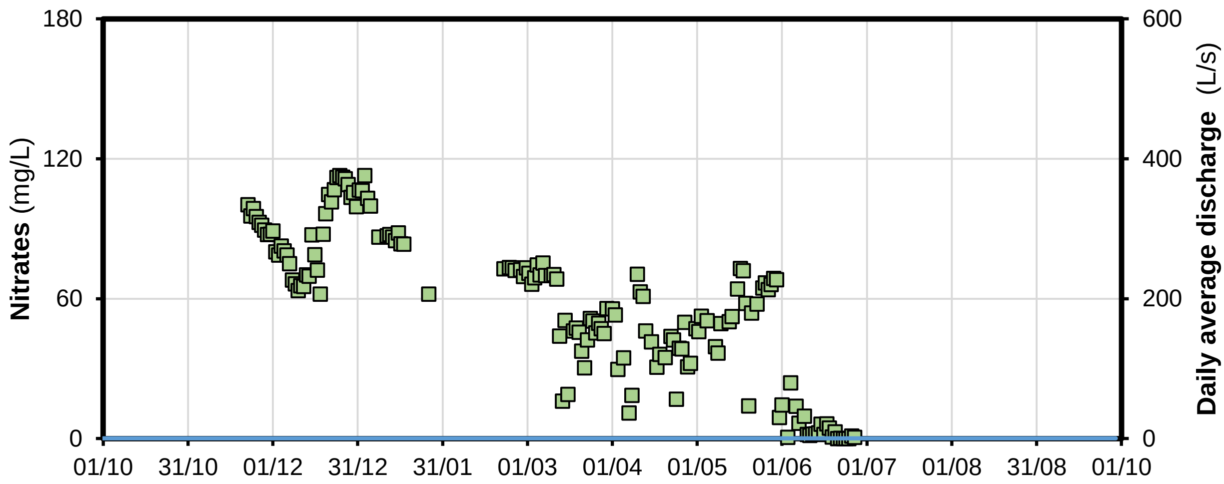

Figure 31. Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during the hydrological year 2012.

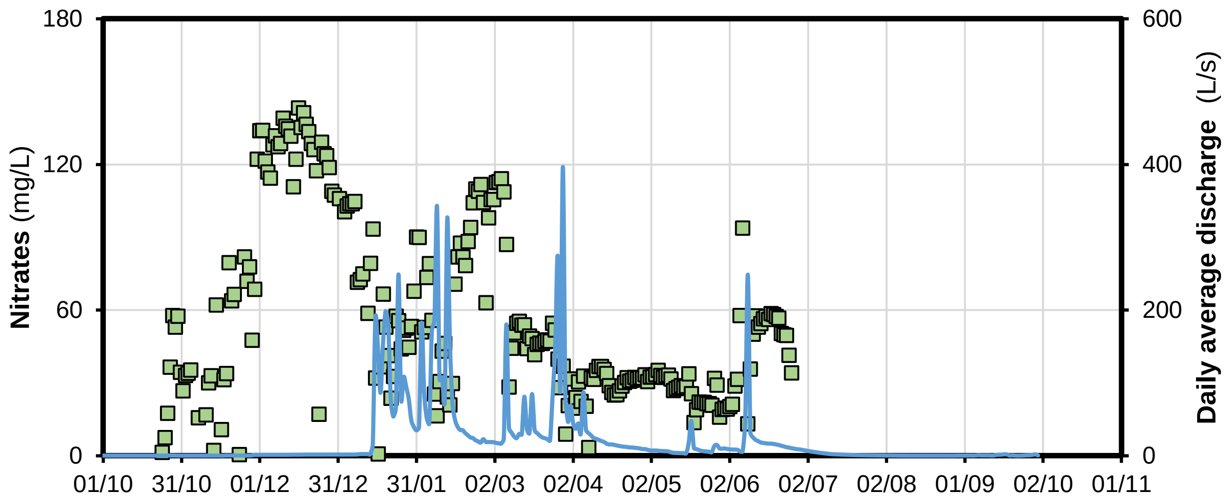

Figure 32. Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during the hydrological year 2013.

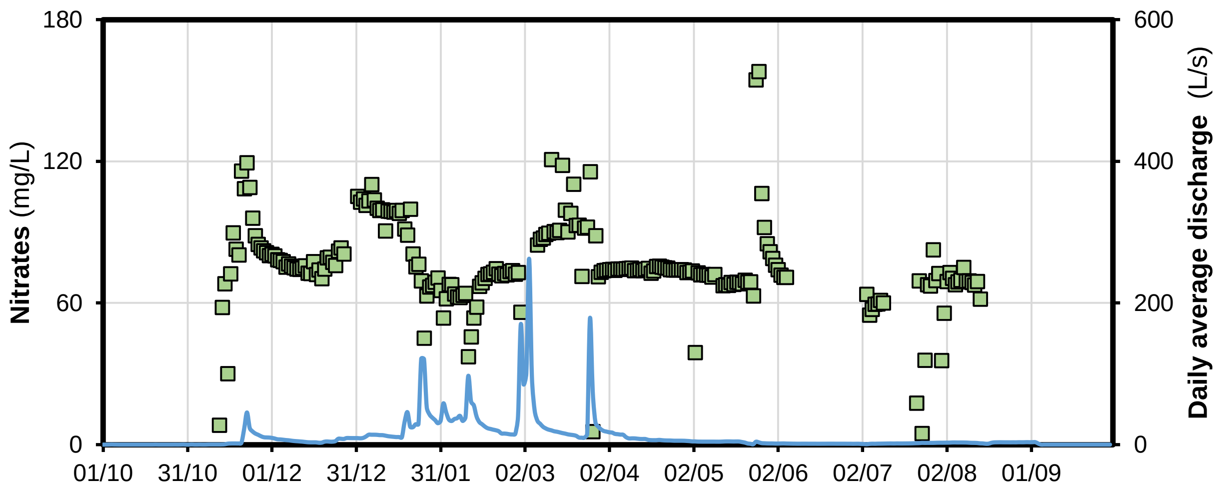

Figure 33. Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during the hydrological year 2014.

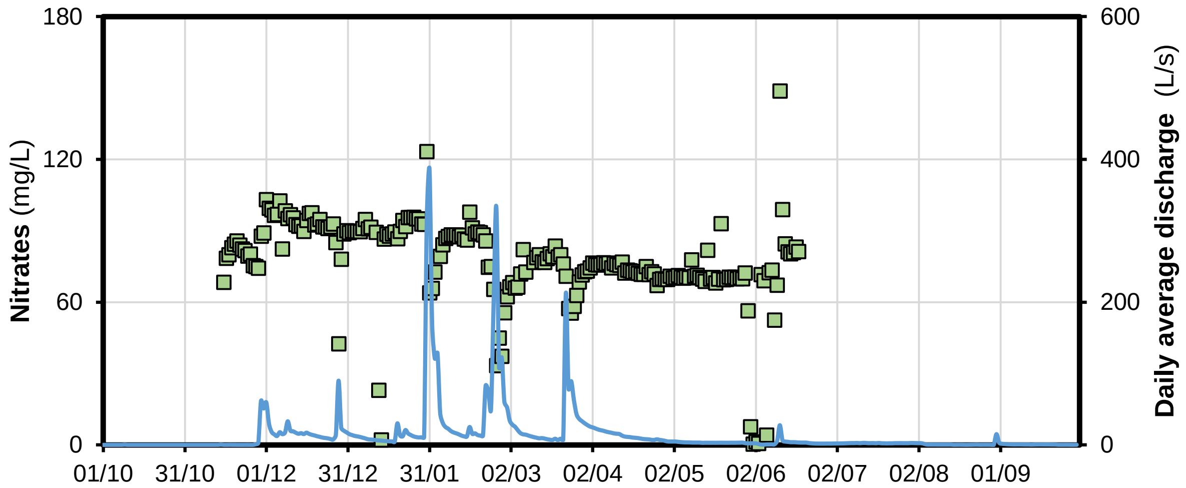

Figure 34. Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during the hydrological year 2015.

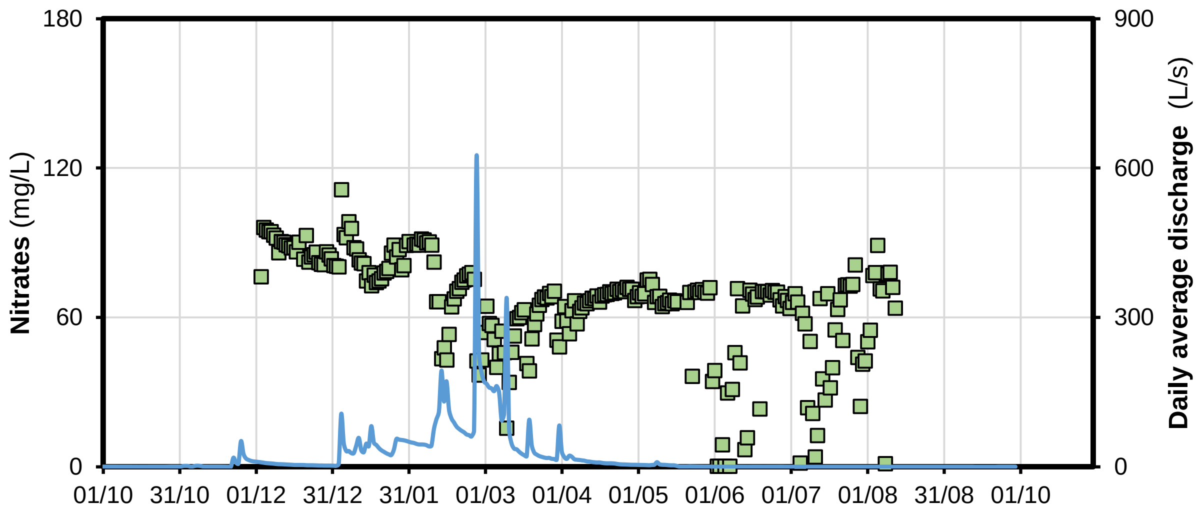

Figure 35. Daily average discharges and nitrate concentrations (mg/L) in La Tejería watershed during the hydrological year 2016.

ANNEX II. Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during each hydrological year of the study period.

ANNEX II. Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during each hydrological year of the study period.

The following graphs represent daily average concentrations (mg/L) and daily average discharge (L/s) for Latxaga watershed during each hydrological year (October – September) of the study period.

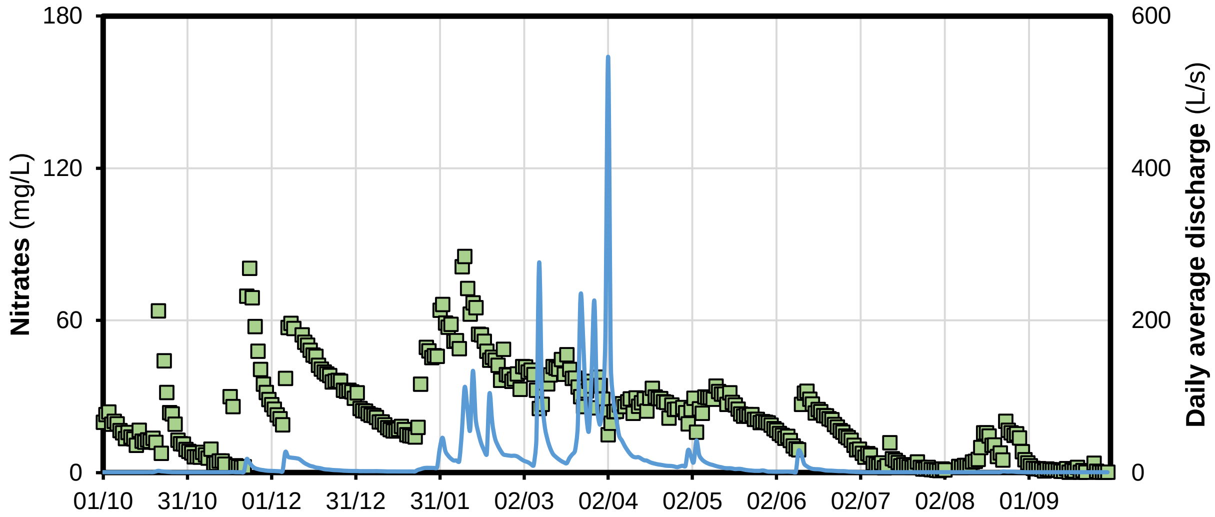

Figure 36. Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during the hydrological year 2007.

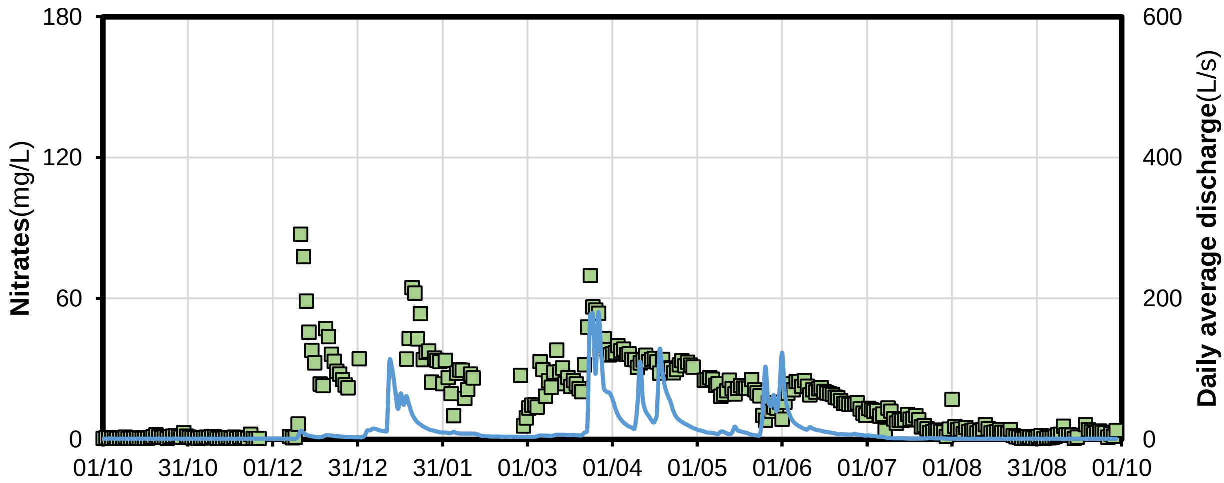

Figure 37. Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during the hydrological year 2008.

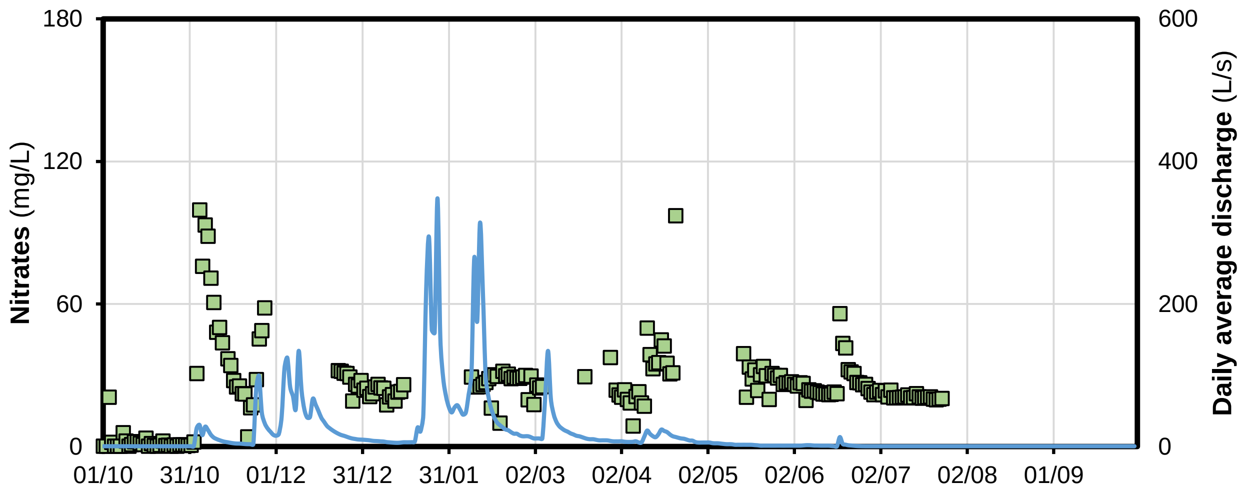

Figure 38. Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during the hydrological year 2009.

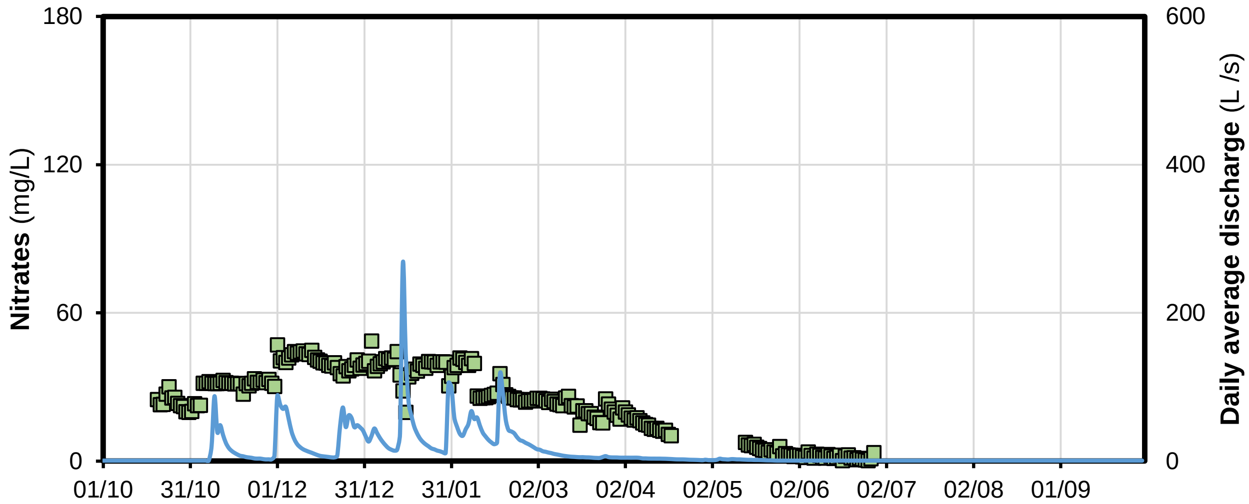

Figure 39. Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during the hydrological year 2010.

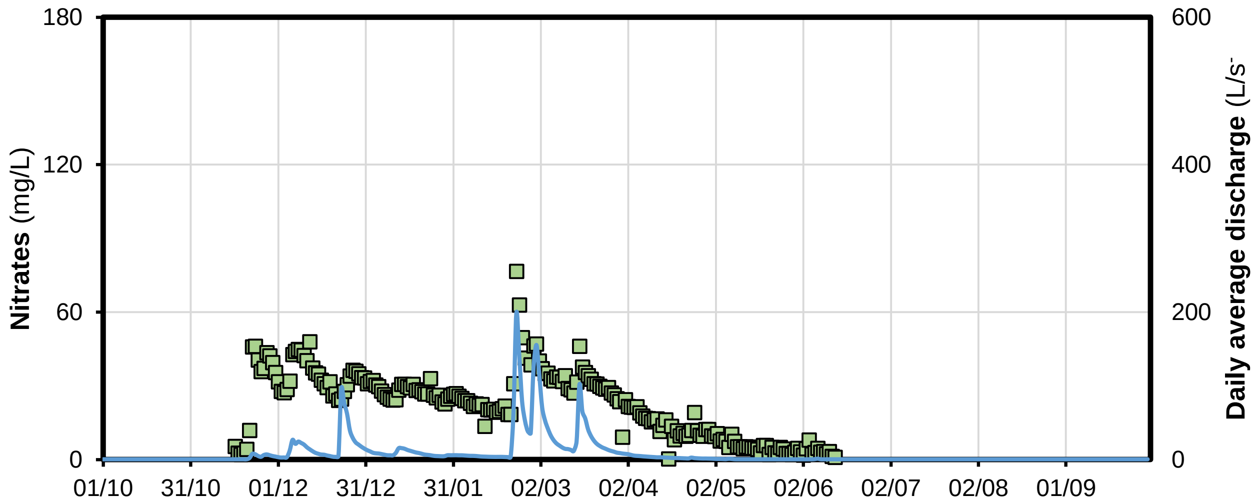

Figure 40. Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during the hydrological year 2011.

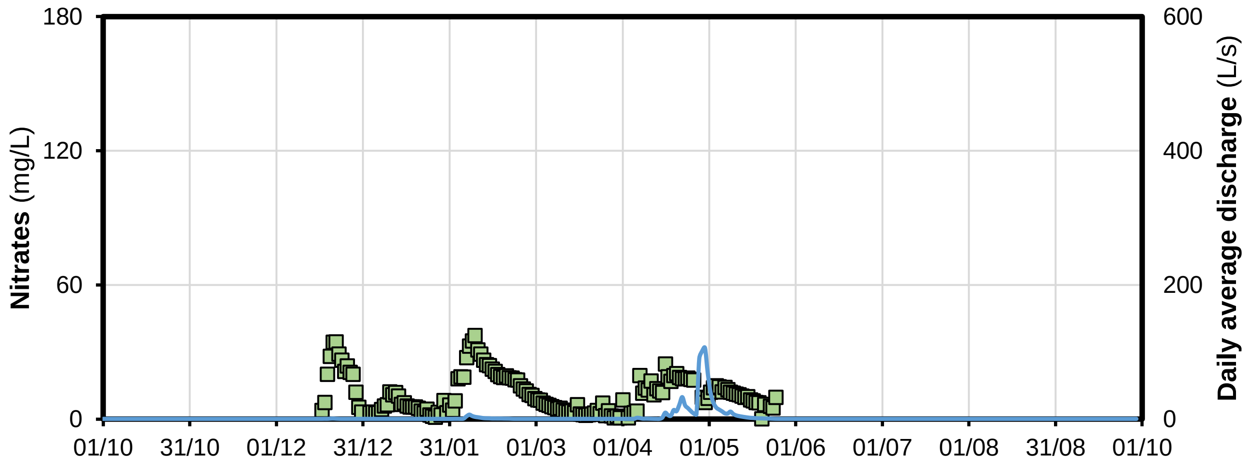

Figure 41. Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during the hydrological year 2012.

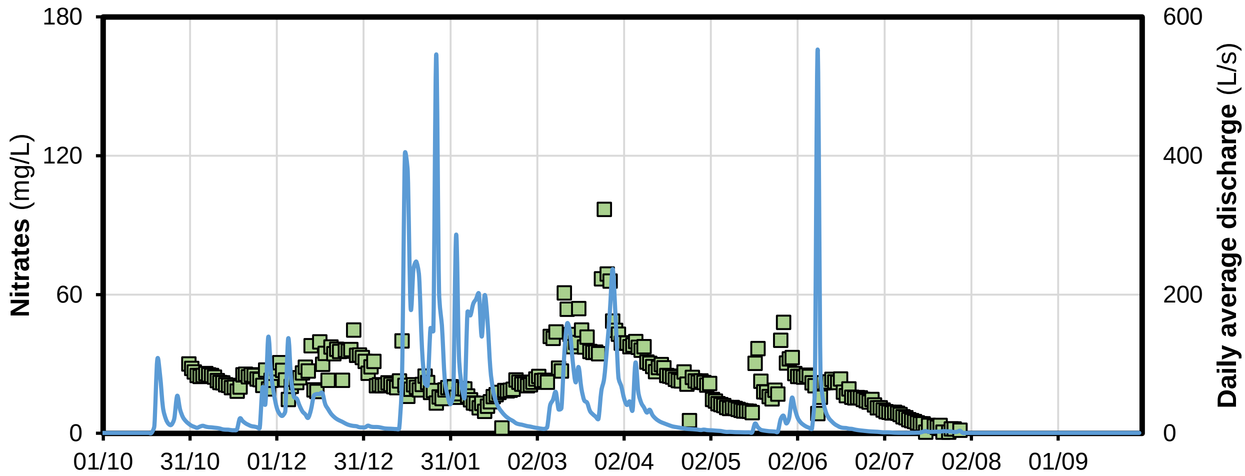

Figure 42. Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during the hydrological year 2013.

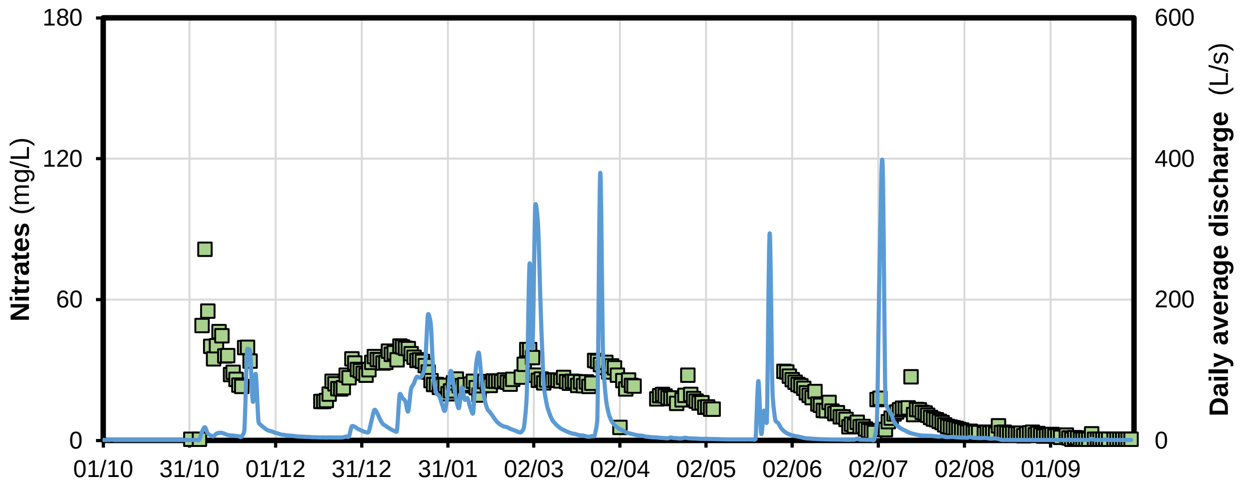

Figure 43. Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during the hydrological year 2014.

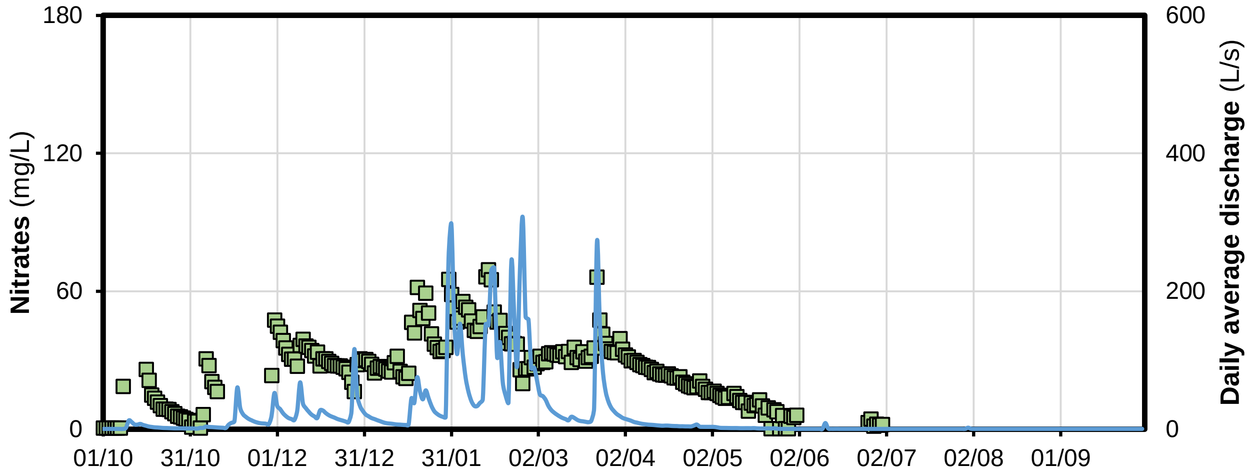

Figure 44. Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during the hydrological year 2015.

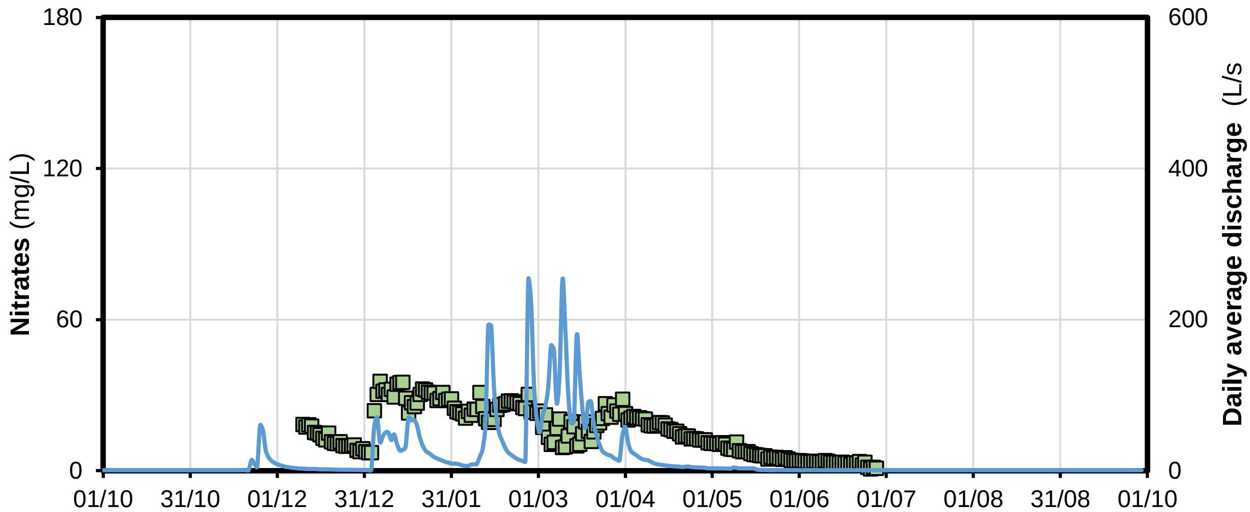

Figure 45. Daily average discharges and nitrate concentrations (mg/L) in Latxaga watershed during the hydrological year 2016.

ANNEX III. Monthly mean phosphate concentrations (mg/L) in La Tejería during each hydrological year of the study period

ANNEX III. Monthly mean phosphate concentrations (mg/L) in La Tejería during each hydrological year of the study period

The following tables show monthly mean phosphate concentrations obtained in La Tejería during each hydrological year of the study period (October 2006 – September 2017). Not available data was expressed as '-', corresponding to those months having less than 50% of the days with available discharge data.

Table 11. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2007.

	2007												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	-	0.00	0.0	0.00	0.03	0.04	0.02	0.01	0.00	0.00	0.00	0.00	0.08
IQR	-	0.01-0.01	0.01-0.01	0.01-0.01	0.02-0.04	0.03-0.08	0.02-0.03	0.01-0.02	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.07-0.12

(-): not available data.

Table 12. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2008.

	2008												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.02	0.02	0.00	0.00	0.00	0.06
IQR	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.02	0.02-0.04	0.02-0.04	0.02-0.03	0.01-0.01	0.01-0.01	0.01-0.01	0.06-0.15

Table 13. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2009.

	2009												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.02	0.02	0.00	0.00	0.00	0.08
IQR	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.02	0.02-0.04	0.02-0.04	0.02-0.03	0.01-0.01	0.01-0.01	0.01-0.01	0.07-0.33

Table 14. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2010.

	2010												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	0.00	0.01	0.03	0.02	0.05	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.32
IQR	0.01-0.01	0.01-0.01	0.03-0.05	0.02-0.07	0.04-0.09	0.01-0.03	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.21-0.89

Table 15. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2011.

	2011												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	0.00	0.00	0.01	0.03	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.26
IQR	0.01-0.01	0.01-0.01	0.01-0.02	0.03-0.04	0.03-0.03	0.01-0.02	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.17-0.28

Table 16. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2012.

	2012												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.46
IQR	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.1-0.79

Table 17. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2013.

	2013												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	0.00	0.00	0.00	0.04	0.04	0.03	0.02	0.01	0.01	0.00	0.00	0.00	0.14
IQR	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.1	0.03-0.11	0.03-0.09	0.02-0.03	0.01-0.01	0.01-0.02	0.01-0.01	0.01-0.01	0.01-0.01	0.12-0.17

Table 18. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2014.

	2014												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	0.00	0.00	0.02	0.01	0.03	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.14
IQR	0.01-0.01	0.01-0.01	0.02-0.02	0.01-0.02	0.02-0.09	0.01-0.04	0.01-0.02	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.12-0.17

Table 19. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2015.

	2015												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	0.00	0.00	0.02	0.01	0.03	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.10
IQR	0.01-0.01	0.01-0.01	0.02-0.02	0.01-0.02	0.02-0.09	0.01-0.04	0.01-0.02	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	0.08-2.04

Table 20. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2016.

	2016												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	0.00	0.00	0.00	0.04	0.07	0.04	0.01	0.00	0.00	0.00	0.00	-	0.11
IQR	0.01-0.01	0.01-0.01	0.01-0.01	0.03-0.06	0.05-0.12	0.03-0.13	0.01-0.02	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01	-	0.1-0.41

(-): not available data.

ANNEX IV. Monthly mean phosphate concentrations (mg/L) in Latxaga during each hydrological year of the study period

ANNEX IV. Monthly mean phosphate concentrations (mg/L) in Latxaga during each hydrological year of the study period

The following tables show monthly mean phosphate concentrations obtained in Latxaga during each hydrological year of the study period (October 2006 – September 2017). Not available data was expressed as '-', corresponding to those months having less than 50% of the days with available discharge data.

Table 21. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2007.

	2007												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	-	-	-	-	-	-	-	-	-	-	-	-	-
IQR	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 22. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2008.

	2008												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	0.07	0.07	0.01	-	-	-	-	-	-	0.12	0.15	-	0.07
IQR	0.07-0.08	0.06-0.07	0.01-0.02	-	-	-	-	-	-	0.1-0.22	0.08-0.18	-	0.07-0.12

Table 23. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2009.

	2009												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	-	-	-	-	-	-	-	-	-	-	-	-	-
IQR	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 24. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2010.

	2010												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	-	-	-	-	-	-	-	-	-	-	-	-	-
IQR	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 25. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2011.

	2011												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	-	-	0.08	0.07	-	0.07	-	-	-	-	-	-	0.07
IQR	-	-	0.08-0.1	0.07-0.09	-	0.06-0.1	-	-	-	-	-	-	0.08-0.08

Table 26. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2012.

	2012												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	-	-	-	0.10	0.06	-	-	0.06	-	-	-	-	0.06
IQR	-	-	-	0.09-0.12	0.05-0.07	-	-	0.06-0.07	-	-	-	-	0.06-0.08

Table 27. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2013.

	2013												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	-	-	0.07	-	-	-	-	-	-	-	-	-	-
IQR	-	-	0.06-0.08	-	-	-	-	-	-	-	-	-	-

Table 28. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2014.

	2014												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	-	-	-	-	-	-	-	-	-	-	-	-	-
IQR	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 29. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2015.

	2015												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	-	-	-	-	-	-	0.06	-	-	-	-	-	-
IQR	-	-	-	-	-	-	0.06-0.06	-	-	-	-	-	-

Table 30. Monthly mean phosphate concentrations (mg/L) in La Tejería watershed during the hydrological year 2016.

	2016												
	Oct.	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sept.**	**Median**
Median	-	-	-	-	-	-	-	-	-	-	-	-	-
IQR	-	-	-	-	-	-	-	-	-	-	-	-	-