



Nitrate and Phosphorus Transport in a Galician River (NW Iberian Peninsula): Insights From Fourteen Years of Monitoring

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The long-term development of water quality metrics is critical to estimate the status of water resources and successful catchment management. This study looks at the temporal evolution of nitrate and phosphorus loads and concentrations in a stream draining rural catchment in Galicia (NW Iberian Peninsula) during 14 hydrological years. The concentrations of both nutrients are relatively low because of the rural nature of the research catchment and low-intensity agriculture. However, catchment nutrient reference levels were widely exceeded. The hydrology controls nutrient fluxes as flow is the main driver of nutrient transfer. For both nutrients there were no consistent trends in nutrient fluxes. The analysed nutrients, however, have been seen to behave differently. As a result, N seems to be decreasing, mainly due to decreased transit in the autumn and spring. Phosphorus, which is primarily transported as particulate matter, exhibits an increase in winter linked to a greater flow and sediment transfer.

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INTRODUCTION

The natural quality of inland waters is related to the geomorphology, climate, and land use in the catchment. Thus, size and slope of the catchment, rainfall, temperatures, vegetation, erosion and soil structure play an important role in water quality. However, due to human activities, the high loads of sediments and nutrients transported by rivers have become one of the greatest problems causing the deterioration of the quality of surface waters on a global scale (Bennet et al., 2001; Worrall et al., 2016; Grizzetti et al., 2021; Kelly et al., 2022), and this explains why in recent years, determined efforts have been made both in the field of research and management and restoration.

Although water management and use has been one of the main concerns of the European Water Policy since the 1960s, it was only in the year 2000 that progress was made in the protection of aquatic resources with the publication of the Water Framework Directive (WFD; Directive, 2000) by the European Parliament and the Council of the European Union, in which a community action framework was established in the field of water policy. The WFD focuses on the protection of all water bodies present in the territory of the European Community. Its objectives are to prevent the deterioration of water resources, protect and improve their condition, promote the sustainable use of the resource, guarantee a reduction in pollution, prevent the effects of floods and droughts, and achieve at least good ecological status by the year 2015. Despite the progress made with the scope of improving the environmental quality of the various water sources in Europe, the last report by the

European Environment Agency (European Environment Agency, 2018) indicated that 47% of European surface waters continue to fail to meet the minimum objective of good ecological status, with agricultural activities and the urbanisation of rural landscapes being the main threats to fluvial courses (European Environment Agency, 2018). Therefore, the frequent use of agrochemicals to meet production demands means that agricultural systems play an important role as a source of contamination (non-point source) of water bodies (Oenema et al., 2005; Sharpley et al., 2008; Lassaletta et al., 2009). Moreover, over the last few decades, the progressive implementation of modern agriculture and livestock methods, with the introduction of increasingly intensive tillage techniques, an increase in the size of plots, the establishment of monocultures, etc. has promoted runoff and soil erosion (Panagos et al., 2015). In general, chemicals from non-point sources are transported to nearby water bodies either in dissolved form or along with sediment during heavy rainfall and erosion events, even in gently sloping areas (Sharpley et al., 2008; Dupas et al., 2017).

The latest reports from the European Environment Agency noted an improvement in 20% of the stations, directly attributed to the implementation of measures to control diffuse (non-point) contamination and increased efficiency in wastewater treatment (Carvahlo et al., 2019). Thus, based on reported long-term data for nitrates in European waters, there was a falling trend for nitrate concentration in rivers, although this has levelled off since 2009. The reason for nitrate persistence is due to overuse of nitrogen, which can remain in the subsurface flow for decades in catchments with long time response and add to increased nitrate loads long after application practices have changed, or mitigation strategies have been implemented (Fovet et al., 2015; Ehrhardt et al., 2021). These and other provenances of nitrate create a heterogeneous patchwork of source areas across the landscape that can be activated and deactivated in response to changing hydrological conditions (Dupas et al., 2019). For phosphorus, a marked decline was reported due to improved wastewater treatment, reduction of P in detergents, as well as reduction in soil fertilization rates and implementation of measures to reduce soil erosion and connectivity to the receiving waters (Oenema et al., 2005; Minaudo et al., 2015; Moatar et al., 2017). However, phosphorus may persist through soil enrichment, and therefore it may take a long time before any major water quality improvements can be detected in the recipient water bodies after decreasing fertilisation of agricultural fields (Withers and Lord, 2002; Ekholm et al., 2015).

Correct assessment of the quality of water resources in the catchment is essential to estimate the status of the resources and start management and planning, if required. In fact, the WFD urges members to carry out studies on trends of different contaminants (with trend understood to be the monotonic variation of the concentration in relation to time) and identify those water bodies exceeding established reference nutrient levels. This requires sufficiently frequent monitoring of the water quality over long periods of time, which is an arduous, costly, and time-consuming task. At present, several countries, including Spain, must improve their control programs to guarantee broad and consistent monitoring of water bodies, with appropriate coverage

of all relevant quality indicators, since there are still significant deficiencies. However, the number of checkpoints has decreased in recent years as compared to the first planning cycles of the WFD. This includes the Galician region, popularly known as “the country of a thousand rivers.” Despite this, the scientific community did not pay much attention to the health of Galician rivers. To date, they have not undergone extensive monitoring because hydrological and hydrochemical studies based on catchment monitoring are relatively recent in the community. This underlines the need to continue long-term monitoring efforts for water quality assessments and to identify trends.

The objective of this paper was to explore the temporal evolution of nitrate and phosphorus loads and concentrations in a stream draining a typical rural catchment in Galicia (NW Iberian Peninsula), i.e., small population centres and low-intensity agriculture. The study is based on information collected over a period of 14 years in which regular manual sampling was combined with automatic sampling during runoff episodes.

MATERIAL AND METHODS

Study Area

The study site is the Corbeira stream headwater catchment located in NW Spain (Figure 1, gauge at 43° 12'58"N, 8° 13'48"W). The Corbeira is a right-bank tributary of the Mero River, the main river contributing to the Cecebre reservoir (water supply for the city of A Coruña and surroundings (about 450,000 inhabitants) discharging into the Ria do Burgo, in the vicinity of the city of A Coruña (Figure 1). The total length of the stream is 10 km, and the whole catchment area covers about 16 km², with altitudes ranging from 65 m a.s.l. at the confluence with the Mero River to 470 m a.s.l. at the highest part. The mean slope is 19%, although approximately 27% of the catchment is steep, i.e., slopes higher than 25%. From a geological point of view, it is located within the Ordenes Complex and is dominated by basic schists (IGME, 1981), with phyllites and biotitic schists the most common petrological types in the area, which confers a certain uniformity to the lithological substrate. Schists are made up of easily alterable minerals, such as biotite (sometimes chlorite), plagioclase, and amphiboles. The soils are Umbrisols and Cambisol (IUSS Working Group WRB, 2014) with a silt and silty loam texture developed. The organic matter content in the upper horizon varies from less than 5.3% in cultivated lands, to 10.5% in forest soils, highlighting the importance of the latter in carbon sequestration. Total N soil concentrations ranged between 0.26% on cultivated land and 0.47% on grassland, whereas forest soils showed a mean value of 0.39% (Rodríguez-Blanco et al., 2015). The P Olsen content varied between 14.0 mg kg⁻¹ in the forest soils and 69.0 mg kg⁻¹ in cultivated fields, with the mean content of grassland 19.5 mg kg⁻¹ (Rodríguez-Blanco et al., 2013).

The main land use is forest, which covers 65% of the catchment area and is mostly used for commercial plantations of eucalyptus and pine. In addition, there is, as in most Galician River catchments, a dense riparian vegetation basically consisting

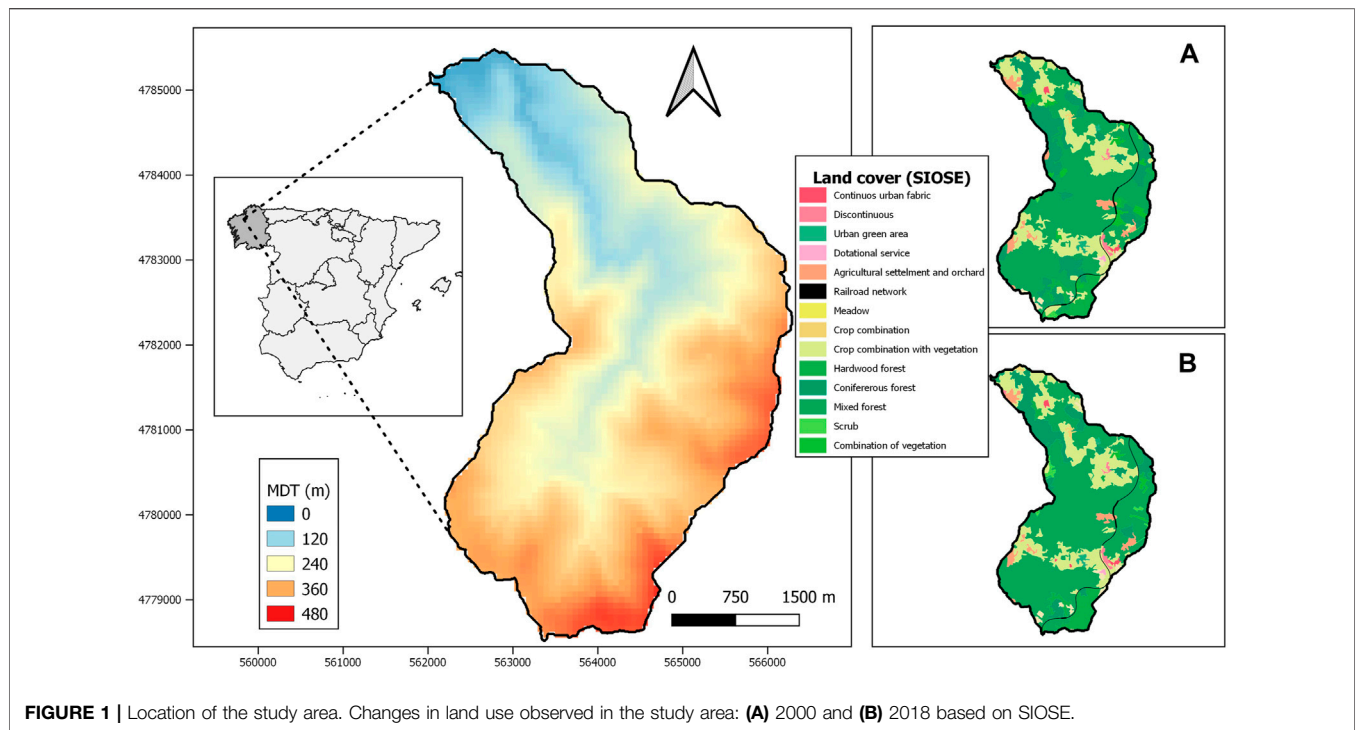
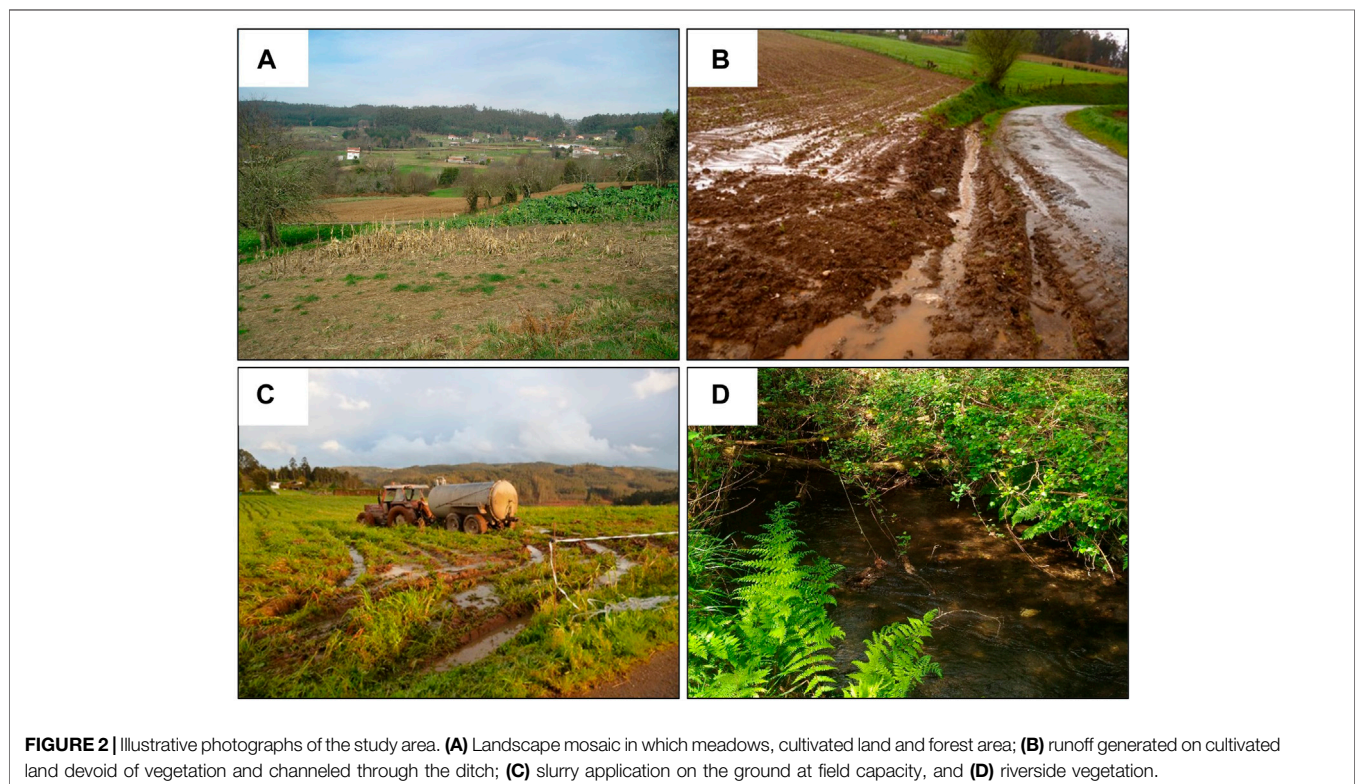
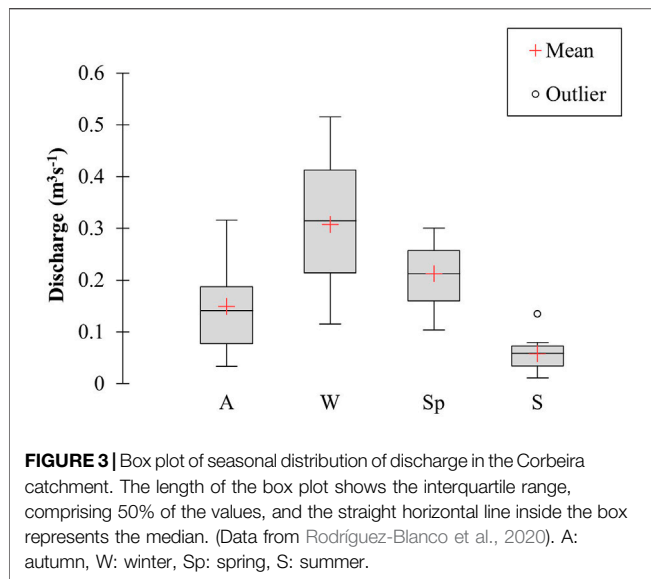


FIGURE 1 | Location of the study area. Changes in land use observed in the study area: **(A)** 2000 and **(B)** 2018 based on SIOSE.



of *Alnus glutinosa*, *Betula alba* and *Salix spp.* The agricultural surface represents 30% of the catchment and is dominated by pasture and meadows (26%), the latter being humid areas mainly

in flood zones. They are used to produce green, dry, or ensiled forage for consumption. Cropland comprises approximately 4% of the catchment area and is essentially used for forage crops, such



as maize and winter cereals. Potatoes, vegetables, and fruit trees are cultivated in small kitchen gardens and orchards. The remaining 5% of the catchment's surface is occupied by impervious areas, mostly road infrastructures (roads and forest paths) distributed throughout the catchment, crossing the main channel and its tributaries at numerous points. This information is based on land use maps from the Spanish Land Cover/Land Use Information System (SIOSE), used to calculate the cover (%) of land use for the years 2004 and 2018. A slight decrease was observed in the agricultural area during this period, whereas forests increased due to the replacement of cultivated land by plantations of fast-growing tree species, mainly eucalyptus. There is also a decrease in stocking density (dominated by cattle) during the study period, going from 0.96 livestock units (LU) per ha of utilised agriculture area (UAA) in 2004 to 0.73 LU per ha of UAA in 2018.

The distribution of land uses in the catchment is characterized by the mosaic presented in agricultural areas (Figure 2), which is generally bordered by meadows and, in some cases, by small stone walls, characteristic of smallholdings in Galicia. This distribution could be classified as a low-intensity agricultural mosaic (cropland and grassland), with a light input of inorganic fertilizer, small field sizes and low livestock density (Dou et al., 2021).

The study area has a marked rural nature (<150 inhab. km⁻²; Organization for Economic Co-operation and Development-OECD, 2007), characterized by a low population density, which has gone from 35 inhab. km⁻² at the beginning of the study (2004) to 32 inhab. km⁻² in 2018 (rates calculated from data of Spanish Statistical Office-INE, 2019)- a 15% decrease in just 15 years. In fact, the Ministry of Agriculture statistics place Galicia at the head of the most isolated communities in rural areas. Between the years 2010–2018, the population in Galician villages fell by 17.9% (INE, 2019). Most of the population is distributed in scattered dwellings that lack a sewage system, so that domestic wastewater is stored in cesspools constituting small sources of contamination.

The climate is temperate oceanic, with an annual average temperature of 13.5°C ranging from 8.9°C in January and February (winter) to 18.8°C in July and August (summer). The rainfall is abundant (1,074 mm- period 1983/1984–2017/2018) and occurs throughout the year, although it is concentrated in the autumn and winter, with October, November and December being the wettest months and July and August the driest. The hydrological regime is pluvial oceanic; which implies two alternate periods: a high-discharge period during the wet period (i.e., late autumn and winter) and a low-discharge period during the dry season (i.e., late spring and summer) (Figure 3; Rodríguez-Blanco et al., 2020). Mean stream discharge is 0.181 m³ s⁻¹, ranging from 0.08 to 0.273 m³ s⁻¹ (Rodríguez-Blanco et al., 2020). Baseflow contribution to the total streamflow (i.e., baseflow index), calculated according to Gustard et al. (1992), varies between 0.61 and 0.78 with an average of 0.71 (unpublished data), indicating that 71% of long-term streamflow in the study area is originated from groundwater.

Field Instrumentation and Water Sampling

The data used in this study covers 14 hydrological years from October 2004 to September 2018. Monitoring within the catchment included rainfall and discharge measurements and automatic and manual sampling of stream water at the catchment outlet. Rainfall was monitored at three locations across the catchment at 10-min intervals using tipping bucket rain gauges (0.2 mm resolution), followed by the Thiessen Polygon method (Linsely et al., 1949) to calculate the mean rainfall in the area. Stream water level was measured at the catchment outlet using a pressure transducer (ISCO 720), and discharge was calculated from the rating curve. Measured water levels at 1 min intervals were aggregated to 10-min values. Water sampling was carried out under baseflow conditions (manual sampling every 2 weeks) and during runoff events (automatic sampling, ISCO 6712-FS). Full details of the design of the monitoring and water sampling can be found in Rodríguez-Blanco et al. (2013, 2015).

Laboratory Analyses

Water samples were immediately brought back to the laboratory and refrigerated (4°C) until analysed for nitrate and total and dissolved phosphorus concentrations. After sample filtration (0.45 μm), nitrate concentrations (expressed as mg NO₃⁻ L⁻¹) were determined by capillary electrophoresis. Total phosphorus (TP) (μg P L⁻¹) was determined in unfiltered water samples by acid digestion with ammonium persulfate (APHA, 1998) followed by colorimetric determination using the molybdate-ascorbic acid method developed by (Murphy and Riley, 1962). Following water sample filtration, dissolved phosphorus (DP) was determined by ICP-MS. Particulate phosphorus (PP) was calculated as the difference between TP and DP.

Data and Statistical Analysis

Since the main objective of this work was to detect trends of nitrate and phosphorus in long time series, the load (of these nutrients) for different periods of time (monthly, seasonal, or annual) was calculated by summing up the products from the

mean concentration between two consecutive samples and cumulative discharge for each time interval between two water samples. The discharge-weighted mean concentration of each nutrient for each specific period (monthly, seasonal, or annual) was calculated as the nutrient load of each period divided by the total discharge of the period. For the seasonal trend, the year was divided into four seasons: autumn (October, November, and December), winter (January, February, and March), spring (April, May, and June) and summer (July, August, and September).

Once the nutrient concentrations were estimated, two different methodologies were used to calculate the trend of nitrate concentrations. The first refers to the approach used by the member states in the context of the Nitrates Directive, which is based on calculating the differences between the average concentration of nitrates taken from two consecutive periods of 4 years. Differences in the range between -1 and 1 mg L^{-1} indicates the absence of trend, whereas those higher than 1 and 5 mg L^{-1} are rated as a positive and strongly upward trend. In the second approach, trend analysis was performed using the non-parametric Mann-Kendall test and the Sen method in the Maksiemen program (developed by the Finnish Meteorological Office). Both tests are widely used for trend detection in hydro-meteorological records and water quality (Bourauoi and Malagó, 2020) and have also been recommended by the World Meteorological Organisation for analysing the trends in hydrometeorological time series (Kumar et al., 2009). The presence of a monotonic upward or downward trend was tested with the Mann-Kendall and the magnitude (i.e., slope of a linear trend) was estimated with the Sen method.

RESULTS

Exploratory Analysis: Annual and Seasonal Nitrate and Phosphorus Loads and Concentrations

The average nitrate and phosphorus export during the study period was $19.04 \text{ kg ha}^{-1} \text{ year}^{-1}$ (7.36 and $30.07 \text{ kg ha}^{-1} \text{ year}^{-1}$) and $0.13 \text{ kg ha}^{-1} \text{ year}^{-1}$ (0.08 and $0.22 \text{ kg ha}^{-1} \text{ year}^{-1}$) for nitrate and phosphorus respectively (Figure 4). In both cases, the highest values were registered in the hydrological year 2009/2010 and the lowest were measured in the hydrological year 2016/17 (Figure 4), similar to discharge variations in the study period. This highlights the importance of the hydrological response in the nutrient export in the study catchment, because small streams can be very sensitive to changes in the precipitation regime and runoff episodes compared to large basins (Bol et al., 2018). The results showed that PP is the main fraction of P mobilized from the catchment, representing approximately 72% of the phosphorus exported, although the proportions vary between 39% in the hydrological year 2013/14 and 86% in 2017/18. This variability is probably related to the characteristics of the rainfall-runoff events, management activities within the

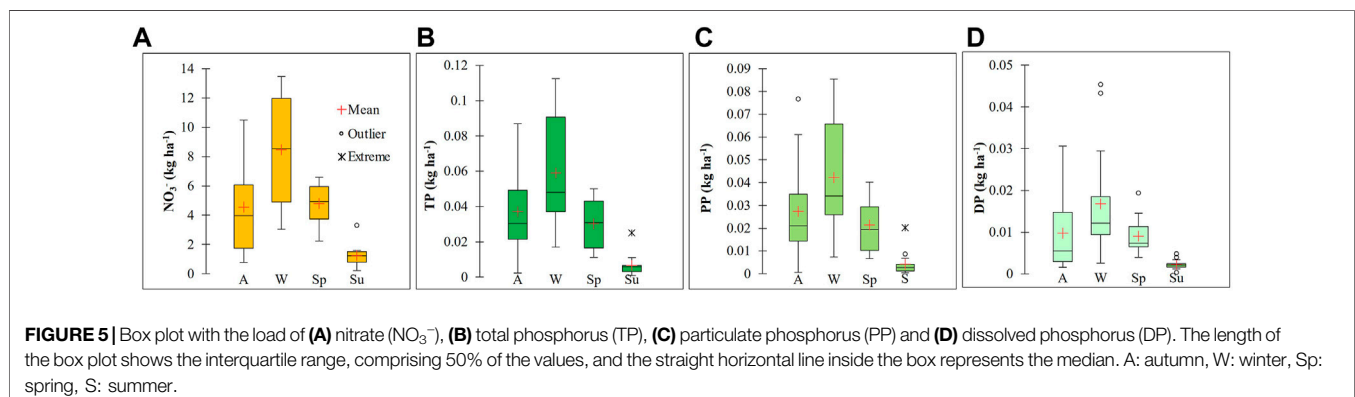
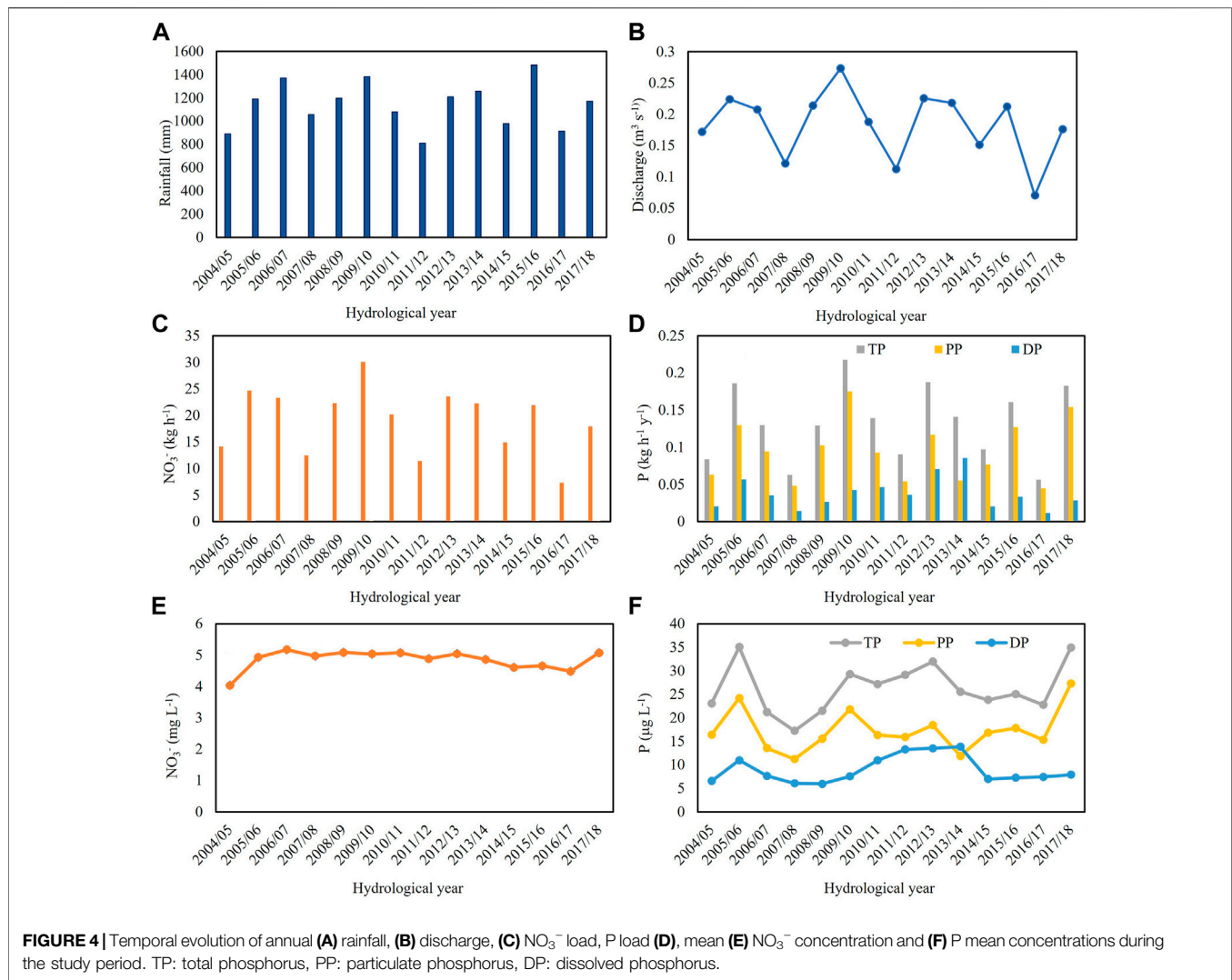
catchment in relation to meteorological conditions, and the source of sediments delivered to the river channel. The P losses occur primarily through erosion and surface runoff as P is mobilized and transported during runoff events (Rodríguez-Blanco et al., 2015).

Mean annual concentrations ranged from 4.1 to 5.2 mg L^{-1} for NO_3^- , and 17.2 and $35.1 \text{ } \mu\text{g L}^{-1}$ for TP (Figure 4), reaching mean values of 4.8 mg L^{-1} and $26.3 \text{ } \mu\text{g L}^{-1}$, respectively, which signifies a greater variability of phosphorus ($\text{CV} = 20\%$) concentrations than nitrate ($\text{CV} = 6\%$). The highest mean concentration of nitrate was recorded in the hydrological year 2006/07, while the lowest values were obtained in 2004/05. For total phosphorus, the highest mean concentrations were recorded in hydrological year 2005/06 while the lowest values, also for dissolved phosphorus, were recorded in 2007/08. Therefore, the lowest concentrations are usually recorded in the driest years and with lower flow rates (Figure 4).

Transport throughout the year (Figure 5) showed that the highest nitrate loads were obtained in winter ($8.45 \text{ kg ha}^{-1} \text{ year}^{-1}$), followed by spring (4.78 kg ha^{-1}) and autumn (4.54 kg ha^{-1}), with the lowest values recorded in summer (1.25 kg ha^{-1}). The pattern for phosphorus was similar, which also returned the highest records in winter (0.050 kg ha^{-1}), followed by autumn (0.030 kg ha^{-1}) and spring (0.031 kg ha^{-1}), with the lowest values observed in summer (0.006 kg ha^{-1}) (Figure 5). The seasonal distribution of the concentrations (Figure 6) followed the same pattern as the loads, meaning that nitrate showed the following decreasing order: winter (5.5 mg L^{-1}) > autumn (5.3 mg L^{-1}) > spring (4.5 mg L^{-1}) > summer (4.1 mg L^{-1}), while phosphorus displayed the sequence: autumn (TP: $32.75 \text{ } \mu\text{g L}^{-1}$; PP: $22.91 \text{ } \mu\text{g L}^{-1}$; DP: $10 \text{ } \mu\text{g L}^{-1}$) > winter (TP: $33 \text{ } \mu\text{g L}^{-1}$; PP: $23 \text{ } \mu\text{g L}^{-1}$; DP: $10 \text{ } \mu\text{g L}^{-1}$) > spring (TP: $24 \text{ } \mu\text{g L}^{-1}$; PP: $15 \text{ } \mu\text{g L}^{-1}$; DP: $8 \text{ } \mu\text{g L}^{-1}$) > summer (TP: $16 \text{ } \mu\text{g L}^{-1}$; PP: $9 \text{ } \mu\text{g L}^{-1}$; DP: $7 \text{ } \mu\text{g L}^{-1}$). Phosphorus concentrations showed large differences between autumn and winter against summer.

Trends in Nitrate and Phosphorus Loads and Concentrations

Tables 1–3 present the results obtained with the Mann-Kendall test. Statistically relevant trends in annual values were not observed for both nutrients (Table 1). Nitrate seems to show a limited downward prospect. The same results were obtained using the Nitrate Directive approach, because the difference between the NO_3^- flow-weighted concentrations of two consecutive reporting periods ranged between -1 and 1 mg L^{-1} , indicating the absence of a trend. On a seasonal scale, a meaningful decrease is only observed in autumn for the nitrate load (Table 2), mainly linked to the decrease in October, as well as an increase in TP concentrations in winter (Table 3). A negative trend is also seen in the load of NO_3^- and P in the month of September, while the concentrations show a positive pattern, which could be related to the lower discharge in this month and the enrichment of the flow due to less dilution.



DISCUSSION

NO_3^- and P loads were similar or lower compared with other studies carried out in Galicia (Bernárdez et al., 2013; Serrano et al.,

2015) and suggest that agricultural activities and forest plantation management in the study area have only a slight impact on surface waters of the Corbeira catchment relative to other mixed land use catchments in Europe (Fovet et al., 2015; Dupas et al.,

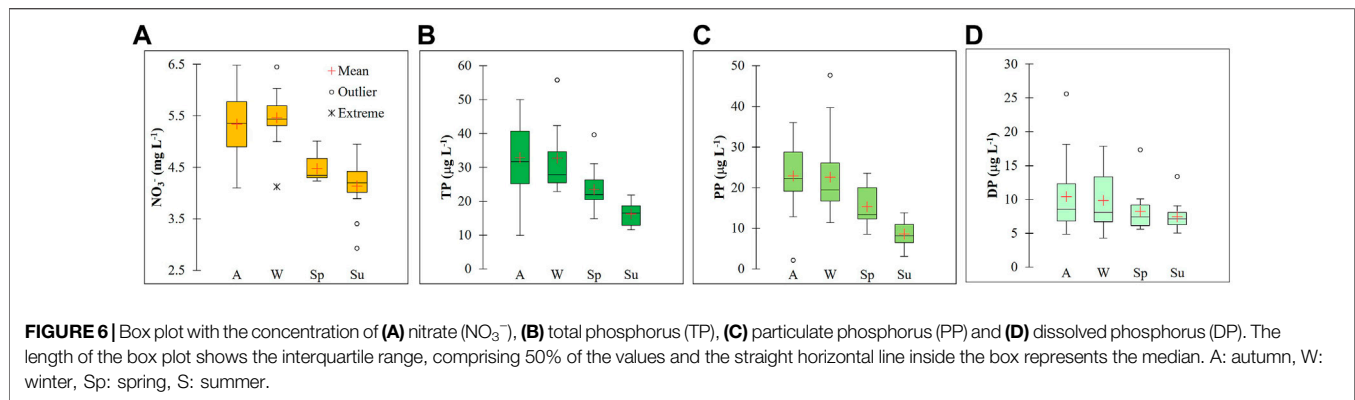


FIGURE 6 | Box plot with the concentration of (A) nitrate (NO_3^-), (B) total phosphorus (TP), (C) particulate phosphorus (PP) and (D) dissolved phosphorus (DP). The length of the box plot shows the interquartile range, comprising 50% of the values and the straight horizontal line inside the box represents the median. A: autumn, W: winter, Sp: spring, S: summer.

TABLE 1 | Mann-Kendall trend test results for nutrient yield and concentrations.

Variable	Mann-Kendall test	Sen's slope
NO_3^- ($\text{kg ha}^{-1} \text{ year}^{-1}$)	-1.20	-0.485
TP ($\text{kg ha}^{-1} \text{ year}^{-1}$)	0.33	0.001
PP ($\text{kg ha}^{-1} \text{ year}^{-1}$)	0.00	0.001
DP ($\text{kg ha}^{-1} \text{ year}^{-1}$)	-0.11	0.000
NO_3^- (mg L^{-1})	-0.99	-0.018
TP ($\mu\text{g L}^{-1}$)	0.55	0.277
PP ($\mu\text{g L}^{-1}$)	0.55	0.176
DP ($\mu\text{g L}^{-1}$)	0.88	0.154

A positive Sen's slope reveals increasing values, whereas a negative slope indicates decreasing values.

2017; Bouraoui and Malago, 2020; Ehrhardt et al., 2021). In fact, annual mean concentrations of both elements were well below the recommendations of WFD, the threshold proposed by Camargo and Alonso (2006) for protecting the most sensitive freshwater species and the threshold established by Carleton et al. (2009) to prevent nuisance level of periphyton and cyanobacteria (Table 4). When the mean nitrate and phosphorus concentrations obtained

in this study are compared to the threshold values reported by Poikane et al. (2021), based on their relationship with macrophytes and phytobenthos, it is observed that mean nutrient concentrations of this study are within the range of predicted nitrogen good-moderate class boundaries for low alkalinity lowland and upland rivers (Table 4). They also are in the boundary values proposed by de Vries et al. (2013) to protect aquatic ecosystems from eutrophication. However, they exceed the threshold reported by Stevenson et al. (2008). In this case, the values reported by this last author coincide with concentrations in the catchment reference site (TP: $15 \pm 7 \mu\text{g L}^{-1}$; mean and standard deviation from 120 water samples collected from 2004 to 2016, unpublished data); i.e., in the headwaters of the studied stream, which drains a forest area and is assumed to be free of nutrient inputs from human activities. So, protection of stream with this threshold was deemed impractical. This highlights the need to adapt the thresholds to individual water bodies to protect aquatic ecosystems from eutrophication.

Nitrate concentration exceeds the concentration collected by Macías et al. (1991) as reference values in slightly polluted rivers

TABLE 2 | Mann-Kendall trend test results for seasonal and monthly nutrient loads.

Variable	NO_3^-		TP		PP		DP	
	Sen's slope	Sen's slope	Sen's slope	Sen's slope	Sen's slope	Sen's slope	Sen's slope	Sen's slope
Autumn	-1.86*	-0.400	-1.31	0.003	-1.42	-0.002	-1.09	0.000
Winter	0.77	0.194	0.99	0.003	1.53	0.002	0.33	0.000
Spring	-0.33	-0.040	0.00	0.000	0.33	0.000	0.33	0.000
Summer	-1.09	-0.052	0.00	0.000	0.00	0.000	-1.64	0.000
October	-2.19*	-114.638	-1.42	-0.582	-1.42	-0.540	-1.86	-0.136
November	-1.53	-199.571	-1.64	-1.773	-1.86*	-1.376	-1.31	-0.381
December	-1.64	-372.552	-1.09	-2.275	-1.09	-0.628	-0.77	-0.387
January	0.55	72.032	1.31	1.558	0.99	1.253	0.33	0.078
February	0.88	104.815	1.31	1.963	1.53	2.083	0.00	0.032
March	0.44	80.935	0.44	0.486	0.33	0.224	0.77	0.240
April	-0.22	-28.660	0.99	1.038	0.55	0.243	0.99	0.206
May	-1.42	-63.505	-0.77	-0.349	-1.09	-0.289	0.11	0.007
June	-0.88	-47.283	-0.44	-0.092	-0.88	-0.172	-0.44	-0.029
July	-0.66	-32.810	-0.66	-0.156	-0.66	-0.072	-1.09	-0.072
August	-1.09	-16.652	-0.99	-0.074	-0.33	-0.022	-1.97*	-0.059
September	-1.86*	-34.130	-1.86*	-0.114	-1.53	-0.044	-2.08*	-0.056

A positive Sen's slope reveals increasing values, whereas a negative slope indicates decreasing values. Significance level: *: 0.05; +: 0.1.

TABLE 3 | Mann-Kendall trend test results for seasonal and monthly nutrient concentrations.

Variable	NO ₃ -		TP		PP		DP	
	Sen's slope		Sen's slope		Sen's slope		Sen's slope	
Autumn	-1.31	-0.080	-0.33	-0.135	-0.55	-0.342	0.22	0.093
Winter	0.11	0.007	2.30*	1.006	1.53	0.832	0.77	0.168
Spring	-0.22	-0.003	0.44	0.228	-0.11	-0.023	1.53	0.150
Summer	0.00	0.006	1.42	0.393	1.31	0.292	-0.22	-0.056
October	-1.53	-0.088	-0.77	-0.855	-1.20	-1.135	-0.22	-0.137
November	-1.75*	-0.124	-0.66	-0.873	-1.09	-1.239	0.00	-0.024
December	-0.66	-0.084	0.77	0.458	0.11	0.173	1.31	0.285
January	0.33	0.011	1.31	1.659	0.77	0.872	0.00	-0.012
February	0.00	-0.011	1.20	0.939	0.99	0.696	0.66	0.165
March	0.00	0.002	0.00	-0.076	-0.33	-0.269	1.42	0.244
April	-1.20	-0.031	0.11	0.144	0.11	0.128	1.31	0.165
May	-0.22	-0.007	0.33	0.129	-0.33	-0.320	1.42	0.251
June	-0.22	-0.013	0.22	0.209	0.00	-0.005	1.75*	0.136
July	0.55	0.014	0.22	0.215	0.00	0.016	-0.22	-0.031
August	0.44	0.033	0.66	0.208	1.42	0.284	-0.33	-0.064
September	0.44	0.017	1.31	0.196	0.88	0.133	0.77	0.220

A positive Sen's slope reveals increasing values, whereas a negative slope indicates decreasing values. Significance level: *: 0.05; *: 0.1.

TABLE 4 | Nutrient thresholds establish by different ecology-based strategies.

Reference	Nutrient criteria	Approach for establishing criteria
Camargo and Alonso (2006)	0.5–1.0 mg TN L ⁻¹	Protect aquatic ecosystems from eutrophication and acidification
Carleton et al. (2009)	100 µg TP L ⁻¹ ; 2.7 mg TN L ⁻¹	Prevent nuisance level of periphyton and cyanobacteria
Poikane et al. (2021)	1.63 mg TN L ⁻¹ (.71–4.19), 32 µg SRP L ⁻¹ (18–58) 1.79 mg N L ⁻¹ (1.02–4.04), 40 µg L ⁻¹ (19–78)	Good moderate class boundary low alkalinity lowland rivers Good moderate class boundary low alkalinity upland rivers
Stevenson et al. (2008)	10–12 µg TP L ⁻¹	Protect high-quality biological conditions in streams (Mid-Atlantic Highlands)
de Vries et al. (2013)	1.0–2.5 mg N L ⁻¹	Protect aquatic ecosystems from eutrophication and acidification

TP, Total phosphorus; SRP, soluble phosphorus; TN, total nitrogen.

(1.19 mg L⁻¹), the background concentration proposed by Meybeck (1982) for the major unpolluted rivers (0.44 mg L⁻¹), as well as the levels suggested for uncontaminated natural rivers in Galicia (1–4 mg L⁻¹, Antelo and Arce, 1996) and the mean concentration in the catchment reference site (1.99 ± 0.54 mg L⁻¹; mean and standard deviation from 120 water sampled collected from 2004 to 2016, unpublished data). Naves et al. (2019) observed nitrate contamination in the groundwaters (concentrations between 2.54 and 47.1 mg L⁻¹) of the study area linked to an inadequate management of the manure in the field and even to an occasional discharge of slurry from local farms. However, the results of this study are far from what was observed by these authors, since nitrate concentrations in summer (mean = 4.13 mg L⁻¹) -when discharge is dominated by groundwater-are well below the values reported by Naves et al. (2019) as a reference in the study area (1.2–9.9 mg L⁻¹).

Loads and the concentrations of both nutrients showed a marked seasonal pattern related to the hydrological behaviour of the catchment, that is, the highest values were recorded in winter and autumn, coinciding with the highest discharge and runoff events (Rodríguez-Blanco et al., 2019), while the lowest were obtained in summer, coinciding with the period of low waters and the greatest influence from the baseflow. This behaviour suggests a greater nutrient mobilization during the wet period (October–March), which is consistent with a predominant diffuse source of

nitrate and phosphorus (Abbott et al., 2018; Dupas et al., 2019; Garzon-Vidueira et al., 2020). Thus, wet periods increase the connectivity between nutrient sources and the stream network (Rodríguez-Blanco et al., 2013; 2015), promoting the transfer of nutrients. Corbeira is a transport-limited catchment, where the nutrient fluxes are controlled by the hydrology, as the flow is the main driver of nutrient transport, since it controls the connectivity between the source (e.g., soils) and the stream. Nitrate is mainly transported in subsurface flow (Rodríguez-Blanco et al., 2015) while P (mainly associated with sediment) in surface runoff (Rodríguez-Blanco et al., 2013).

The results showed the lack of consistent trends of N and P over time, although a decreasing trend appears for N loads, mainly linked to the reduction of nitrate transport during autumn and spring (Table 2), although it might also be linked to a decline in agricultural activities in the catchment, which leads to a decrease in the application of manure and fertilisers—ideally in the autumn and spring. Forest plantation cutting cycles should also be considered since forest cut decrease nutrient uptake, making more nutrients available for leaching into water courses (Thompson et al., 2009). Forest roads, especially when intercepting the stream can be an important source of nutrients associated (mainly P) with sediments in plantation areas. Phosphorus points to an upward trend, mainly in winter, which could be related to the positive flow trend in the study area (Rodríguez-Blanco et al., 2020). An increase in discharge levels

translates into a greater flow velocity and movement of sediments, which is essential for the transport of P in the catchment since it is intrinsically related to the particulate fraction. A similar pattern was observed in another mixed land use catchment (Minaudo et al., 2015; Bol et al., 2018), demonstrating the significance of suspended sediment in the dynamics of P. The results also show an increase in the nutrient concentrations, despite the fact that discharge and nutrient load decrease in the summer, meaning that the flow is being enriched owing to lesser dilution. As has been reported in several other catchments with forestry and agricultural uses (e.g., Abbott et al., 2018), this could be indicative of surplus nutrients applied to the soil being available for export to water bodies by drainage or runoff.

Despite the decline in population and reduced agricultural activities in the catchment, only a limited improvement in nitrate concentrations was observed. This may be due to the potentially long transit time in the catchment, so reducing non-point source nutrients may take decades to affect the water chemistry of rivers (Fovet et al., 2015; Dupas et al., 2017). The increase in winter flow could also counteract the effect of the reduction in the number of people, so that no trend at annual scale will be detected.

CONCLUDING REMARKS

The concentrations of N and P measured in the catchment are relatively low, which shows that agricultural practices and the forest plantation management in the catchment do not jeopardise (for the moment) the water quality, although the catchment nutrient reference levels were widely exceeded. The variability of export fluxes is high, despite their “natural nature,” due to the fact that connectivity between the nutrient source area and the stream is dependent on flow conditions. A lack of consistent trends of N and P over time was observed, but the nutrients analysed behaved differently. Thus, N appeared to show a downward trend, mainly associated with declining transport in autumn and spring. Phosphorus showed an upward trend in winter linked to a greater flow and sediment transfer. As a result, any increase in erosion and runoff will almost certainly result in an increase phosphorus load in the study area.

Despite the decrease in population and abandonment of agricultural land in the catchment, the concentrations of

nitrate do not show a sizable reduction, which could be indicative of surplus nutrients provided to the soil being available for export to water bodies *via* drainage or runoff. As a result, a decrease in inputs from various sources does not result in rapid improvement in riverine water quality.

DATA AVAILABILITY STATEMENT

The datasets presented in this article are not readily available because the data are part of a large database. Requests to access the datasets should be directed to maria.luz.rodriguez.blanco@uvigo.es.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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CONFLICT OF INTEREST

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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