



# Approach to the Water Quality in a Catchment Framed in a Rural-Agroforestry Landscape Slightly Degraded by the Agro-Livestock Activity

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## Abstract

*The headwater streams constitute landscapes with their own entity and are strongly influenced by their environment. They have a large impact on health and integrity, both for water quality and wildlife downstream. Studies on water quality from atlantics agroforestry catchments are scarce. Knowledge about water quality in agroforestry headwater catchments is important for assessing downstream effects and as a baseline for net impacts of land-use change. We analyzed physicochemical water variables of a headwater stream framed in a rural-agroforestry catchment with very little agricultural area, low livestock density and very little human population in NW Spain. Stream water samples were collected at the catchment outlet at approximately biweekly intervals over three years. All water samples were analyzed for the following quality parameters: pH, water temperature (T), electrical conductivity (EC), dissolved oxygen (DO), chemical oxygen demand (COD), major cations (Ca, Mg, Na, K), anions (Cl, SO<sub>4</sub>), nutrients [total dissolved carbon (TDC), dissolved organic carbon (DOC), nitrites nitrogen (NO<sub>2</sub>-N), nitrate nitrogen (NO<sub>3</sub>-N), ammonium nitrogen, Kjeldahl nitrogen (KN), total nitrogen (TN), dissolved, particulate and total phosphorus (DP, PP, TP)], and suspended solids (SS). Discharge was also measured. The mean concentrations of major anions, cations and different forms of carbon, nitrogen and phosphorus were rather low compared to global "average" values. Overall, the mean values of the main physicochemical water quality indicators offers similar values to those found in other rural catchment in humid temperate climates with low agricultural activity and demography, although such concentrations could have been underestimated as they mostly correspond to regular sampling and therefore ignore the influence of rainfall-runoff events.*

*Keywords: water quality, catchment, agroforestry, land-use*

## Introduction

Water quality plays a significant role in public health, habitat protection, agriculture, fisheries, and industry [1]. The degradation of fresh water quality is a global issue, affecting their physicochemical properties, biodiversity, and economic activities. Water composition in rivers is fundamentally dependent on the natural and anthropogenic characteristics of the surrounding landscapes, as well as on the biogeochemical processes that occur in rivers [2, 3]. Headwater streams are critical areas for organic matter and nutrient dynamics and, in pristine state, they host an important component of biodiversity in catchments and play a key role in ecosystem services delivery [4,5]. Headwater systems are also important for understanding and protecting downstream ecosystems, because they have a considerable influence over the whole hydrographical network [6], but they are highly vulnerable to a host of human impacts Agriculture is a mayor disturbing factor of aquatic systems [7]., Headwater streams, especially those well connected to agricultural land, are more vulnerable to the inputs of sediment, nutrients, organic matter and other pollutants than large rivers because their low discharge [4,8]. For this reason, diagnosis of the headwater streams is a key requirement to assess their role within the basin river network, and if necessary, mitigate the harmful impacts on them.

The current research focused on assessing the physicochemical water quality of a headwater stream (Corbeira stream) linked to an agroforestry catchment with low contribution of stressors derived from both the agro-livestock sector and the human population. The Corbeira stream belongs to the Mero river basin, which is included in the Coastal Galicia Hydrographic District (NW of Spain). The particularity of this stream is that it is located upstream of the Abegondo-Cecebre reservoir, which serves as a settling basin and it is cataloged as Special Area of Conservation under Natura 2000. In addition to its ecological value, this reservoir stands out for being a source of drinking water supply to a population of around 450,000 inhabitants. Knowledge of the impact of agro-livestock on Corbeira stream quality is crucial for a proper protection strategy for this area.

## Material and Methods

### Description of the Study Area

The Corbeira stream (catchment area of 16 km<sup>2</sup>) is a perennial stream located in the A Coruña Province, NW Spain. The climate is oceanic and the hydrological regime is mainly pluvial-oceanic. Stream discharge (mean annual: 0.20 m<sup>3</sup> s<sup>-1</sup>) is mainly supplied by baseflow [9]. The soils are derived from schist of basic composition [10] and are classified as Umbrisols and Cambisols. The land use consists of commercial forest (65%, mainly eucalyptus plantations), agriculture fields (30%) and impervious areas (5%). Approximately 87% of the agricultural fields comprise grasslands, while the remaining part is devoted to

cultivated land, mostly maize and winter cereals. Agricultural production is structured around the family farm, and the tillage is traditional. The catchment has a small and highly dispersed rural population (about 35 inhabitants km<sup>2</sup>, with the Spanish mean being 93 inhabitants/km<sup>2</sup>), and the stocking density is 0.29 livestock units ha<sup>-1</sup>. Fertilization organic (mainly slurry) and inorganic and liming practices are routinely applied to maintain or improve the agricultural production. The topsoil is characterized by acid pH (4.5-5.6), high organic matter content (4.4 to 10.5%), and silt and silt-loam texture. [11-16].

#### Water sampling and laboratory analysis

Water samples were collected at the catchment outlet at approximately biweekly intervals over a 3-year period, mainly in baseflow conditions. Twenty three water quality physicochemical parameters, including pH, temperature, electrical conductivity, dissolved oxygen (DO), chemical oxygen demand (COD), total dissolved carbon (TDC), dissolved organic carbon (DOC), calcium, magnesium, sodium, potassium, chlorides, sulfates, nitrite nitrogen (NO<sub>2</sub>-N), nitrate nitrogen (NO<sub>3</sub>-N), ammonium (NH<sub>4</sub>), Kjeldahl nitrogen (KN), total nitrogen (TN), dissolved phosphorus (DP), particulate phosphorus (PP), total phosphorus (TP), suspended solids (SS) and discharge were analyzed.

The analytical methods used were as follows: temperature was measured in the field using a glass thermometer. pH, electrical conductivity, and DO were determined on unfiltered samples using standard electrochemical techniques. After samples filtration (0.45 µm), concentrations of Ca, Mg, Na, K, and DP were analyzed by ICP-MS and Cl, SO<sub>4</sub>, NO<sub>2</sub> and NO<sub>3</sub> by capillary electrophoresis while the NH<sub>4</sub> concentrations were measured using an ammonia-selective electrode. NO<sub>2</sub> and NH<sub>4</sub> concentrations were below the detection limit in all cases. The KN concentrations were analyzed by Kjeldahl digestion of unfiltered samples [17]. TP was determined for colorimetry [18] after digesting unfiltered water samples with sulfuric acid solution and potassium persulfate [17]. Particulate P was estimated as the difference between TP and DP. COD was determined by volumetry. An gravimetric method was used for calculation of SS. DOC after sample filtration was analyzed using a Shimadzu TOC analyzer. The DOC concentration was obtained as the difference between total dissolved carbon and dissolved inorganic carbon. The stream water level was measured at the catchment outlet using a differential pressure transducer sensor connected to an automatic sampler as indicated in [9].

#### Statistic analysis

The statistical measures were calculated in order to understand the central tendency of the analyzed parameters. The mean annual flow-weighted nutrient concentrations was estimated. The range of variability was measured by estimating the dispersion in the data by computing the standard deviation and the coefficient of variation (CV).

### Results and Discussion

#### Basic physicochemical variables and discharge

A statistical summary of the physicochemical constituents analyzed in the stream water is shown in Table 1. The values of the basic physicochemical parameters (EC, DO, COD, T) fit within the typical values of non-intensive agricultural catchments as reported by previous studies for this area [19] and also in UK rivers [20]. The mean pH was neutral and ranged from 6.5 to 7.5. The oxygen saturation levels rarely exceeding 100% saturation, that is, the water becomes oversaturated for short periods of time. COD showed mean values indicative of good water quality, although occasionally it reached relatively high values (88 mg/L) coinciding with the highest value of SS which could be attributed to rainfall runoff episodes with the capacity to mobilize materials into the drainage network. The water temperature showed satisfactory values (mean 13°C) and consistent with good oxygenation, being always below the maximum limits allowed for salmonid waters (21.5°C) and for cyprinid waters (28°C) [21] as corresponds to uncontaminated waters.

The mean ion concentrations generally were low, as reflected in the low values of electrical conductivity (ranged from 90 to 117 µS cm<sup>-1</sup>), which indicates a weak mineralization of the stream water, characteristic of unpolluted natural catchments and with moderate or low solubility of soil materials and geological substrate. The salinity is clearly dominated by Cl and Na concentrations (31% and 23% of the total salinity, respectively), which can be attributed to the spray from the sea (oceanic influence) due to the catchment proximity to the sea (about 30 km), followed by the concentrations of NO<sub>3</sub> (10.5%) and SO<sub>4</sub> (9.9%). Basic divalent cations, which were present in low and similar concentrations had limited contributions to the total salinity (Ca: 7.6%, Mg: 5%) in accordance with the soft character of the region waters [22]. Much less significant is the contribution of K, which only account for 1.4%.

Tab. 1. Mean and variability of physicochemical parameters in the studied water stream.

Water quality parameters	Units	Mean ± standard deviation				
		Mean ± standard deviation	Minimum	Maximum	Range	CV (%)
Discharge	m <sup>3</sup> s <sup>-1</sup>	0.23 ± 0.19	0.02	1.20	1.18	82.61
pH	Unit pH	7 ± 0.19	6.5	7.50	1	2.71
T	°C	12.19 ± 3.13	6	18	12	25.70
EC	µS cm <sup>-1</sup>	101 ± 5.02	90	117.4	27	4.97
DO	%	97.60 ± 2.63	88	102	14	2.70
COD	mg L <sup>-1</sup>	15.6 ± 15.5	0.70	89	88.3	99.40
TDC	mg L <sup>-1</sup>	5.54 ± 1.08	2.77	10.19	7.42	19.49
DOC	mg L <sup>-1</sup>	2.06 ± 0.95	0.60	6.80	6.2	46.12
Ca	mg L <sup>-1</sup>	3.65 ± 0.58	0.70	5.14	4.44	15.89
Mg	mg L <sup>-1</sup>	2.43 ± 0.19	2.10	3	0.9	7.82
Na	mg L <sup>-1</sup>	11.0 ± 1.15	8.11	16	7.89	10.45
K	mg L <sup>-1</sup>	0.68 ± 0.42	0.34	3.78	3.44	61.76
Cl	mg L <sup>-1</sup>	15.00 ± 0.90	12.63	17.64	5.01	6.00
SO <sub>4</sub>	mg L <sup>-1</sup>	4.74 ± 0.75	3.25	7.66	4.41	15.82
NO <sub>3</sub> -N	mg L <sup>-1</sup>	1.14 ± 0.30	0.59	2.66	2.07	26.32
KN	mg L <sup>-1</sup>	0.28 ± 0.47	0.03	4.34	4.31	167.86
TN	mg L <sup>-1</sup>	1.42 ± 0.65	0.72	5.85	5.13	45.77
DP	µg L <sup>-1</sup>	9.07 ± 5.48	1.00	33.2	32.2	60.42
PP	µg L <sup>-1</sup>	22.78 ± 45.86	2.96	433.17	430.21	201.32
TP	µg L <sup>-1</sup>	31.86 ± 46.85	4.68	444.32	439.64	147.05
SS	mg L <sup>-1</sup>	17.32 ± 56.97	0.50	511	510.5	328.93

The discharge is presented as one of the most fluctuating parameters during this study, oscillating between 0.02 and 1.20 m<sup>3</sup> s<sup>-1</sup>, with an annual mean value of 0.23 m<sup>3</sup> s<sup>-1</sup>. The mean discharge-weighted SS concentration was 17 mg L<sup>-1</sup>, a value very similar to that calculated [16] for this catchment based on a 12-year dataset from high resolution monitoring. The SS concentration was characterized by strong variability (CV = 329%) during the monitoring period (table 1). Like other authors [23] in order to assess the impact of SS in the stream, SS concentrations were compared with the repealed EU Freshwater Fish Directive (FFD) [24] target (25 mg L<sup>-1</sup>) due to the absence of explicit thresholds within the Water Framework Directive [25, 26]. Concentrations remained below 25 mg L<sup>-1</sup> for the 94% of the water samples, so that the FFD threshold was only exceeded by 6% of the samples, coinciding with rainfall-runoff events.

### Carbon, N and P concentrations

Table I shows a statistical summary of the carbon, nitrogen and phosphorus analyzed in the Corbeira stream. The mean TDC concentration accounted for 5.54 mg L<sup>-1</sup> with similar proportions of organic and inorganic carbon. DOC values fluctuated between 0.60 and 6.80 mg L<sup>-1</sup>, with a mean of 2.06 mg L<sup>-1</sup>. This value is almost an order of magnitude higher than the levels determined for natural waters in Galicia [22]. However, is very close to that reported by [27] for Corbeira stream under baseflow conditions, and it is typical for non-intensive agricultural catchments [20].

With respect to TN, the mean annual flow-weighted NT concentration reached 1.42 mg L<sup>-1</sup> and was dominated by NO<sub>3</sub>-N (1.14 mg L<sup>-1</sup> of highly bioavailable N; 80.3% of TN), with KN (0.27 mg L<sup>-1</sup>) only contributing to 19.7% of the TN. These low N levels are characteristic of streams draining rural catchments of mainly forest use, with low agro-livestock development, and low N deposition, as occurs in the study catchment [11, 19, 28]. In fact, the Corbeira stream showed considerably lower concentrations than those obtained in the same region for the Abelar agricultural catchment whose soils supported massive slurry applications [29]. Compared to the nitrates limits stipulated by the Drinking Water Directive [30], our study area always exhibited noticeably lower NO<sub>3</sub>-N concentrations than the allowed limit in drinking water (11.2 mg L<sup>-1</sup> NO<sub>3</sub>-N or 50 mg L<sup>-1</sup> NO<sub>3</sub>), in spite of that some temporal variability in the NO<sub>3</sub>-N levels was observed during the study period (range from 0.59 to 2.66 mg L<sup>-1</sup>). However, the NO<sub>3</sub>-N levels for rivers draining catchments with low anthropic pressure in the same region (0.2-0.7 mg L<sup>-1</sup> NO<sub>3</sub>-N), as well as the global reference values (mean 0.1 mg L<sup>-1</sup>) for pristine rivers [31]) were exceeded, suggesting some N enrichment in the Corbeira stream water, probably as a consequence of the agricultural practices in the catchment. In addition, in all the water samples, the TN concentration, considered by some authors [32] as a more appropriate criterion than dissolved inorganic N concentration for preventing impacts by inorganic nitrogen pollution in aquatic environment, exceeded the critical limit over which potential risk exists for water eutrophication (0.5-1.0 mg TN L<sup>-1</sup>), but only 10% of the samples exceeded the threshold of 2 mg TN L<sup>-1</sup> identified in the European Nitrogen Assessment [33] as an appropriate target for the delivery of good ecological status for European waters. These findings indicate that control of N concentrations will be needed to improve the ecological status of the Corbeira stream.

In relation to P, the mean annual flow-weighted concentrations were 31.86, 22.78, and 9.07 µg L<sup>-1</sup> for TP, PP, and DP, respectively, showing a strong range of variation over the study period, especially particulate fraction (2.96-433.17 µg L<sup>-1</sup>), in part reflecting the high variability in SS levels (table 1). The maximum TP and PP values occurred at the same time as the maximum SS concentration (511 mg L<sup>-1</sup>) coinciding with an erosive rainfall event, which activated sediment sources close to the stream (rills and ephemeral gullies developed in an agricultural field next to the stream) producing a high SS concentration [28, 34]. Therefore, the highest TP and PP concentrations can be attributed to the rapid mobilization and arrival of the sediment adsorbed P to the stream.

The mean P concentrations are low compared to those reported for other small streams draining low-intensity agricultural catchments and the median European levels [35], but the Corbeira mean concentrations are higher when they are compared to DP background values (2 µg L<sup>-1</sup>) of natural waters in Galicia (NW Spain), suggesting a P enrichment in the stream water. Despite the amplitude in the range of concentrations of the different forms of P, only 10% and 2% of the samples exceeded the value of 50 µg L<sup>-1</sup> for TP and 20 µg L<sup>-1</sup> for DP, respectively, threshold considered to pose a threat for freshwaters eutrophication (50 µg L<sup>-1</sup> for TP or 20 µg L<sup>-1</sup> for DP) [36]. These results indicating that only occasionally the P can negatively affect the water quality of the Corbeira stream. However, it is likely that these results may be underestimated in a study based only on data from regular sampling. Previous studies carried out on this same catchment showed that runoff events can compromise the stream water quality during short time intervals [28, 37].

### Conclusions

Overall, the mean values of the main physicochemical water quality indicators offers similar values to those found in other rural catchment in humid temperate climates with low agricultural activity and demography, and similar to the median European levels. Highlight that only occasionally N and P concentrations can negatively affect the water quality of the Corbeira stream. However the nutrient concentrations could have been underestimated as they mostly correspond to regular sampling and therefore ignore the influence of rainfall-runoff events.

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