



N and P behaviour in alluvial aquifers and in the soil solution of their catchment areas: How land use and the physical environment contribute to diffuse pollution



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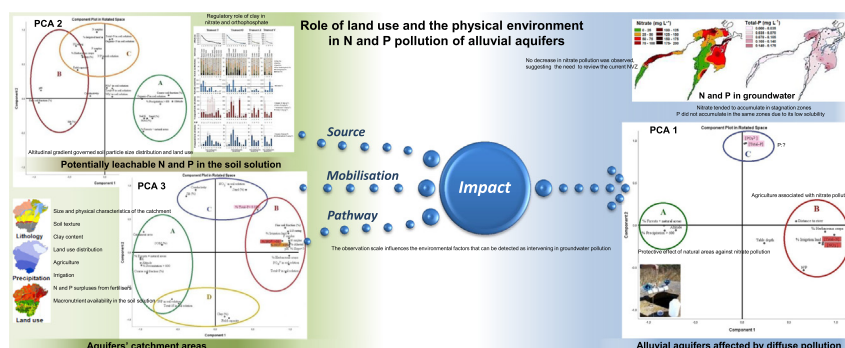
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HIGHLIGHTS

- Designated NVZ did not meet expectations of significantly improving water quality.
- Due to its low solubility P did not accumulate in the same stagnation zones as NO₃.
- The regulatory role of clay on NO₃ and PO₄³⁻ in the soil solution was verified.
- The intensive agricultural pressure on sandy loam soils favoured P-leaching.
- N and P diffuse pollution were analysed from an aquifer–soil–catchment perspective.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 February 2021

Received in revised form 8 July 2021

Accepted 27 August 2021

Available online 1 September 2021

Editor: Christian Herrera

Keywords:

Nitrate
Orthophosphate
N-surplus
P-surplus
Nitrate Vulnerable Zones
PCA

ABSTRACT

The role of land use and the physical environment in N and P pollution of alluvial aquifers was analysed at three levels of information: (1) aquifer (N and P in groundwater), (2) soil transect (potentially leachable N and P in the soil solution) and (3) aquifer's catchment area. The study was carried out in the Oja and Tirón alluvial aquifers and their catchment areas (northern Spain).

Nitrate was the dominant N form, both in groundwater and the soil solution of aquifers' catchment areas. Orthophosphate and organic-P were the codominant P forms in the aquifers. Orthophosphate was the main form in the soil solution.

During the period 2005–2017 no significant decrease in nitrate pollution was observed, suggesting the need to review current Nitrate Vulnerable Zone (NVZ) designations. Since nitrate is highly mobile, it tended to accumulate in stagnation zones at the lower reaches of the aquifers. P did not accumulate in the same zones due to its low solubility.

Principal component analyses (PCAs) of the aquifers, soil transects and aquifers' catchment areas revealed that the observation scale influences the environmental factors that can be detected as intervening in groundwater pollution. At the aquifer scale, links were found between nitrates and land use, topographic, hydrogeological and climatic factors. The protective effect of natural areas against nitrate pollution was noteworthy, while agriculture was associated with pollution. At the soil transect scale, an altitudinal gradient governed soil particle size distribution and land use, separating mountain forest soils from agricultural soils. The negative relationship between clay contents vs. nitrate and orthophosphate in the soil solution pointed to a regulatory role of clay. At the

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catchment scale, the size and physical characteristics of the catchments and land use distribution determined macronutrient availability in the soil solution and, in turn, N and P groundwater distribution.

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1. Introduction

Diffuse source fluxes of macronutrients in the vadose zone, groundwaters, and at their interface with surface waters affect the quality of drinking water, the health of aquatic ecosystems and global change. These are critical issues covered in the sixth goal of the 2030 Agenda for Sustainable Development to ensure the availability and sustainable management of water and sanitation for all (Economic and Social Council of the United Nations, 2018). To ensure a more effective restoration and protection of water quality, a better understanding is needed of the hydrogeochemical, ecological and anthropogenic factors affecting diffuse pollution by nitrogen (N) and phosphorus (P) compounds generated by human activities.

N and P are macronutrients that play essential roles for all living organisms. They are the main growth-limiting nutrients in aquatic ecosystems, but their concentrations can be greatly modified by human action. Excess N and P inputs lead to the eutrophication of water bodies, while high levels of nitrate in drinking water are considered dangerous to human health (European Environment Agency, 2017; Sutton et al., 2011).

Agricultural diffuse loss is currently the dominant source of pollution with N and P in most of the European Union (EU), partly as a result of the efforts made to reduce point source pollution during the past few decades (by improving wastewater treatment systems; European Environment Agency, 2016). More specifically, most groundwater pollution by N and P comes from diffuse sources, while surface water pollution is still attributable to both point and diffuse sources (European Environment Agency, 2016). In the EU, the estimates of agricultural diffuse losses of N and P range from about 0–30 kg N ha⁻¹ and 0–1 kg P ha⁻¹, while the background losses are around 1–2 kg N ha⁻¹ and 0.1 kg P ha⁻¹ (European Environment Agency, 2005). The European Environment Agency (2017) has warned that EU countries still maintain a surplus of N unacceptable in agricultural land, which is reflected in increasing N-leaching affecting nitrate levels in many EU waters. Although less studied than N, it has also been documented that the high amounts of P applied for many years in EU countries have increased P-leaching in sandy soils (Crouzet et al., 1999).

The limit values of N and P established to reduce and prevent eutrophication vary considerably across the EU counties, suggesting that setting consensus criteria is not an easy task. A thorough review of the nutrient criteria for surface waters under the European Water Framework Directive by Poikane et al. (2019) reported values for good/moderate threshold concentrations of total nitrogen (total-N) varying from 0.25 to 35 mg L⁻¹ and of total phosphorous (total-P) from 0.008 to 0.660 mg L⁻¹ for EU rivers. These authors found a clear influence of the relatively widespread use of the concentration of 11.3 mg L⁻¹ as limit value for total-N in most EU countries, probably attributable to the nitrate guideline value fixed by the Nitrates Directive (91/676/EEC; Council of the European Communities, 1991). The Nitrates Directive establishes that both surface freshwater and groundwater are affected by nitrate pollution when its concentration exceeds 50 mg L⁻¹ (=11.3 mg N L⁻¹). The directive requires areas of land that drain into waters polluted by nitrates to be designated as Nitrate Vulnerable Zones (NVZs). In NVZs, action programmes must be implemented limiting N-fertilization and animal manure application to prevent nitrate leaching and runoff. Within the range of 25–50 mg L⁻¹ of nitrate, water is considered at risk of becoming polluted if no protective measures are taken (European Commission, 2000). Unlike N, a guideline limit value for P in groundwater remains to be established,

perhaps because the transport of P is not as well understood as that of N (Hinsby et al., 2019). Until now, the threshold value of 0.035 mg L⁻¹ of total-P has been widely used in the scientific literature for the transition from mesotrophic to eutrophic state (OECD, 1982) in temperate zones.

N and P in water are generally present in soluble inorganic forms, as well as in soluble and particulate organic forms. Nitrate is usually the dominant form of N, being very soluble and highly mobile. Nitrate leaching depends on natural factors such as soil and vadose zone characteristics and climate, as well as human factors such as crop type, irrigation method and doses and the utilisation regime of fertilisers and manure (Arauzo and Valladolid, 2013). Unlike N, P does not move quickly through soil. The application of P to soil (as fertiliser, manure or in sewage effluent) results in an immediate rise in the level of water-soluble P, which declines rapidly with time due to adsorption and precipitation reactions taking place in the soil (Yaron et al., 1996). These processes mainly depend on the soil texture and soil hydraulic properties. Therefore, the actual level of water-soluble P in soil is usually very low and the movement of P through the soil is very restricted, with runoff being considered the main route for phosphate transport to surface waters (Yaron et al., 1996). Even so, it has been documented that the application of high amounts of P can result in soils saturated with P and hence significantly increased P-leaching through preferential flow in coarse/sandy soils (Crouzet et al., 1999; Platineau et al., 2021; Yaron et al., 1996) and cracked heavy-clay soils (Paltineau, 2001). There are, therefore, a variety of biogeochemical processes involved in the transport of N and P compounds of the soil solution, via leaching and subsurface runoff, until reaching the receptor aquifer.

Aquifers exposed to pollutants from diffuse sources present a greater or lesser level of pollution depending on their degree of intrinsic vulnerability. According to Witkowski et al. (2007), intrinsic vulnerability is based on an assessment of natural hydrogeological and climatic attributes, whereas specific vulnerability is mostly assessed in terms of the risk of the groundwater system becoming exposed to contaminant loading. Among all types of aquifers, alluvial aquifers are probably the ones with the highest degree of intrinsic and specific vulnerability (Arauzo, 2017; Arauzo et al., 2011, 2019). This is explained by the combination of certain risk factors inherent to alluvial aquifers, including a shallow water table, abundant sand and gravel in alluvial deposits and intensive agriculture (typically undertaken on lower terraces and floodplains along riverbanks).

All these considerations highlight the need to analyse in depth the role of land use and the physical environment (hydrology, soils, topography, geology and weather conditions) in the distribution of N and P compounds in alluvial aquifers. This task requires an interdisciplinary approach, as diffuse N and P pollution of groundwater occurs at different organisational levels that involve a variety of interrelated variables and scales. To do this, we used Principal Component Analysis (PCA) applied at different spatial scales, looking for relationships between variables. We focused on three scales that provide essential levels of information: (1) aquifer scale (N and P in groundwater), (2) soil scale (potentially leachable N and P in the soil solution) and (3) catchment scale (role of land use and the physical environment in the aquifer's catchment area). For this purpose, a study area comprising two alluvial aquifers (the Oja Alluvial Aquifer and the Tirón Alluvial Aquifer; north of Spain) and their catchment areas was selected. These aquifers are recognised examples of water bodies that have been chronically affected by pollution from diffuse sources (Arauzo et al., 2011) but only the Oja aquifer has a designated NVZ. Intensive agriculture is widely

implanted in the area, while forests and natural areas are preserved at the headwaters. This provides a variety of environmental scenarios to analyse diffuse source fluxes of macronutrients in the vadose zone and groundwaters in the context of the aquifers' catchment areas.

Summarizing, the main objectives of this study are as follows: (1) to determine if there has been any significant decrease in nitrate pollution in the Oja and Tirón alluvial aquifers since the 2006 NVZ designation (does the designated NVZ meet expectations?); (2) to analyse and compare the chemical forms of N and P in groundwater of both aquifers, as well as their spatial distribution and seasonality; (3) to analyse and compare the chemical N and P forms in the soil solution (as potential leachable pollutants into groundwater) and their distribution along altitudinal soil transects (representing different soils and land uses of the aquifers' catchment areas); (4) to determine the role of land use and the physical environment on the N and P distribution, applying PCAs to identify links between environmental variables under a cross-scale perspective (aquifers–soil transects–aquifers' catchment areas). These objectives are in line with the sixth goal of the 2030 Agenda for Sustainable Development (Economic and Social Council of the United Nations, 2018).

2. Material and methods

2.1. Study area

The study area comprises the Oja Alluvial Aquifer, the Tirón Alluvial Aquifer and the catchment areas that drain into them (Fig. 1). It has a

total extension of 1397 km² that is located on the right bank of the upper Ebro River basin (north of Spain). The general climate is continental–Mediterranean, although a mountain climate dominates in the headwaters of the selected catchments (which belong to the Iberian System; Fig. 1). Administratively, the territory depends on the Spanish regions of La Rioja and Castilla y León. The regional Governments have the competence to designate NVZs and to implement the corresponding action programmes in the area.

Recharge of the Oja and Tirón aquifers depends on the infiltration from precipitation and irrigation returns from their respective catchment areas. Discharge occurs towards the rivers and by pumping extractions. The dynamics of both aquifers is closely linked to that of their associated rivers, which can be influent or effluent at different segments along the watercourse with their alluvial deposits, depending on the seasonal water inputs and extractions for irrigation (Arauzo et al., 2011). The Oja aquifer is hydraulically linked to the Oja and Tirón rivers (aquifer's catchment area C-1), the Zamaca stream (aquifer's catchment area C-2) and the Valpierre stream (aquifer's catchment area C-3) (Fig. 1). The Oja and Tirón rivers meet together 9 km before draining into the Ebro River. The Zamaca and the Valpierre streams are minor tributaries of the Ebro River and both remain permanently dry in their mid–upper sections. Besides nitrate pollution, the Oja aquifer is strongly affected by groundwater over–extraction during the peak spring and summer irrigation demand periods (Arauzo et al., 2011). The Tirón aquifer is hydraulically linked to the mid–upper reaches of the Tirón River (aquifer's catchment area C-1'; Fig. 1). As a whole, the Oja–Tirón fluvio–alluvial system discharges into the River Ebro a water volume

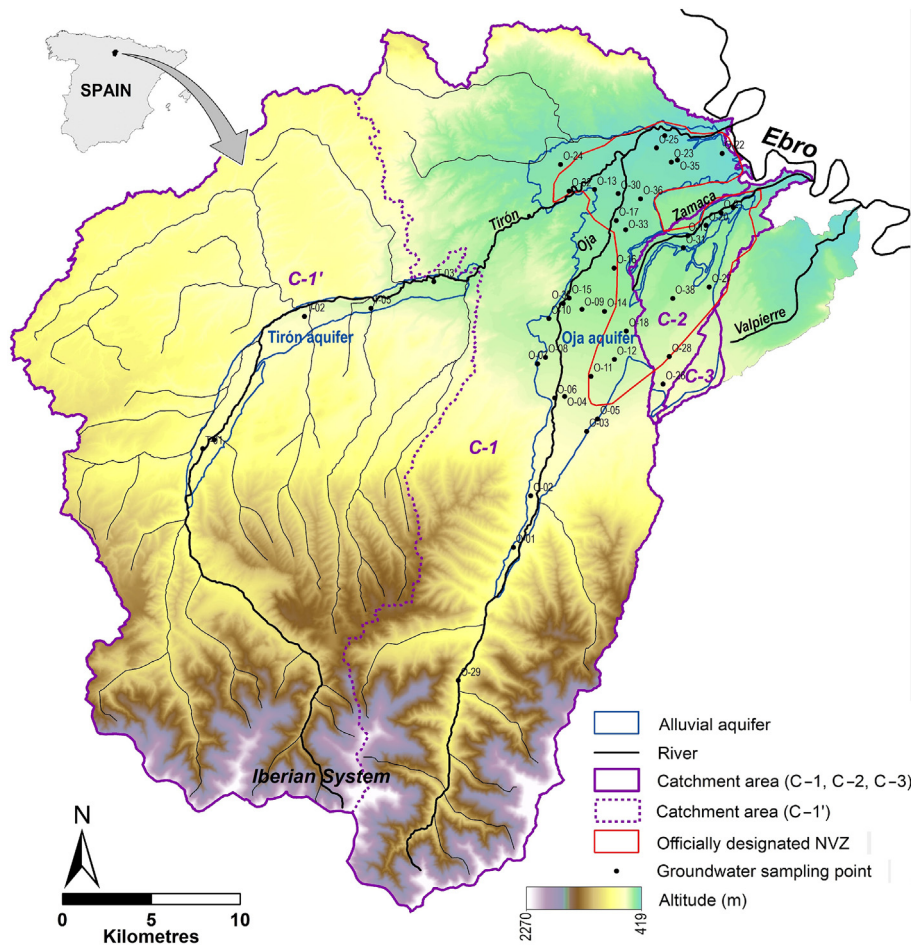


Fig. 1. Study area, which includes the Oja Alluvial Aquifer, the Tirón Alluvial Aquifer and their respective catchment areas (C-1, C-2 and C-3, for the Oja aquifer, and C-1', for the Tirón aquifer). The location of the groundwater sampling points (O-01 to O-39 in the Oja aquifer and T-01 to T-05 in the Tirón aquifer), the elevation map and the NVZ designated by the Spanish Regional Government are shown.

of around 240 hm³ year⁻¹ and a nitrogen load of around 2.4 kt year⁻¹ (Arauzo et al., 2011).

N and P contributions from municipal sewage and industrial effluents in the area are not significant, since they are mainly channelled to a central wastewater treatment plant that empties into the River Ebro outside the study area (Gobierno de La Rioja, 2010). This made it easier to solely focus on diffuse pollution processes.

The main characteristics of the aquifers and their catchment areas (C-1, C-2 and C-3 for the Oja aquifer; C-1' for the Tirón aquifer) are shown in Tables 1 and 2. The maps of lithology, annual precipitation and land use are shown in Fig. 2. The prevailing soil types in the area are fluvisols, cambisols and regosols according to the FAO classification system (FAO, 2006a), mostly with slightly alkaline pH (from 7.2 to 7.9) except in the headwater areas of the rivers Oja and Tirón (from 4.1 to 5.9).

To date, an area of 94 km² has been designated as an NVZ on the Oja aquifer by La Rioja Government (Gobierno de la Rioja, 2006; Fig. 1 and Table 2), in which action programmes to restore groundwater quality are being implemented. The designated area coincides with the most polluted areas of the Oja aquifer (Arauzo et al., 2011), suggesting that this was the criterion for the designation. No designations have been made in the Tirón aquifer.

2.2. Groundwater and soil sampling campaigns

Four sampling campaigns were conducted in the Oja and Tirón alluvial aquifers during April and October of 2013 and 2017 to analyse the contents and distribution of N and P compounds in groundwater. The four resulting datasets, together with those from another previous four campaigns (in April and October of 2005 and 2009; Arauzo et al., 2011), were used to determine if there had been any significant improvement in groundwater quality during the 2005–2017 period (note that the existing NVZ in the area was designated in 2006;

Gobierno de la Rioja, 2006). A total of eight datasets were therefore analysed, corresponding to four years (2005, 2009, 2013 and 2017) and two campaigns each year (spring and autumn). Early spring (April) and autumn (October) periods were selected because they correspond to when the depth of the water table reaches its minimum and maximum annual levels, respectively, which in turn correspond to when groundwater nitrate pollution presents its annual lowest and highest values (Arauzo et al., 2006, 2011).

At each groundwater sampling campaign, 44 sampling points (mainly irrigation wells) were sampled. Sampling points were labelled from O1 to O39 in the Oja aquifer and from T1 to T5 in the Tirón aquifer (Fig. 1). Subsurface groundwater samples (1 m depth) were collected using a 2.5-litre Wildco Beta Plus Water Bottle (Forestry Suppliers; Inc.; Jackson; Mississippi; USA). The depth of the water table was measured using a Nordmeyer water level indicator (Nordmeyer, Overveen, The Netherlands). In situ subsurface measurements of dissolved oxygen, pH, conductivity and temperature of groundwater were performed using a YSI 556 Multi-Probe System (YSI Inc., Yellow Springs, Ohio, USA).

In addition, a soil sampling campaign was carried out during April–May 2017 to analyse and compare the chemical N and P forms in the soil solution as potential leachable pollutants into groundwater. For this, soil samples were collected at 28 sampling points distributed along four altitudinal transects (Fig. 3) that represented the different soils and land uses of the study area. The transects were arranged parallel to the rivers Tirón and Oja and the streams Zamaca and Valpierre, and were designated as Transect T, Transect O, Transect Z and Transect V, respectively. Two replicate topsoil samples were collected at a depth of 0–20 cm from each soil sampling point. To adequately estimate the degree of stoniness, 3–10 kg of soil per sample were taken (depending on the abundance of coarse elements). Two in situ measurements of soil hydraulic conductivity (K) were performed at the soil surface of each sampling point using a hand-held tension Mini Disk Infiltrometer (Decagon Devices, Pullman Washington, USA; Decagon Devices, 2016). The Mini Disk Infiltrometer measures the unsaturated hydraulic conductivity at different applied tensions (adjustable suction from 0.5 to 7 cm). Infiltrating water under a tension prevents the filling of the macropores and gives a hydraulic conductivity characteristic of the soil matrix that is less spatially variable (Everst and Kanwar, 1993).

2.3. Physical analysis of the soils

The most common subdivision of soil granulometry into classes is the fine-earth fraction (clay, silt and sand) and the coarse fraction (fine, medium and coarse gravel and stones). According to this classification, the following particle size fractions were measured on the soil samples: clay ($\emptyset \leq 0.002$ mm), silt ($0.002 \leq \emptyset < 0.02$ mm), sand ($0.02 \leq \emptyset < 2$ mm), fine-medium gravel ($2 \leq \emptyset < 20$ mm), coarse gravel ($20 \leq \emptyset < 60$ mm) and stones ($\emptyset \geq 60$ mm). Soil samples were previously air-dried and sieved to separate and weigh the fine-earth fraction and the coarse fraction. The sieving and sedimentation method (ISO 11277:1998) was used for determining the particle size distribution of the fine-earth fraction. Soil texture was determined by the relative abundance of the three particle size classes of the fine-earth fraction. The particle size distribution of the coarse fraction was determined according to FAO (2006b) guidelines. Estimation of field capacity was based on soil texture and organic matter (USDA, 2018).

2.4. Chemical analysis of groundwater and soils

Spectrophotometric determinations of total-N (Koroleff digestion with peroxodisulphate and detection with 2,6-dimethylphenol method according to EN ISO 11905-1), nitrate (2,6-dimethylphenol method according to ISO 7890-1-2-1986), ammonium (indophenol blue method according to ISO 7150-1), nitrite (diazotisation method according to ISO 26777), total-P and orthophosphate (phosphomolybdenum blue

Table 1
Characteristics of the Oja Alluvial Aquifer and the Tirón Alluvial Aquifer.

Parameter	Oja Alluvial Aquifer	Tirón Alluvial Aquifer
Hydrogeological Domain	Ebro Depression, Ebro River basin (NE of Spain)	Ebro Depression, Ebro River basin (NE of Spain)
Associated rivers	Oja and Tirón rivers; Zamaca and Valpierre streams	Tirón River
Aquifer use	Irrigation; human consumption	Irrigation; human consumption
Extent	Floodplains, alluvial fans, first terrace and lower terraces hydraulically connected to the main aquifer	Floodplain, alluvial fans and first terrace
Lithology	Coarse gravels, polygenic gravels and sands with a variable content of silt	Coarse gravels and sands with a variable content of silt
Geology	Quaternary alluvial deposits	Quaternary alluvial deposits
Underlying geology	Conglomerates, sandstones and Miocene shales	Marls and Miocene gypsums
Degree of confinement	Unconfined	Unconfined
Code of groundwater mass ^a	045	044
Regional Administration	La Rioja	Castilla y León and La Rioja
Total area (km ²)	144	29
Average thickness (m) ^b	12 (saturated thickness: 7.6)	Not assessed
Resources (hm ³ year ⁻¹) ^b	48–57	Not assessed
Total reserves (hm ³) ^b	170	Not assessed

^a Code assigned by the Hydrographic Confederation of the Ebro (Spain's Ministry for the Ecological Transition).

^b Source: Arauzo et al. (2011).

Table 2
Characteristics of the aquifers' catchment areas.

Parameter	Catchment C-1'	Catchment C-1	Catchment C-2	Catchment C-3
Receptor aquifer	Tirón aquifer	Tirón aquifer and main body of Oja aquifer	Eastern zone of Oja aquifer	Extreme eastern zone of Oja aquifer
Associated rivers	Upper-middle reaches of Tirón River	Oja and Tirón Rivers	Zamaca Stream	Upper reaches of Valpierre Stream
Total catchment area (km ²)	675	1295	49	8
Altitude (max.–mean– min.; m)	2039–948–547	2270–911–433	699–567–427	695–639–605
Coverage of lithology types ^a				
Alluvial deposits	16%	19%	81%	85%
Limestones	2%	2%	0%	0%
Sandstones, conglomerates	27%	36%	19%	15%
Marlstones	36%	22%	0%	0%
Clays	3%	2%	0%	0%
Slates, schists	16%	19%	0%	0%
Coverage of slope ranges ^a				
0–5%	31%	35%	82%	92%
5–9%	16%	13%	12%	8%
> 9%	53%	52%	6%	0%
Coverage of precipitation ^a				
600–900 mm y ⁻¹	70%	59%	0%	0%
400–600 mm y ⁻¹	30%	41%	100%	100%
Soil characteristics ^b				
Dominant soil texture	Sandy loam /Loam /Clay loam	Loam /Clay loam	Loam	Loam
Fine soil fraction: Sand–Silt–Clay (%)	34 (14) –26 (1) –40 (6)	42 (14)–37 (8)–21 (10)	42 (3)–33 (2)–25 (4)	38 (10)–20 (8)–42 (2)
Coarse soil fraction (%)	34 (25)	33 (27)	18 (12)	24 (27)
Soil hydraulic conductivity (K; cm s ⁻¹)	0.0004 (0.0003)	0.0004 (0.0003)	0.0002 (0.0001)	0.0002 (0.0000)
Total-N in the soil solution (mg kg ⁻¹)	368 (225)	99 (66)	94 (34)	109 (70)
Total-P in the soil solution (mg kg ⁻¹)	9 (7)	8 (4)	10 (4)	11 (5)
N/P in the soil solution	64 (76)	15 (11)	10 (5)	10 (1)
Coverage of land use types ^{a, c}				
Horticultural crops	0.2%	0.2%	1%	0%
Irrigated herbaceous crops	5%	10%	73%	62%
Rainfed herbaceous crops	40%	34%	7%	34%
Vineyards	0.1%	3%	10%	1%
Meadows, pastures	2%	2%	1%	1%
Forest, natural areas, shrubland, unproductive land	53%	51%	7%	2%
Coverage of irrigated land (sprinkling or furrow) ^a	5%	10%	74%	62%
N and P surpluses ^d				
N surplus (kg N ha ⁻¹ year ⁻¹)	12.2	12.8	25.9	26.0
N surplus per catchment (t N year ⁻¹)	823	1658	127	21
P surplus (kg P ha ⁻¹ year ⁻¹)	0.0	0.1	1.4	1.1
P surplus per catchment (t P year ⁻¹)	0	13	7	1
Coverage of polluted alluvial areas ^e				
[NO ₃] in groundwater >25 mg L ⁻¹	68%	69%	100%	100%
[NO ₃] in groundwater >50 mg L ⁻¹	44%	29%	90%	65%
[Total-P] in groundwater >0.035 mg L ⁻¹	0%	87%	83%	100%
[Total-P] in groundwater >0.2 mg L ⁻¹	0%	0%	0%	0%
Area officially designated as NVZ (km ²)	0	56	38	0

^a Percent coverage relative to the total catchment area.^b Average estimated from the soil transects in Figs. 3 and 5; standard deviations in brackets.^c Extracted from the Crops and Land Use map of Spain (MARM, 2009).^d The mean annual N and P surpluses by crop type (Table 3) were assigned to polygons of the land use map in Fig. 2C.^e Percent coverage relative to the total alluvial area (mean annual values extracted from maps in Fig. 4A, B); NO₃ threshold values according to Council of the European Communities (1991) and European Commission (2000); Total-P threshold values according to OECD (1982) and BOE (1988).

method according to ISO 6876–1986) were performed on groundwater samples. Analyses were carried out using a DR 2800 spectrophotometer (Hach Lange GmbH, Düsseldorf, Germany; Hach Company, 2008). Organic-N in groundwater was estimated as the difference between total-N and the concentrations of soluble inorganic forms (nitrate, nitrite and ammonium) expressed as mg N L⁻¹. Organic-P in groundwater was estimated as the difference between total-P and soluble reactive phosphorus (orthophosphate) expressed as mg P L⁻¹. N and P organic fractions include soluble organic forms such as proteins, amino acids, urea and complex high molecular weight compounds, and particulate organic forms such as bacteria, microalgae, microfungi and detritus (most of them are easily mineralizable labile forms). Small amounts of pyrophosphate (unstable in aqueous solution) and orthophosphate adsorbed onto the organic fraction can be counted as organic-P.

The above-mentioned chemical determinations were also performed on the soil solution samples. For this, soil solution samples were previously prepared from the fine-earth fraction subsamples by water extraction, stirring at 150 rpm for 2 h and centrifugation at 3000 rpm for 10 min. Depending on the degree of soil moisture, the compounds in the soil solution may be available both to be assimilated by plants and to be leached (if field capacity is exceeded). Since we are specifically interested in this latter aspect, extractions of the soil solution were carried out using water as a solvent in order to emulate natural field conditions (precipitation and irrigation).

The nitrogen-to-phosphorus ratio (N/P ratio) was calculated from the total-N and total-P determinations, both for groundwater and soil solution samples. The resultant N/P ratios were compared with the Redfield N/P ratio (Redfield, 1958). Redfield described the relatively

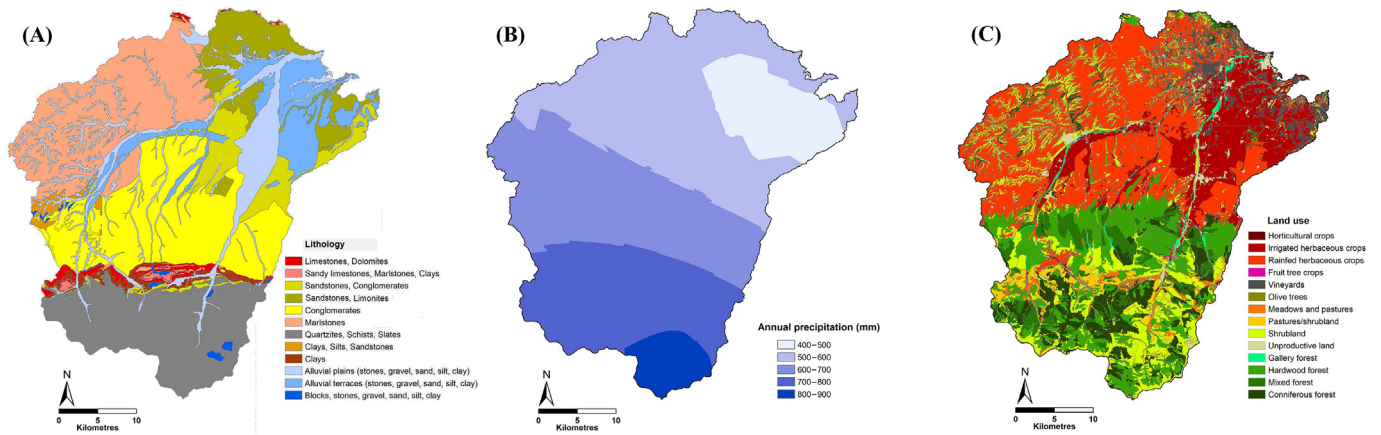


Fig. 2. (A) Lithological map, (B) Annual precipitation map, (C) Land use map.

consistent ratio of nutrients in marine planktonic biomass and found that, on average, planktonic biomass contains N and P in an atomic ratio of 16/1. Biomolecular analyses by *Loladze and Elser (2011)* reinforced Redfield's argument when concluding that the ratio of 16/1 is the N/P ratio of the major biochemical constituents of a microbial cell growing in balance at its maximal capacity, confirming it as one of the most robust stoichiometric patterns in the biosphere. When compared to the Redfield N/P ratio, the variability of the N/P ratio in groundwater

and soil solution samples could help to understand macronutrient fluxes at the catchment scale and determine when, and under what circumstances, N or P act as limiting factors.

Determination of soil organic matter (SOM) was based on the Walkley–Black chromic acid wet oxidation method (*Walkley and Black, 1934*). Soil pH and electrical conductivity were measured in a 1:2.5 soil/water suspension ratio, using a Crison MicropH 2001 meter (Crison Instruments SA, Barcelona, Spain) for the former and a Crison

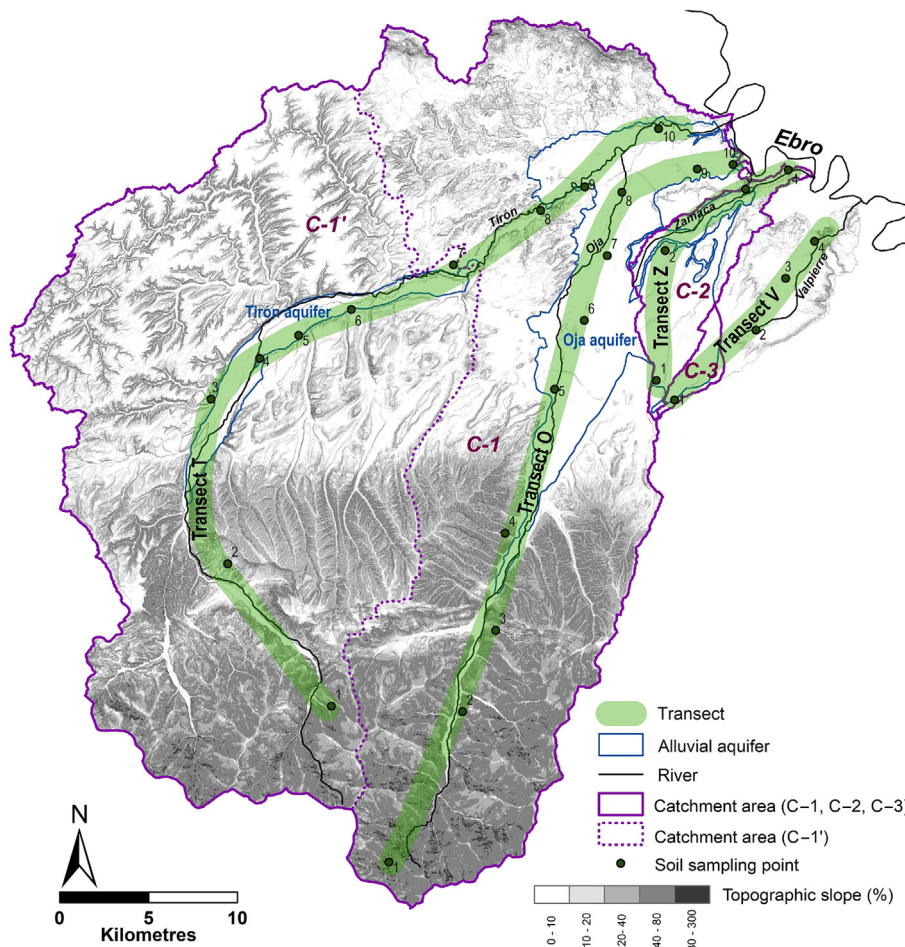


Fig. 3. Location of the soil sampling points along the altitudinal transects T, O, Z and V. The map of topographic slope is shown.

Conductimeter Basic 30 (Crison Instruments SA, Barcelona, Spain) for the second.

2.5. GIS spatial analysis and mapping

The thematic maps were prepared with the Geographic Information System (GIS) ArcGIS 10.3 for Desktop (ESRI, Redlands, CA, USA; ESRI, 2015), using the ETRS89 UTM Zone 30 N coordinate reference system.

The catchments that drain into the Oja and Tirón alluvial aquifers (C-1, C-2 and C-3, and C-1', respectively; Fig. 1) were delineated from a digital elevation model (DEM) of 25 m resolution, using the Hydrology toolset in the Spatial Analyst Toolbox (ArcGIS 10.3). The lowest elevation point of each aquifer was used as pour point for watershed calculation.

The maps of nitrate and total-P concentrations, N/P ratio and water table depth were generated applying kriging interpolation (Spatial Analyst Tools) of data of the 39 sampling points over the Oja aquifer and the five points over the Tirón aquifer (Fig. 1). These maps were generated for both the April and October 2017 sampling campaigns.

The lithological map of the study area (Fig. 2A) was extracted from the digital geological map of Spain (IGME, 2015).

The map of annual precipitation (Fig. 2B) was generated applying kriging interpolation of 22 data points with average annual precipitations obtained from the network of the Spanish Meteorological Agency (Botey et al., 2013).

The land use map of the study area (Fig. 2C) was extracted from the digital version of the Crops and Land Use map of Spain 2000–2009 (MARM, 2009).

The map of topographic slope (Fig. 3) was generated from a DEM of 25 m resolution using the Slope tool (Spatial Analyst Tools).

2.6. N and P surpluses and land use

Identifying the risks of N- and P-losses from agricultural land provides essential support for assessing groundwater vulnerability to pollution from fertilisers. In this task, N and P balances in crops are useful environmental indicators of N and P pressures (Arauzo et al., 2019). The annual N and P balances depict the difference between the N or P inputs (from mineral fertilisers, manure, other organic fertilisers, seed and planting materials, biological and atmospheric deposition) and their respective outputs (removal with the harvest of crops and grazing of fodder, crop residuals removed from the field, and emissions) per hectare of utilised agricultural land and year (European Commission, 2018). As N and P losses by leaching and runoff are not included in these calculations, a positive balance (surplus) reflects inputs that are in excess of crop needs, and which could potentially result in pollution of water resources (Arauzo et al., 2019).

In this research, the annual N and P balances in the agricultural crops of the Spanish region of La Rioja during 2015 and 2016 were used to estimate the mean annual N and P surpluses, by crop type, in the study area (Table 3). This information was extracted from the annual reports of the Spanish Ministry of Agriculture, Fisheries, Food and Environment on the N and P balances in Spanish agriculture (MAPAMA, 2017a, 2017b, 2018a, 2018b), according to the guidelines of the EU referred to above (European Commission, 2018). The corresponding information for Spanish forests was extracted from Forest Europe (2015).

The annual surpluses of N and P by catchment area, were estimated by assigning the annual surpluses of N and P by crop type (Table 3) to their respective polygon on the land use map of the study area (Fig. 2C). The resulting map was then clipped to the boundaries of the different catchment areas (C-1, C-1', C-2 and C-3) and the surpluses were estimated for each catchment.

Assignment of ratings to different land uses and crop types, according to their N-surplus and risk of N-loss to groundwater, has been used to assess the risks of groundwater nitrate pollution (Arauzo, 2017; Arauzo et al., 2019). In this research, land use (LU) ratings (Table 3) were assigned following the procedure of Arauzo et al. (2019), using empirical data on the N surpluses in crops of La Rioja during 2015 and 2016 (MAPAMA, 2017a, 2018a). LU ratings represent the risk of nitrate pollution associated with land use on a scale from 1 to 10 (from negligible to extreme).

2.7. Statistical analysis

IBM SPSS Statistics 25.0 software (IBM Corp. Released, 2017) was used for the statistical analyses.

Four two-way repeated measures ANOVAs (RM ANOVAs) were conducted to analyse possible changes in nitrate and total-P concentrations in groundwater of the Oja and Tirón aquifers during the period 2005–2017. This period was selected because February 2006 marked the beginning of the current NVZ designated in the area (Gobierno de la Rioja, 2006). The objective was to assess if there has been any significant improvement in groundwater quality as a result of the implementation of the action programmes within the NVZ (the year 2005, prior to implementation, was included in the analyses). Each two-way RM ANOVA was performed on eight datasets, corresponding to four years (2005, 2009, 2013, and 2017) and two sampling campaigns per year (spring and autumn), using a general linear model for repeated measures (full factorial model). The first within-subjects factor of the RM ANOVAs was interannual variability, with four levels: years 2005, 2009, 2013 and 2017. The second within-subjects factor was seasonal variability, with two levels: spring and autumn. Conditions of normality and sphericity were checked for each data group in order to verify the assumptions required by the RM ANOVA. The sphericity assumed

Table 3

Mean annual surplus of N and P by crop types; extracted from the annual reports on the N and P balances in crops of La Rioja region during 2015 and 2016 (MAPAMA, 2017a,b, 2018a,b); standard deviations in brackets.

Land use	Crop type	P surplus (kg P ha ⁻¹ year ⁻¹)	N surplus (kg N ha ⁻¹ year ⁻¹)	LU rating ^a
Horticultural crops	Vegetables	16 (2)	207 (15)	10
	Root crops	40 (0)	156 (20)	9
Herbaceous crops	Forage crops	68 (0)	291 (28)	10
	Cereals	-2 (5)	25 (19)	6 (7 if watered)
	Dried pulses	-2 (4)	11 (7)	5 (6 if watered)
Woody crops	Industrial crops	-2 (3)	-103 (3)	1
	Fruit tree crops	8 (0)	83 (9)	8
	Vineyards	12 (0)	45 (0)	7
Meadows and pastures	Grazing areas	1 (0)	11 (0)	5 (6 if watered)
Forest and natural areas ^b	-	0.1	1	1

^a LU ratings represent the risk of nitrate pollution associated with land use (in a range of 1 to 10) according to Arauzo et al. (2019); ratings were slightly adapted to the N surpluses in crops of La Rioja 2015–16.

^b According to the European Environment Agency, 2005 and Forest Europe (2015).

model was used for reporting the results, since Mauchly's test of sphericity showed no violation of the assumption of sphericity. To refine the results, the sampling points where nitrate did not exceed 25 mg L^{-1} , or total —P did not exceed 0.035 mg L^{-1} , were not included in the RM ANOVAs.

To better understand the role of land use and the physical environment in the distribution of N and P in the alluvial aquifers and in the soil solution of the soils of their catchment areas, three PCAs were performed on three different datasets from the sampling campaigns conducted in 2017, including: (1) variables of groundwater quality and environmental characteristics of the surroundings of the sampling sites in the Oja and Tirón aquifers (PCA 1), (2) variables of the physical and chemical properties of the soil and environmental characteristics of the surroundings of the soil sampling sites along the transects T, O, Z and V (PCA 2) and (3) variables that characterise the catchment areas of the Oja and Tirón aquifers (C-1, C-2, C-3, and C-1'; PCA 3). PCA is a multivariate procedure to reduce dimensionality so that the dataset is easier to visualize, searching for links between the variables analysed. Each resulting principal component represents a linear combination of the original variables, explaining a part of the original sample variance. PCAs were performed using the Varimax rotation method with Kaiser normalisation. The Kaiser–Meyer–Olkin measure of sampling adequacy and Bartlett's test of sphericity were previously carried out to check the suitability of the data.

The variables used in the principal component analyses PCA 1, PCA 2 and PCA 3 are shown in Table 4. For PCA 1, coverage variables were estimated locally over an area of 1.5 km^2 , corresponding to the surface of an inverted isosceles triangle of height 2 km, upstream of the sampling point, following the flow direction. For PCA 2, coverage variables and the N and P surpluses were estimated locally over a circular area of 1.5 km^2 around the sampling point.

3. Results and discussion

3.1. N and P in groundwater. Has water quality improved since the NVZ designation?

The two-way RM ANOVAs to analyse the variability in nitrate and total-P concentrations in the Oja and Tirón alluvial aquifers during the period 2005–2017 did not show significant differences between the years analysed (2005, 2009, 2013 and 2017) nor between the seasons (spring and autumn) in either aquifer, both for nitrate and for total-P contents (Table 5). The mean values of nitrate were always above the threshold of 50 mg L^{-1} in the analysed points of the two aquifers (Table 5). However, the mean values of the total-P did not exceed the threshold value of 0.035 mg L^{-1} (OECD, 1982) in the Tirón aquifer, although it was slightly exceeded in the upper and middle sections of the Oja aquifer (Tables 5 and 6). These results reveal the higher impact of nitrate on groundwater quality over time compared to phosphorus. Regarding nitrate, several studies suggest a link between poor NVZs designations and the persistence of nitrate pollution in groundwater bodies (Arauzo and Martínez-Bastida, 2015; Arauzo et al., 2011; Orellana-Macías et al., 2020; Richard et al., 2018; Worrall et al., 2009), even though EU countries have been making significant efforts to reduce nitrate pollution during the last few decades. Likewise, Cameira et al. (2021) highlight the need to apply efficient methods to determine the effectiveness of N mitigation measures in reducing groundwater nitrate pollution and, where necessary, fine-tune the action programmes within each NVZ. Given the results, it is clear that the NVZ designation in the study area did not meet expectations of significantly reduce groundwater nitrate pollution. This suggests the need to review and expand the NVZ in the Oja catchment areas and undertake a further ZVN designation in the Tirón catchment area, fine-tuning the designation criteria and action programmes for the NVZs.

Nitrate was the dominant inorganic N form in the two aquifers (Table 6), a common fact in well oxygenated waters; ammonia was

Table 4
Variables used in the Principal Component Analysis (PCAs).

PCA 1	<ul style="list-style-type: none"> ○ Nitrate concentration in groundwater (mean annual values) ○ Total-N concentration in groundwater (mean annual values) ○ Orthophosphate concentration in groundwater (mean annual values) ○ Total-P concentration in groundwater (mean annual values) ○ N/P in groundwater (mean annual values) ○ Altitude ○ Groundwater table depth (mean annual values) ○ Distance from sampling point to river ○ Coverage of territory with precipitation over 600 mm y^{-1} ○ Coverage of forest and natural areas ○ Coverage of herbaceous crops (rainfed cereal, vegetables and root crops) ○ Coverage of irrigated land (vegetables, root crops and winter cereals in rotation)^a ○ Local risk associated to land use (LU rating)
PCA 2	<ul style="list-style-type: none"> ○ Altitude ○ Coarse soil fraction ○ Fine soil fraction ○ Sand soil content ○ Silt soil content ○ Clay soil content ○ Soil organic matter ○ Soil pH ○ Soil electrical conductivity ○ Field capacity ○ Soil hydraulic conductivity (K) ○ Nitrate concentration in the soil solution ○ Organic-N concentration in the soil solution ○ Total-N concentration in the soil solution ○ Orthophosphate concentration in the soil solution ○ Organic-P concentration in the soil solution ○ Total-P concentration in the soil solution ○ N/P in the soil solution ○ Annual N surplus ○ Annual P surplus ○ Coverage of territory with precipitation over 600 mm y^{-1} ○ Coverage of forest and natural areas ○ Coverage of herbaceous crops ○ Coverage of irrigated land^a ○ LU rating
PCA 3	<ul style="list-style-type: none"> ○ Total catchment area ○ Coverage of alluvial area (relative to the total catchment area) ○ Coverage of alluvial area with nitrate concentration $> 50 \text{ mg L}^{-1}$ ○ Coverage of alluvial area with nitrate concentration $> 25 \text{ mg L}^{-1}$ ○ coverage of alluvial area with total-P concentration $> 0.035 \text{ mg L}^{-1}$ ○ Mean altitude ○ Average coarse soil fraction ○ Average fine soil fraction ○ Average sand soil content ○ Average silt soil content ○ Average clay soil content ○ Average soil organic matter ○ Average soil pH ○ Average soil electrical conductivity ○ Average field capacity ○ Average soil hydraulic conductivity (K) ○ Average nitrate concentration in the soil solution ○ Average organic-N concentration in the soil solution ○ Average total-N concentration in the soil solution ○ Average orthophosphate concentration in the soil solution ○ Average organic-P concentration in the soil solution ○ Average total-P concentration in the soil Solution ○ Average N/P in the soil solution ○ Annual N surplus ○ Annual P surplus ○ Coverage of territory with precipitation over 600 mm y^{-1} ○ Coverage of territory with slope $< 5\%$ ○ Coverage of forest and natural areas ○ Coverage of herbaceous crops ○ Coverage of irrigated land^a ○ LU rating

^a Mainly by sprinkler irrigation and to a lesser extent by furrow irrigation.

present at a very low concentration, as the necessary geological and redox potential conditions did not occur (Scheidleder et al., 2000); and nitrite was undetectable, indicating absence of faecal pollution

Table 5

Two-way RM ANOVAs to analyse the interannual variability (first within-subjects factor, with four levels: years 2005, 2009, 2013 and 2017) and the seasonal variability (second within-subjects factor, with two levels: spring and autumn) on nitrate and Total-P concentrations in the Oja and Tirón alluvial aquifers during the period 2005–2017.

Two-way RM ANOVA				
Within-subjects effects (sphericity assumed)				
NO ₃ ⁻ in Oja aquifer	df	F	P-value	Mean (SD) (mg L ⁻¹) ^a
Interannual variability	3	0.97	0.45	2005: 105 (19); 2009: 107 (36); 2013: 89 (31); 2017: 81 (13)
Seasonal variability	1	1.16	0.36	Spring: 100 (25); Autumn: 91 (24)
Interaction	3	1.16	0.39	
NO ₃ ⁻ in Tirón aquifer	df	F	P-value	Mean (SD) (mg L ⁻¹) ^a
Interannual variability	3	2.71	0.14	2005: 143 (39); 2009: 104 (42); 2013: 94 (9); 2017: 50 (23)
Seasonal variability	1	1.07	0.41	Spring: 88 (24); Autumn: 104 (23)
Interaction	3	7.94	0.05	
Total-P in Oja aquifer	df	F	P-value	Mean (SD) (mg L ⁻¹) ^a
Interannual variability	3	2.90	0.09	2005: 0.07 (0.01); 2009: 0.04 (0.01); 2013: 0.05 (0.01); 2017: 0.05 (0.02)
Seasonal variability	1	3.40	0.16	Spring: 0.04 (0.01); Autumn: 0.06 (0.02)
Interaction	3	1.13	0.39	
Total-P in Tirón aquifer	df	F	P-value	Mean (SD) (mg L ⁻¹) ^a
Interannual variability	3	0.48	0.70	2005: 0.03 (0.01); 2009: 0.02 (0.00); 2013: 0.02 (0.00); 2017: 0.02 (0.00)
Seasonal variability	1	20.25	0.05	Spring: 0.01 (0.01); Autumn: 0.04 (0.07)
Interaction	3	8.75	0.09	

df: degrees of freedom.

^a Post hoc tests were not needed.

(Scheidleder et al., 2000). Nitrate was also the dominant fraction with respect to organic-N, ranging between 73%–97% of the total-N in the Oja aquifer and between 90%–95% in the Tirón aquifer (Table 6). As nitrate was the main N fraction, we focused on analysing this form. Unlike N, inorganic and organic forms of P were more balanced; orthophosphate ranged between 54%–76% of the total-P in the Oja aquifer and between 43%–53% in the Tirón aquifer (Table 6). As there was no clear dominance of either of the two fractions, we focused on analysing total-P.

Maps of nitrate concentration in groundwater during April and October 2017 (Fig. 4A) allowed verification that four polluted areas previously described by Arauzo et al. (2011) still persist in the Oja aquifer, as follows: (1) northern area (lower reaches of the main aquifer; recharged by catchment C-1), (2) eastern area (branch of the stream

Zamaca; recharged by catchment C-2 and upper section of catchment C-3), (3) mid-eastern edge (recharged by catchment C-1) and (4) mid-western edge (on the left bank of the river Oja; recharged by catchment C-1). In accordance with observations by Arauzo et al. (2011), zones above 50 mg L⁻¹ of nitrate were seasonally stable in the first three areas, while zones above 25 mg L⁻¹ had greater extension during autumn (as a result of nitrate loss from spring-summer fertilisers); a non-permanent polluted zone appeared in the fourth area after summer, but the quality of groundwater recovered with the aquifer recharge at the end of winter (due to the snowmelt), as in previous years (Arauzo et al., 2011). Nitrate pollution did not show any seasonal variability in the Tirón aquifer during 2017 (Fig. 4A). The wide extent of nitrate pollution in both aquifers can be explained by its high solubility

Table 6

Groundwater characteristics in the upper, middle and lower reaches of the Oja Alluvial Aquifer (selected points: O-01, O-09 and O-25; Fig. 1) and the Tirón Alluvial Aquifer (selected points: T-01, T-02 and T-03; Fig. 1); the mean values and standard deviations (in brackets) for the sampling campaigns of April and October 2017 are shown.

Parameter	Oja Alluvial Aquifer			Tirón Alluvial Aquifer		
	Upper section (O-01)	Middle section (O-09)	Lower section (O-25)	Upper section (T-01)	Middle section (T-02)	Lower section (T-03)
Altitude (m) ^a	743	571	460	759	656	580
Table depth (m)	3.2 (0.9)	10.4 (2.4)	4.2 (1.5)	1.5 (0.1)	4.5 (0.8)	2.4 (0.0)
Groundwater temperature (°C)	11.6 (1.2)	13.4 (1.3)	14.2 (3.1)	12.4 (2.9)	13.0 (4.1)	13.3 (2.1)
Electrical conductivity (µS cm ⁻¹)	215 (25)	226 (30)	1160 (106)	680 (102)	1800 (209)	1610 (226)
pH	7.2 (0.2)	7.3 (0.4)	7.4 (1.0)	7.3 (1.9)	7.3 (1.2)	7.5 (0.3)
Dissolved oxygen (%)	92 (10)	90 (13)	84 (26)	92 (11)	92 (27)	95 (16)
Total-N (mg N L ⁻¹)	1.0 (0.0)	3.3 (0.2)	27.7 (11.5)	1.4 (0.6)	25.2 (4.3)	10.0 (2.0)
NO ₃ ⁻ (mg L ⁻¹)	3.2 (0.0)	11.3 (3.0)	120.0 (54.4)	5.8 (2.6)	100.6 (10.4)	42.0 (6.9)
NO ₂ ⁻ (mg L ⁻¹)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
NH ₄ ⁺ (mg L ⁻¹)	0.03 (0.01)	0.02 (0.01)	0.02 (0.00)	0.02 (0.00)	0.01 (0.01)	0.04 (0.01)
Organic-N (mg N L ⁻¹)	0.2 (0.5)	0.7 (0.9)	0.6 (0.8)	0.1 (0.0)	2.5 (0.3)	0.5 (0.3)
NO ₃ ⁻ -N out of total-N (%)	73 (0)	79 (27)	97 (4)	91 (2)	90 (4)	95 (5)
Total-P (mg P L ⁻¹)	0.07 (0.00)	0.04 (0.01)	0.02 (0.00)	0.03 (0.01)	0.02 (0.01)	0.03 (0.00)
PO ₄ ³⁻ (mg L ⁻¹)	0.17 (0.02)	0.08 (0.03)	0.04 (0.00)	0.04 (0.00)	0.03 (0.00)	0.04 (0.01)
Organic-P (mg P L ⁻¹)	0.02 (0.01)	0.01 (0.00)	0.01 (0.00)	0.01 (0.01)	0.01 (0.01)	0.02 (0.00)
PO ₄ ³⁻ -P out of total-P (%)	76 (11)	65 (1)	54 (4)	53 (17)	47 (7)	43 (8)
N/P ratio	14 (0)	83 (21)	1385 (402)	57 (9)	126 (390)	333 (66)
Type of water ^b	Calcium-bicarbonate	Calcium-bicarbonate	Calcium-sulphate	Calcium-sulphate	Calcium-sulphate	Calcium-sulphate

^a Above the sea level.

^b Source: Arauzo et al. (2011).

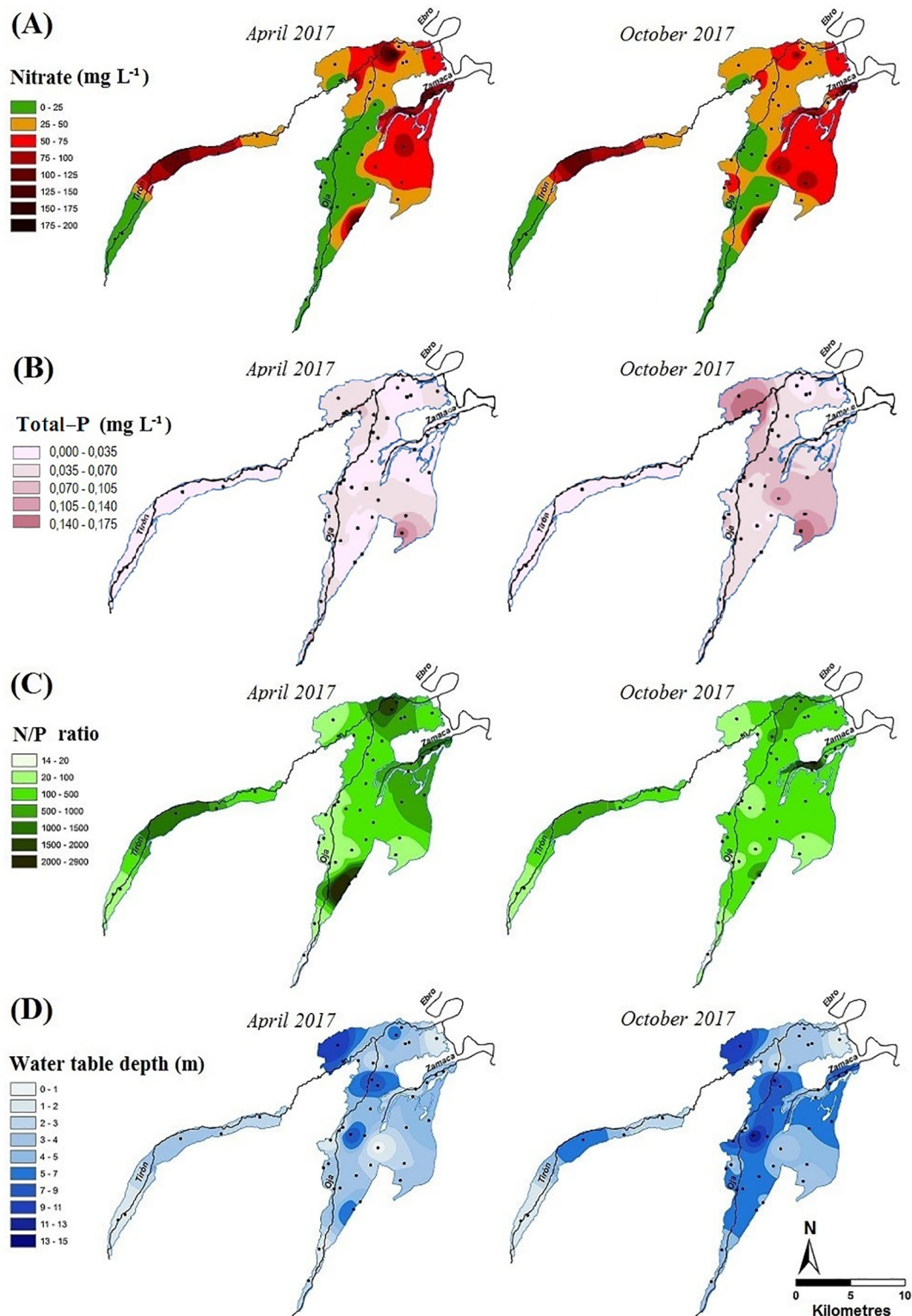


Fig. 4. Thematic maps of the Oja and Tirón aquifers during April and October 2017: (A) Nitrate concentration in groundwater, (B) Total phosphorous concentration in groundwater, (C) N/P ratio in groundwater, (D) Water table depth. The sampling points are shown as black dots.

and mobility, making it easily leachable and transportable through the vadose and saturated zone. The shallow depth of the water table (Fig. 4D) and the high permeability of the vadose zone (Fig. 2A) favour leaching. Then, the high groundwater flow velocity at the upper reaches of the aquifers favour advective transport of nitrate towards their lower reaches, where it tends to accumulate in stagnation zones (Arauzo et al., 2011).

Spatial distribution of total-P in groundwater during April and October 2017 (Fig. 4B) did not show any similarity with that of the nitrate maps (Fig. 4A). Unlike nitrate, water-soluble P in soil is very low, so it is expected that movement through the soil is very restricted. We hypothesised that the areas with the highest concentration of total-P in the saturated zone came mainly from direct leaching (by preferential flow) in coarse/sandy soils (Crouzet et al., 1999; Platineau et al., 2021;

Yaron et al., 1996) or cracked heavy-clay soils (Paltineau, 2001). The scope of advective transport of P in the saturated zone also had to be more restrictive than that of nitrate since P did not appear accumulated in the same stagnation zones as nitrate (Fig. 4A, B). In general terms, it can be said that P levels in groundwater did not constitute a contamination problem in either the Oja or Tirón aquifers. In both, the maximum limit established of 0.4 mg L⁻¹ of phosphate for the production of drinking water (BOE, 1988) was not exceeded (Fig. 4B and Table 6). Furthermore, the threshold value of 0.035 mg L⁻¹ for total-P (OECD, 1982) was never reached in the Tirón aquifer (Fig. 4B), although it was slightly exceeded in the Oja aquifer (in the upper and middle reaches of the branch of the Zamaca stream and at the confluence of the Oja and Tirón rivers; Fig. 4B and Table 6). The different scenarios that affect the N and P distribution in groundwater will be addressed in Section 3.3.

The maps of N/P ratio in groundwater (Fig. 4C) showed a distribution of the N/P ratio dominated by nitrate concentrations (Fig. 4A). The N/P ratio was close to the Redfield N/P ratio (=16) in the upper sections of the two aquifers, while it was up to 85 times higher in the lower section of the Oja aquifer, and up to 20 times higher in the lower section of the Tirón aquifer (Table 6). The explanation for these results lies in the higher solubility and mobility of nitrate in the vadose and saturated zone, in contrast to those of P. It should be noted that these high N/P ratios pose ecological implications, since P will become the limiting factor for primary production in the fluvial ecosystems that receive inflows from the lower sections of the aquifers (main discharge areas to the associated rivers; Arauzo et al., 2011).

3.2. N and P in the soil solution and soil hydraulic properties

Soil texture, particle size distribution and soil hydraulic conductivity along the altitudinal transects T, O, Z and V (Fig. 3) are shown in Fig. 5. Transects T and O (corresponding to the two larger river basins) presented soils of sandy loam and loam texture at the higher elevations, generally with a high content of gravel and stones, and clay loam textured soils at the lower elevations, with a lower content of coarse elements. Transects Z and V (corresponding to the two smaller river basins and covering a more restricted altitude range) presented soils of loam and clay loam texture, with moderate to low content of gravel and stones. Hydraulic conductivity showed a high variability along transects, tending to be greater in soils with abundant coarse elements and sand, with a lower proportion of clay and silt.

Total-N in the soil solution of the four transects ranged from 25 to 550 mg kg⁻¹ (Fig. 5). Nitrate was the most abundant form of N in the soil solution in most sampling points, except points 4–7 of Transect T (in which organic-N was higher). In any case, since the organic-N of the soil solution is composed of easily mineralizable labile forms, the principal N compound finely accumulated in groundwater was always nitrate (Table 6). Total-P in the soil solution ranged from 2.4 to 26 mg kg⁻¹, being mainly dominated by the orthophosphate, except in the higher altitudes where organic-P was the dominant form (Fig. 5). A difference between N and P behaviour in soil systems is that N is more mobile and is subject to various microbial processes which make it more prone to variation, whereas P behaviour is more governed by physico-chemical processes such as adsorption to clay particles (Kadlec and Wallace, 2009). According to Arauzo (2017), Arauzo and Valladolid (2013), Arauzo et al. (2019), Cameira et al. (2021), Misra and Tyler (1999) and Sánchez-Pérez et al. (2003), the potential for N and P leaching from the soil profile to the saturated zone depends on factors such as: (1) the amounts of N and P available in the soil solution (which depend, in turn, on the soil N and P reserves, on the N and P surpluses from the crops, and on their solubility and biochemical transformations), (2) soil moisture (which depends on water inputs by precipitation and irrigation, soil hydraulic properties, weather conditions and crop growth features), (3) the depth of the water table (4) the soil texture and structure and (5) the lithology of the vadose

zone. In addition to vertical leaching processes, advective transport also constitutes a transport pathway for solutes. Advective transport occurs both in the saturated and vadose zone by subsurface runoff. The latter depends on the substrate, slope and hydrological characteristics of the aquifer's catchment area (Arauzo, 2017).

The N/P ratio in the soil solution was relatively close to the Redfield N/P ratio (Fig. 5). It was slightly below it in Transects Z and V, and slightly above or below it in Transects T and O (with the only exception of point 7 of Transect T, which was 13 times higher). But, when comparing N/P ratios in the soil solution and in groundwater (Section 3.1) much higher values were found in groundwater (Fig. 4C; Table 6), particularly in the middle and lower alluvial reaches. This divergence can be explained again by the higher solubility and mobility of nitrate. Nitrate is poorly adsorbed by the soil particles and is easily transported from the soil solution through the vadose zone. Once nitrate reaches the saturated zone, it can be transported by groundwater flow over long distances, to later accumulate at the lower reaches of the aquifers in stagnation zones (Fig. 4A; Arauzo, 2017; Arauzo et al., 2011). However, P does not move quickly through soil. It is rapidly adsorbed and precipitated, so that water-soluble P in soil is usually very low (Yaron et al., 1996). In calcareous soils (which are majority in the study area), the high contents of Ca produce tricalcium and tetracalcium phosphates, of difficult solubility, but also the presence of clay minerals and organic matter can contribute significantly to P soil adsorption (Díez, 1979); Al and Fe phosphates are formed at low pH (Domagalski and Johnson, 2012; Yaron et al., 1996). Therefore, P pathways are much more limited than those of nitrate. However, despite the low solubility of P, Crouzet et al. (1999) and Yaron et al. (1996) pointed out that the application of high amounts of P results in soils being saturated with P and hence significantly increased P-leaching through preferential flow in coarse soils; Misra and Tyler (1999) observed that, in neutral and alkaline soils, soil solution P and pH increase with increasing soil moisture; Paltineanu (2001) documented P preferential flow (mainly in suspension) in swell-shrink, heavy-clay soils, mainly through cracks and large macropores; recent studies on P and K movement through the soils by Paltineanu et al. (2021) have also shown significant amounts of such fertilisers leached from the crop rooting system depth, at high soil water contents and rich fertilisations, in sandy and even in loamy soils. In general, we must bear in mind that, although runoff tends to be considered the main pathway for P transport (Yaron et al., 1996), special attention to the risk of P-leaching must be paid when factors such as (1) the presence of coarse, sandy or cracked heavy-clay soils, (2) high P surpluses from agriculture and (3) high levels of soil moisture converge.

3.3. Sources and pathways of N and P under a cross-scale perspective

PCAs applied to datasets of the aquifers (PCA 1), the soil transects (PCA 2), and the aquifers' catchment areas (PCA 3) allowed us to explore the relationships between variables (Table 4) at different scales of information.

PCA 1 was performed on variables of groundwater quality and environmental characteristics of the sampling sites in the Oja and Tirón aquifers (Fig. 6). The first two components explained 63.4% of the total variance. Component 1, explaining 45.2% of the variance, included information items that relate the altitudinal gradient and land use with N distribution in groundwater. Component 1 correlated negatively with variables in group A and positively with variables in group B. Group A represents the non-polluted areas of the aquifers (Fig. 4A), influenced by a higher altitude and precipitation and protected by forests and natural areas at the headwaters (which do not contribute to a significant N surplus to the environment; Table 3; European Environment Agency, 2005; Forest Europe, 2015). On the positive side of Component 1, group B represents the areas polluted by nitrate (Fig. 4A). In this group, nitrate and total-N concentrations in groundwater are positively related to the percent coverage of irrigated land and herbaceous crops

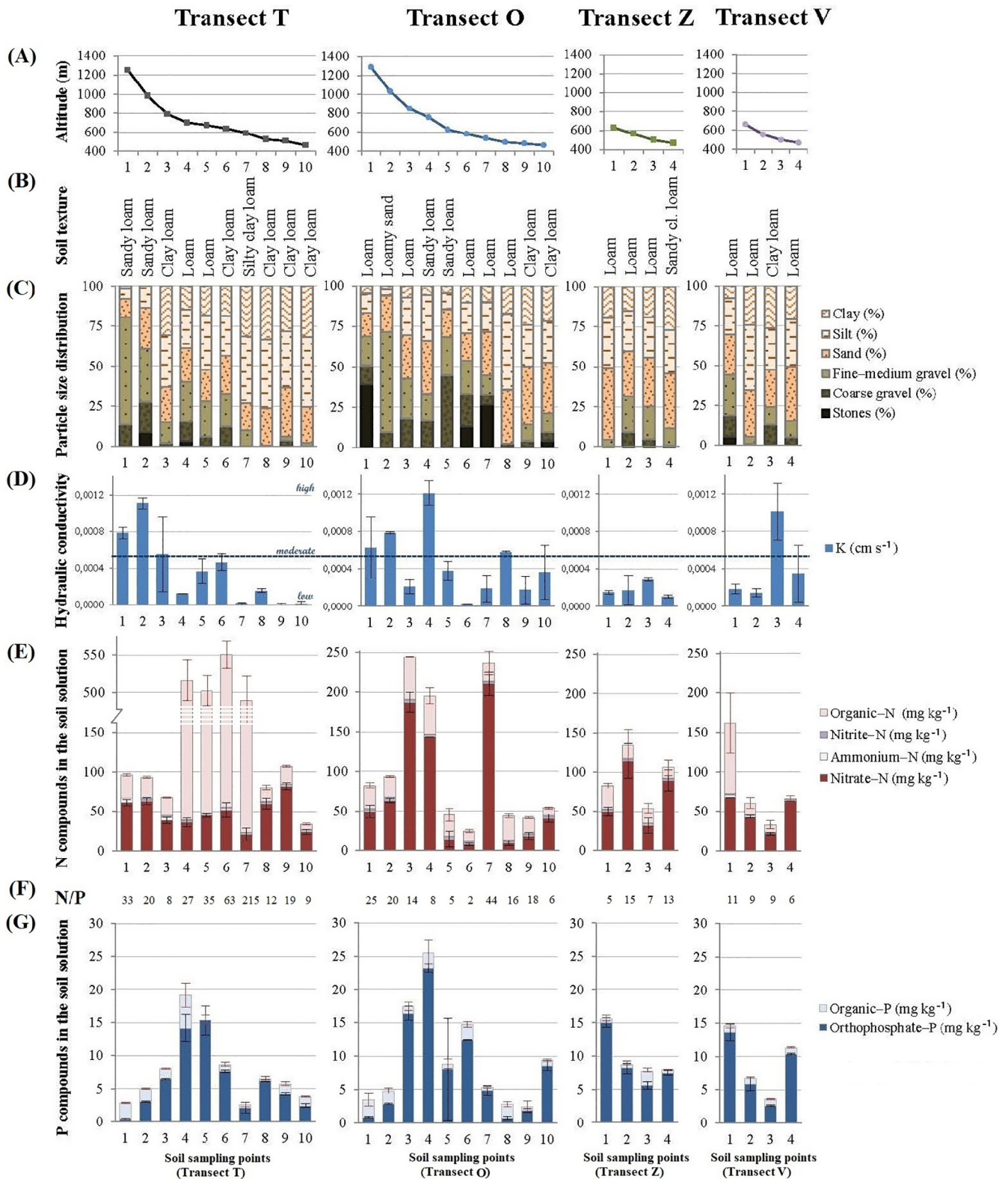
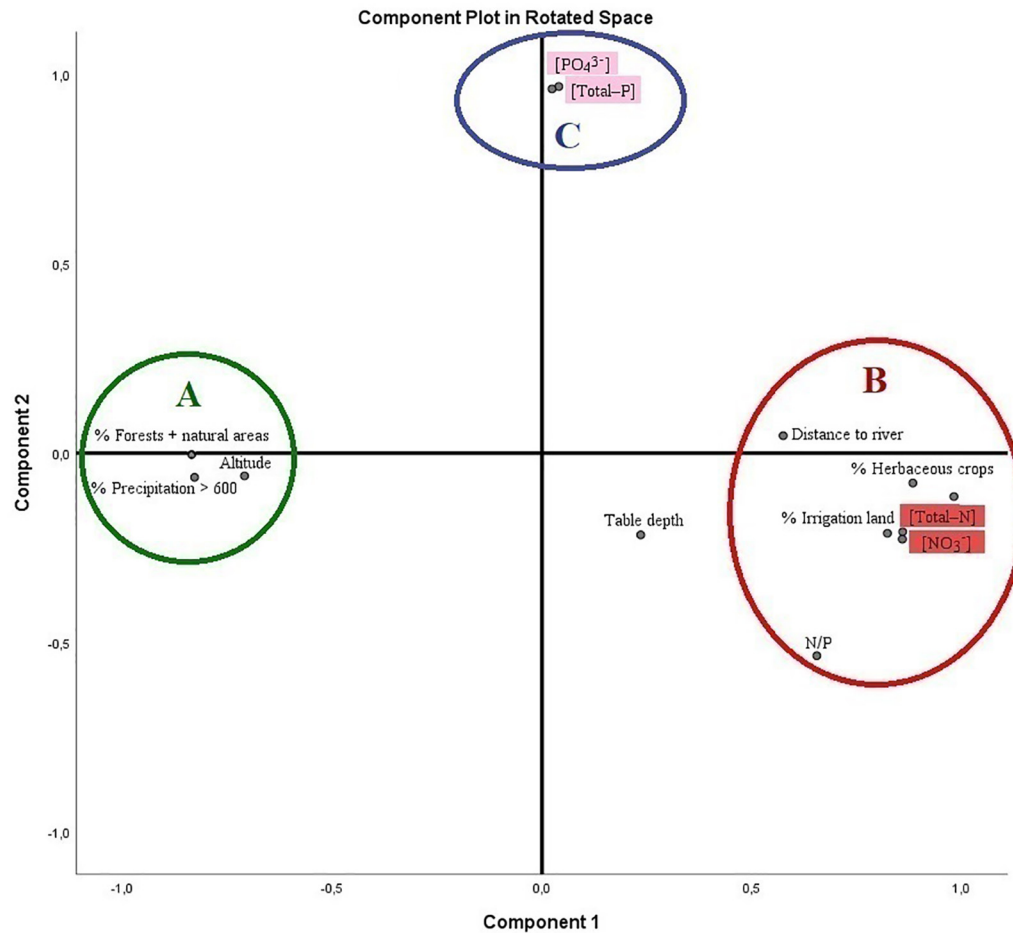


Fig. 5. Soil characteristics along the altitudinal transects T, O, Z and V: (A) Altitude at the soil sampling points, (B) Soil texture, (C) Soil particle size distribution, (D) Soil hydraulic conductivity, (E) N compounds in the soil solution (nitrate-N, ammonium-N, nitrite-N and organic-N), (F) N/P ratio in the soil solution, (G) P compounds in the soil solution (orthophosphate-P and organic-P).

(Fig. 2C), the LU rating (risk of N-loss to groundwater associated with land use; Table 3), the N/P ratio (Fig. 4C) and the distance between the sampling point and the river (the greater the distance the lower

the flow velocity, which increases the risk of stagnation). From the opposite arrangement of groups A and B it is inferred that the areas with the highest nitrate concentration correspond to the lower and flatter



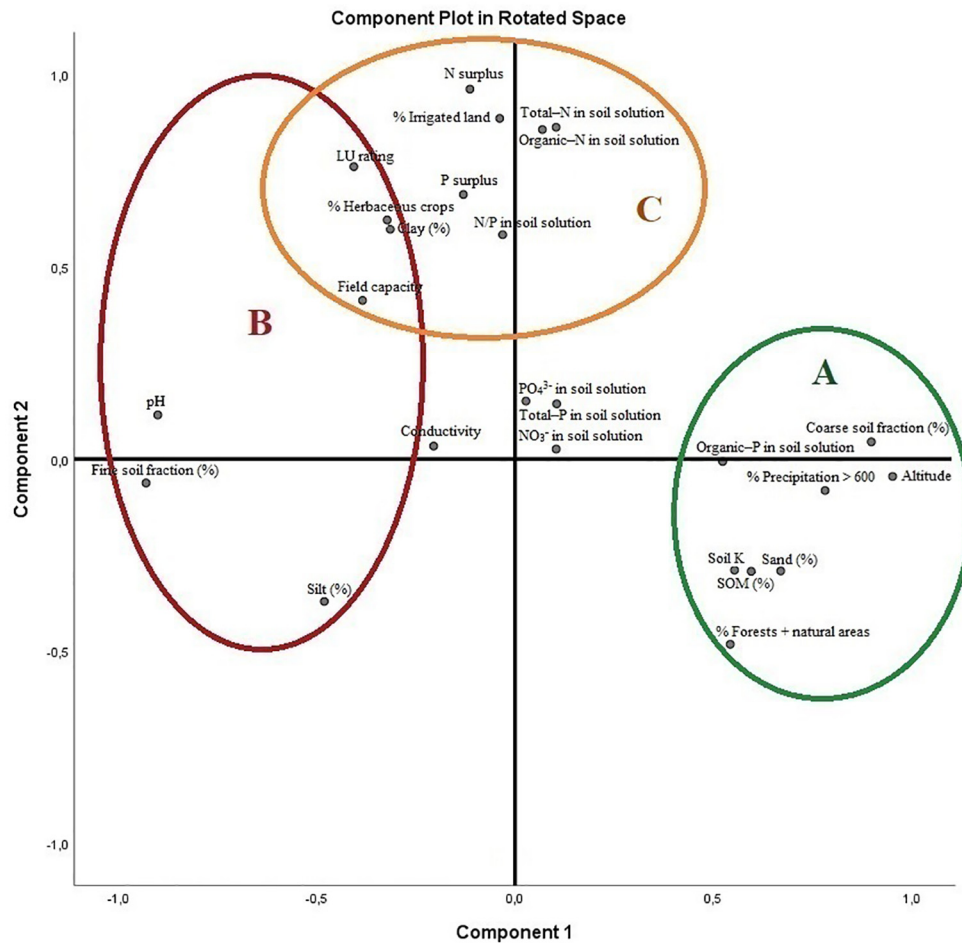
PCA 1

Rotated Component Matrix			
Extraction Method: Principal Component Analysis.			
Rotation Method: Varimax with Kaiser Normalization.			
Parameter	Label in the plot	Component 1 (45.2% of variance) ^a	Component 2 (18.2% of variance) ^a
Local risk associated to land use	LU rating	0.930	-0.127
Coverage of herbaceous crops ^b	% Herbaceous crops	0.818	-0.052
Coverage of forests and natural areas ^b	% Forests + natural areas	-0.800	-0.009
Nitrate concentration in groundwater (mg L^{-1})	[NO ₃ -]	0.797	-0.246
Total-N concentration in groundwater (mg L^{-1})	[Total-N]	0.796	-0.227
Coverage of territory with precipitation > 600 mm y^{-1} ^b	% Precipitation > 600	-0.773	-0.067
Coverage of irrigated land (sprinkling or furrow) ^b	% Irrigation land	0.745	-0.204
Altitude (m)	Altitude	-0.695	-0.056
N/P in groundwater	N/P	0.651	-0.569
Distance from sampling point to river (m)	Distance to river	0.582	0.049
Groundwater table depth (m)	Table depth	0.186	-0.174
Total-P concentration in groundwater (mg L^{-1})	[Total-P]	0.063	0.959
Orthophosphate concentration in groundwater (mg L^{-1})	[PO ₄ ³⁻]	0.051	0.952

^a Total variance explained.

^b Percent coverages were estimated over an area of 1.5 km^2 (inverted isosceles triangle of height 2 km, located upstream of the sampling point and following the flow direction).

Fig. 6. Principal component analysis on variables of groundwater quality and environmental characteristics of the surroundings of the sampling sites in the Oja and Tirón aquifers (PCA 1); plot and rotated component matrix of the first two components (63.4% of the total variance explained) are shown; groups of related variables are displayed in different colors.



PCA 2

Rotated Component Matrix
Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

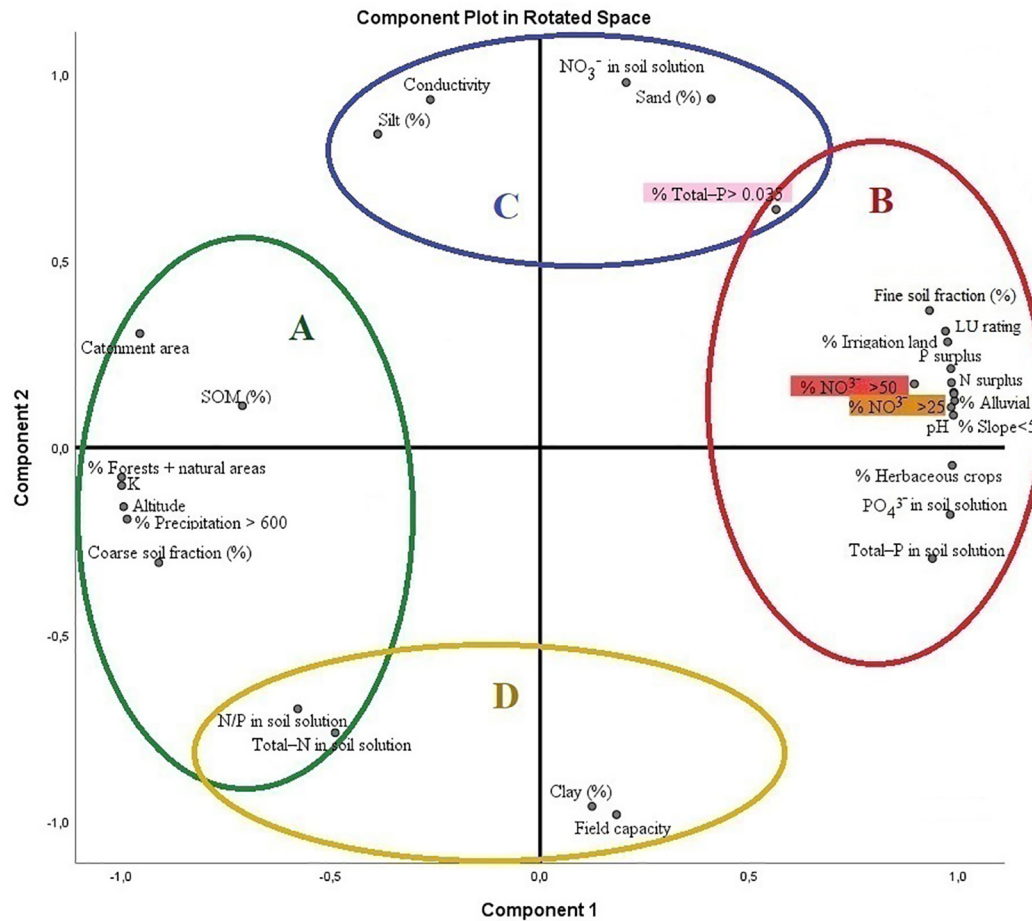
Parameter (catchment scale)	Label in the plot	Component 1 (26.1% of variance) ^a	Component 2 (24.9% of variance) ^a	Component 3 (12.9% of variance) ^a
Altitude (m)	Altitude	0.921	-0.054	-0.044
Coarse soil fraction (%)	Coarse soil fraction (%)	0.880	0.063	0.084
Fine soil fraction (%)	Fine soil fraction (%)	-0.880	-0.063	-0.084
Soil pH	pH	-0.869	0.187	-0.106
Coverage of territory with precipitation > 600 mm ^b	% Precipitation > 600	0.804	-0.105	0.129
Sand content (%)	Sand (%)	0.684	-0.265	0.282
Soil organic matter content (%)	SOM (%)	0.581	-0.260	0.494
Soil hydraulic conductivity (cm s ⁻¹)	K	0.566	-0.257	0.046
Organic-P in the soil solution (mg P kg ⁻¹)	Organic-P in soil solution	0.564	0.001	-0.094
Coverage of forests and natural areas ^b	% Forests + natural areas	0.544	-0.465	0.026
Silt content (%)	Silt (%)	-0.471	-0.385	0.229
N surplus (kg ha ⁻¹ y ⁻¹) ^{b,c}	N surplus	-0.117	0.938	0.146
Coverage of irrigated land (sprinkling or furrow) ^b	% Irrigated land	-0.077	0.886	0.164
Total-N in the soil solution (mg kg ⁻¹)	Total-N in soil solution	0.123	0.873	0.162
Organic-N in the soil solution (mg N kg ⁻¹)	Organic-N in soil solution	0.082	0.870	-0.107
Local risk associated to land use	LU rating	-0.431	0.775	0.162
P surplus (kg ha ⁻¹ y ⁻¹) ^{b,c}	P surplus	-0.152	0.674	0.353
Coverage of herbaceous crops ^b	% Herbaceous crops	-0.369	0.638	0.033
Clay content (%)	Clay (%)	-0.366	0.616	-0.506
N/P in the soil solution	N/P in soil solution	-0.018	0.592	-0.145
Nitrate in soil solution (mg N kg ⁻¹)	NO ₃ ⁻ in soil solution	0.129	0.014	0.864
Soil conductivity (µS cm ⁻¹)	Conductivity	-0.235	0.043	0.671
Orthophosphate in the soil solution (mg P kg ⁻¹)	PO ₄ ³⁻ in soil solution	0.032	0.198	0.642
Total-P in the soil solution (mg kg ⁻¹)	Total-P in soil solution	0.129	0.193	0.608
Field capacity (m ³ m ⁻³)	Field capacity	-0.399	0.393	-0.557

^a Total variance explained.

^b Percent coverages and N and P surpluses were estimated over a circular area of 1.5 km² around the sampling point.

^c N and P surpluses were estimated from the annual N and P balances in agricultural crops in La Rioja region during 2015 and 2016 (MAPAMA, 2017a,b, 2018a,b; Table 3) and applied to the land use map (Fig. 2C).

Fig. 7. Principal component analysis on variables of the physical and chemical properties of the soil and the environmental characteristics of the surroundings of the soil sampling sites along the transects T, O, Z and V (PCA 2); plot of the first two components and rotated component matrix of the first three components (63.9% of the total variance explained) are shown; groups of related variables are displayed in different colors.



PCA 3

Rotated Component Matrix
Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

Parameter (catchment scale)	Label in the plot	Component 1 (67.7% of variance) ^a	Component 2 (25.1% of variance) ^a
Average soil hydraulic conductivity (cm s ⁻¹) ^b	K	-0.997	-0.082
Coverage of alluvial area (%) ^c	% Alluvial	0.995	0.084
Coverage of forests and natural areas (%) ^c	% Forests + natural areas	-0.995	-0.064
Coverage of alluvial area with [NO ₃ ⁻] > 25 mg L ⁻¹ (%) ^d	% NO ₃ ⁻ > 25	0.995	0.100
N surplus (kg ha ⁻¹ y ⁻¹) ^e	N surplus	0.994	0.105
Coverage of territory with slope < 5% ^c	% Slope < 5	0.990	0.050
Mean altitude (m)	Altitude	-0.989	-0.144
Average soil pH ^b	pH	0.988	0.056
Coverage of territory with precipitation > 600 mm ^c	% Precipitation > 600	-0.982	-0.180
Coverage of herbaceous crops ^c	% Herbaceous crops	0.981	-0.066
Coverage of irrigated land (sprinkling or furrow) ^c	% Irrigated land	0.975	0.207
Average orthophosphate in the soil solution (mg P kg ⁻¹) ^b	PO ₄ ³⁻ in soil solution	0.971	-0.228
P surplus (kg ha ⁻¹ y ⁻¹) ^e	P surplus	0.967	0.226
Risk associated to land use	LU rating	0.964	0.243
Total catchment area (km ²)	Catchment area	-0.934	0.283
Average total-P in the soil solution (mg kg ⁻¹) ^b	Total-P in soil solution	0.928	-0.365
Average fine soil fraction (%) ^b	Fine soil fraction (%)	0.923	0.303
Average coarse soil fraction (%) ^b	Coarse soil fraction (%)	-0.923	-0.303
Coverage of alluvial area with [NO ₃ ⁻] > 50 mg L ⁻¹ (%) ^d	% NO ₃ ⁻ > 50	0.887	0.101
Average soil organic matter (%) ^b	SOM (%)	-0.688	0.133
Average field capacity (m ³ m ⁻³) ^b	Field capacity	0.139	-0.990
Average nitrate in soil solution (mg N kg ⁻¹) ^b	NO ₃ ⁻ in soil solution	0.215	0.973
Average clay content (%) ^b	Clay (%)	0.079	-0.948
Average soil electrical conductivity (μS cm ⁻¹) ^b	Conductivity	-0.219	0.923
Average sand content (%) ^b	Sand (%)	0.435	0.900
Average silt content (%) ^b	Silt (%)	-0.347	0.830
Average total-N in the soil solution (mg kg ⁻¹) ^b	Total-N in soil solution	-0.510	-0.749
Average N/P in the soil solution ^b	N/P in soil solution	-0.596	-0.678
Coverage of alluvial area with [Total-P] > 0.035 mg L ⁻¹ (%) ^d	% Total-P > 0.035	0.562	0.604

^a Total variance explained.
^b Estimated from the soil transects (Figs. 3 and 5).
^c Percent coverage relative to the total catchment area.
^d Percent coverage relative to the total alluvial area.
^e Estimated from the annual N and P balances in agricultural crops in La Rioja region during 2015 and 2016 (MAPAMA, 2017a,b, 2018a,b; Table 3) and applied to the land use map (Fig. 2C).

Fig. 8. Principal component analysis of the variables characterising the aquifers' catchment areas (C-1, C-1', C-2 and C-3; PCA 3); plot and rotated component matrix of the first two components (92.8% of the total variance explained) are shown; groups of related variables are displayed in different colors.

sections of the aquifers, where nitrate tends to accumulate in stagnation zones (Arauzo, 2017; Arauzo et al., 2011). Component 1, therefore, reflects the effects of land use and topographic, hydrogeological and climatic factors on the distribution of nitrate at the aquifer scale. However, the pathways of nitrate and its tendency to accumulate in stagnation zones cannot be explained from PCA 1. This will be discussed later, with results of PCAs 2 and 3. Component 2 of PCA 1 explained 18.2% of the variance, situating together in group C the variables related to P contents in groundwater (orthophosphate and total-P). These variables did not show any relationship with other environmental variables, except for the weak negative correlation with the depth of the water table (explainable by the low mobility of P in the vadose zone). Results of PCAs 2 and 3 will also shed some more light on P behaviour and pathways.

PCA 2 was carried out on variables of the soil properties and environmental characteristics of the surroundings of the soil sampling sites along the transects T, O, Z and V (Fig. 7). The first three components explained 63.9% of the total variance. Component 1, explaining 26.1% of the variance, collected information items that relate the altitudinal gradient with the soil particle size distribution and the land use. Component 1 correlated positively with variables in group A and negatively with variables in group B. Group A represents the mountain forest soils, located at higher altitude, exposed to higher precipitation and mostly covered by natural areas of hardwood and mixed forests (Fig. 2C). Here coarse soils predominate, with abundant sand, gravel and stones, high hydraulic conductivities, and high levels of organic matter (Anyanwu et al., 2015). These soils presented high amounts of organic-P in the soil solution (which is composed of highly mineralizable labile forms), constituting a natural source of potentially leachable P through the coarse material (first finding for a possible P-leaching pathway). On the negative side of Component 1, group B represents the soils of the middle and lowlands, located at lower altitude, exposed to lower precipitation and mostly covered by agricultural land (irrigated and rainfed herbaceous crops, with medium to extreme LU ratings; Fig. 2C; Table 3). These are fine textured soils, with abundant silt and clay and higher field capacity and pH than those of group A. Component 2 of PCA 2 explained 24.9% of the variance. Group C represents soils with the highest levels of total-N and organic-N in the soil solution (highly mineralizable forms potentially available to be leached), associated with agricultural environments. These are soils with high clay content and field capacity, where irrigation land and herbaceous crops dominate, with fertilisers the main source of N and P surpluses. Note that nitrate, orthophosphate and total-P of the soil solution appear in the middle of the plot, showing no relationship with Components 1 and 2 (Fig. 7). These three variables are better described by Component 3 (not represented in the plot, but shown in the rotated component matrix; Fig. 7), which explained 12.9% of the variance. Component 3 positively correlated with nitrate, orthophosphate and total-P in the soil solution and soil conductivity, and negatively with clay content and field capacity. These findings, observed at the scale of soil transects, point to a regulatory role of the clay content in the availability of nitrate and orthophosphate in the soil solution, which would affect their leaching possibilities. In this regard, Loganathan et al. (2013) pointed out that most natural clay minerals have low to medium anion adsorption capacity, but their high surface area and ion exchange capacity facilitate physical or chemical surface modification to improve their anion exchange capacity and surface characteristics. Kadlec and Wallace (2009) also suggested that P is partly governed by the adsorption process to clay particles, while more than four decades ago Díez (1979) had already observed that clay minerals and organic matter contributed significantly to P soil adsorption. Accordingly, low clay contents in the soil could favour a greater availability of anions such as nitrate and orthophosphate in the soil solution.

The PCA 3 was performed on variables that characterise the catchment areas that drain into the aquifers (Fig. 8). The aim here was to analyse the role of the catchment's characteristics in regulating

groundwater pollution by nitrate and P from diffuse sources. The first two components explained 92.8% of the total variance. Component 1, which explained 67.7% of the variance, included information on the physical characteristics and land use of the catchments, and how these affect groundwater pollution by nitrate and P. Component 1 correlated negatively with variables in group A and positively with variables in group B. Group B represents the smallest catchment areas, with a large relative coverage of alluvial zones, lower altitudes and slopes, soils with little coarse fraction, practically devoid of forests and natural areas, and having a large relative coverage of irrigated land and herbaceous crops. In group B, agricultural pressure implies high LU ratings and, therefore, high N and P surpluses from crops that, in turn, contribute to the high levels of orthophosphate and total-P in the soil solution (nitrate and total-N in the soil solution, however, were better represented in the other groups). The catchments represented by group B (C-2 and C-3) showed the largest coverages of alluvial areas affected by nitrate and P pollution ($\% \text{NO}_3^- > 50 \text{ mg L}^{-1}$, $\% \text{NO}_3^- > 25 \text{ mg L}^{-1}$ and $\% \text{total-P} > 0.035 \text{ mg L}^{-1}$; Fig. 8). On the negative side of Component 1, group A relates the largest catchment areas (C-1 and C-1'), with a large relative coverage of forest and natural areas, higher altitudes and precipitation and soils with abundant coarse fraction (gravel and stones) and higher hydraulic conductivity. Group A showed that the catchments with high coverage of forest and natural areas harboured more soil organic matter than those of the agricultural areas of group B (as observed in PCA 2). This is in agreement with observations by Anyanwu et al. (2015), who suggested that farmlands tend to deplete the organic matter content of the soil. The abundance of organic matter in forest soils would also explain the higher amounts of total-N in the soil solution in group A, due to microbial activity associated with soil organic matter decomposition (ectomycorrhizal fungi, leaf decomposers, saprotrophic bacteria; Nicolás et al., 2019). Component 2, explaining 25.1% of the variance, included information on the role of soil texture at the catchment scale. Component 2 correlated positively with variables in group C and negatively with variables in group D. Group C positively associated the coverage of alluvial area affected by P pollution ($\text{total-P} > 0.035 \text{ mg L}^{-1}$), the high nitrate contents in the soil solution and the high levels of soil electrical conductivity to the abundance of silt and sand, and negatively to the clay content and the field capacity of group D. Note that PCA 2 (for the soil transects) indicated the possible regulatory role of the clay content in the availability of nitrate and orthophosphate in the soil solution and its potential effects on nutrient leaching. Group C of PCA 3 (for the catchment areas) corroborates the first statement for nitrate in the soil solution and the second one (effects on leaching and pollution) for P pollution in groundwater. Why does group C not corroborate the same for orthophosphate in the soil solution and nitrate pollution in groundwater? In these two cases, it seems that the variables associated with agricultural activity, represented in group B of PCA 3, had a much greater weight on those variables. It should also be noted that the variable that represents the coverage of alluvial areas affected by P pollution ($\text{total-P} > 0.035 \text{ mg L}^{-1}$) was present both in group B and group C of PCA 3. As mentioned previously, the P impact on groundwater (observed at the catchment scale) can be explained by the joint action of agricultural pressure (irrigation and P surplus from fertilisers, which favour P presence in the soil solution; group B) and soils with abundant sand, scarce clay and low field capacity (group C). This scenario favours P-leaching. In the same way, total-N content in the soil solution (mainly organic-N, Fig. 5) appeared both in group A and group D of PCA 3, and so would depend on both the abundance of organic matter of forests and natural areas (group A) and the high clay content and field capacity (group D), which help to minimise N-leaching.

4. Conclusions

- The impact of nitrate pollution on groundwater was much higher than that of phosphorus. During the period 2005–2017 no significant

decrease in nitrate pollution was observed in the alluvial aquifers. The persistence of pollution justifies the need for a review of the current NVZs in the area, fine-tuning the designation criteria and action programmes. For more effective implementation of the Nitrates Directive in the area, the role of land use and the physical environment at the catchment scale need to be considered.

- Since nitrate is highly mobile, it tended to accumulate in stagnation zones at the lower reaches of the aquifers, where groundwater flow is slow. Due to its low solubility, P did not accumulate in the same stagnation zones as nitrate. However, although runoff is usually considered the main pathway for P transport, our results indicate that special attention to the risk of P-leaching must be paid when factors such as (1) coarse/sandy or cracked heavy-clay soils, (2) high P surpluses from agriculture and (3) high levels of soil moisture converge.
- The N/P ratio in the soil solution of soils of the aquifers' catchment areas was relatively close to the Redfield N/P ratio (=16). The N/P ratio in groundwater was also near the Redfield ratio in the upper reaches of the aquifers but was 20–85 times higher in the lower sections of the aquifers. The low solubility of phosphorus compared to nitrate would explain that fact. The high N/P ratios pose ecological implications since phosphorus will be the limiting factor for primary production in the fluvial ecosystems that receive inflows from the lower sections of the aquifers, which are discharge areas to their associated rivers.
- Diffuse pollution by N and P can be understood within a source-mobilization-pathway-impact framework. The main sources of N and P losses were the N and P surpluses from fertilization. However, organic-P in the soil solution of the forests soils was found as a potentially leachable natural P source. The low mobility of phosphorus, compared to nitrate, was considered the main factor explaining its lower impact on groundwater quality.
- Studies of the impact of land use and the physical environment on diffuse pollution by N and P under a cross-scale perspective (aquifers-soil transects-aquifers' catchment areas) using PCAs, showed that the observation scale has a decisive influence on the type of environmental factors that can be detected as intervening in groundwater pollution.
- At the aquifer scale (PCA 1), links were found between groundwater nitrate contents and land use, topographic, hydrogeological and climatic factors. The protective effect of forests and natural areas against nitrate pollution was noteworthy, while agriculture was associated with the most polluted zones. P distribution in groundwater, however, did not show any relationship with other variables at this observation scale.
- Soil conditions determine N and P in the soil solution and, therefore, their leaching potential. At the soil transect scale (PCA 2), the altitudinal gradient governed soil particle size distribution and land use, separating the mountain forest soils from the agricultural soils of the middle and lowlands. Mountain forest soils presented high organic-P levels in the soil solution that constitute a natural source of P-leaching. At this scale, it was remarkable the consistent negative relationship between nitrate and orthophosphate in the soil solution vs. clay content. This indicates the regulatory role of the clay content in the availability of nitrate and orthophosphate in the soil solution, which affects their leaching possibilities.
- At the catchment scale (PCA 3), the size and physical characteristics of the catchments and land use distribution determined the availability of macronutrients (susceptible to being leached) and, therefore, their final effects on groundwater quality.
- These results provide consistent information on the importance of analysing diffuse pollution from an aquifer-soil-catchment perspective, highlighting the need to consider the catchment scale for a more effective groundwater quality management of alluvial aquifers.

CRediT authorship contribution statement

Mercedes Arauzo: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Writing –

review & editing, Visualization, Supervision, Project administration, Funding acquisition. **María Valladolid:** Conceptualization, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Gema García:** Methodology, Formal analysis, Investigation, Writing – review & editing, Visualization. **Delia M. Andries:** Formal analysis, Investigation, Writing – review & editing, Visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors acknowledge the Spanish State Research Agency and the European Regional Development Fund for their financial support of Project CGL2016-81110-R (AEI/FEDER, UE). We thank the Spanish Ministry of the Environment and Rural and Marine Affairs for providing the digital Crops and Land Use map of Spain.

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