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Spatio-temporal dynamics of nitrogen in river-alluvial aquifer systems affected by diffuse pollution from agricultural sources: Implications for the implementation of the Nitrates Directive

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SUMMARY

Reducing nitrate pollution from diffuse agricultural sources is the major environmental challenge in the two adjacent catchments of the Oja–Tirón and Zamaca rivers (La Rioja and Castilla y León, northern Spain). For this reason, part of their territory was designated a Nitrates Directive. The Oja Alluvial Aquifer, the Tirón Alluvial Aquifer and their associated rivers are particularly vulnerable to nitrate pollution due to the shallow water table, the high permeability of alluvial deposits, interconnections between the alluvial aquifers and surface waters and pressures from agriculture. To this end, nine sampling campaigns, organised on a semi-annual basis and focused on the rivers and alluvial aquifers of the two catchments, were carried out from April 2005 to April 2009. The main objectives of the study were: (1) to investigate the chemical forms of nitrogen in river-alluvial aquifer systems of the Oja–Tirón and Zamaca catchments, (2) to improve our understanding of the spatio-temporal patterns of nitrogen distribution in the alluvial aquifers and associated rivers by integrating hydrochemical data and hydrogeological and environmental parameters, (3) to estimate the amount of nitrogen exported from the rivers and alluvial aquifers to the River Ebro, and (4) to evaluate the suitability of the current method of designating NVZs in the area.

High groundwater flow velocities in the upper alluvial zones favoured the advective transport of nitrate and generated a dilution effect. In these areas, inter-annual variations in nitrate concentrations were observed related to precipitation and N-input from agriculture. However, low flow velocities favoured processes of accumulation in the lower alluvial zones. Our results demonstrated that the entire alluvial surface was highly vulnerable, according to dynamics of the nitrogen in the river-alluvial aquifer systems being studied. The amount of nitrogen exported from these river-alluvial aquifer systems to the River Ebro was estimated at 2.4 ± 0.2 kt year\(^{-1}\). Findings from this investigation highlight the need to include the alluvial aquifer corresponding to the Tirón aquifer as a NVZ, particularly as the Tirón sub-catchment provides more than half of the nitrogen exported from the River Tirón to the River Ebro. Based on these results, at least the entire alluvial surface in the study area should be considered a NVZ in order to address the recovery of water quality.

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1. Introduction

Nitrate pollution from diffuse agricultural sources is the main cause of the deterioration of surface freshwater and groundwater quality and this poses a serious problem for drinking water supplies and contributes to the process of eutrophication (Crouzet et al., 1999; European Environmental Agency, 2005; Nixon et al., 2000; Sutton et al., 2011). In Europe, the reduction and prevention of water pollution caused by nitrate from agricultural sources was addressed by Directive 91/676/EEC (Nitrates Directive; Council of the European Communities, 1991), which is an integral part of the EU Water Framework Directive (WFD; 2000/60/EC). The Nitrates Directive establishes that both surface freshwaters and groundwaters can be considered affected by nitrate pollution when they contain, or could potentially contain, more than 50 mg L\(^{-1}\) of nitrate; the recommended limit for nitrate in drinking water and for the eutrophication of freshwaters is 25 mg L\(^{-1}\) (European Commission, 2000). The Nitrates Directive also defines Nitrate Vulnerable Zones (NVZs) as the areas of land draining into waters affected by nitrate pollution. In these areas farmers are required to comply with the measures laid out in action programmes designed to improve water quality. However, large discrepancies have been observed in the way that NVZs are designated within the framework of the
European Union (European Commission, 2010), partly because the Nitrates Directive does not provide explicit criteria for designation (De Clercq et al., 2001). This can lead to variations in the efficiency of the action programmes implemented. Thus, some of the physical and environmental factors involved in nitrogen dynamics in catchments affected by diffuse pollution (such as flows and solute transport in the saturated zone, nutrient transport by runoff, the behaviour of nitrogen compounds in the environment, and the distribution of risky land uses) often fail to be taken into account when NVZs are designated.

Alluvial aquifers are particularly vulnerable to nitrate diffuse pollution (Arauzo et al., 2008, 2010) due to a combination of factors including: the shallow water table, the high permeability of the alluvial deposits, interconnections with surface waters and the land uses usually undertaken on the lower terraces and floodplains along river banks, which are mainly associated with irrigated agriculture (European Environmental Agency, 2007). Furthermore, most private and small communal groundwater supplies of drinking water are derived from shallow groundwater sources in areas where there is a high risk of nitrate pollution of groundwater (Nixon et al., 2000).

Several relevant studies on groundwater–surface water interactions have been focused on the understanding and modelling of such processes (Abesser et al., 2008; Hubb, 2004; Lewandowski et al., 2009; Nützmann and Lewandowski, 2009). However, despite the high vulnerability of alluvial areas, the dynamics of nitrogen compounds in river-alluvial aquifer systems affected by diffuse pollution has been much less studied at the catchment scale (Arauzo et al., 2006a,b, 2008; Burt et al., 2010; Majumder et al., 2008; Peterjohn and Correll, 1984) in stark contrast to the numerous reports on nitrogen pollution in surface waters (Broussard and Turner, 2009; Causapé et al., 2004; Kyllmar et al., 2006; Lassaletta et al., 2009, 2010; Liu et al., 2000).

The alluvial aquifers and associated rivers in the Oja–Tirón and Zamaca catchments (Autonomous Communities of La Rioja and Castilla y León, northern Spain) constitute a good example of water bodies chronically affected by nitrate pollution from agricultural sources (Arauzo et al., 2006a,b; Confederación Hidrográfica del Ebro, 2007a,b; Gobierno de La Rioja, 2010a). Here, NVZ designation was restricted to some areas where groundwater was affected by nitrate pollution (Gobierno de La Rioja, 2010a) without considering the horizontal movement of the pollutant within the saturated zone, or other environmental factors. Studies by the Confederación Hidrográfica del Ebro, 2007a,b pointed out the high risk associated with not achieving the environmental objectives of the WFD in this area by 2015; it would therefore seem necessary to explore different approaches to water quality recovery in greater detail. With this in mind, an interdisciplinary approach was adopted to study the spatio-temporal dynamics of nitrogen in the river-alluvial aquifer systems at the catchment scale. This entailed exploring some of the physical and environmental factors involved in diffuse pollution from agriculture. The main objectives of the study were: (1) to investigate the chemical forms of nitrogen present in the river-alluvial aquifer systems of the Oja–Tirón and Zamaca catchments, (2) to obtain a better understanding of the spatio-temporal patterns of nitrogen distribution in the alluvial aquifers and associated rivers by integrating hydrochemical data and hydrogeological and environmental parameters, (3) to estimate the quantity of nitrogen exported from rivers and alluvial aquifers to the River Ebro, and (4) to evaluate the suitability of the current method of designating NVZs in the area and to suggest more efficient alternatives. These objectives are consistent with one of the main conclusions of the European Nitrogen Assessment report (Sutton et al., 2011) highlighting an urgent need for research papers relating science and policy issues.

2. Material and methods

2.1. Study area

The study area covered 1349 km², covering two adjacent catchments (Oja–Tirón and Zamaca) located in the neighbouring Autonomous Communities of La Rioja and Castilla y León (northern Spain; Fig. 1). The climate in the area is continental Mediterranean, with an annual precipitation of 520 ± 134 mm (mean ± standard deviation from 2005 to 2009).

The Rivers Oja and Tirón and their respective tributaries constitute the Oja–Tirón catchment (1278 km²). They originate in the mountains of Sierra de la Demanda, are relatively short (48 and 68 km, respectively) and are characterised by high slopes in their upper courses, with heights of 900 m in their first 10 km (Fig. 2). The two rivers meet 9 km before draining into the River Ebro (Figs. 1 and 3), providing a total combined flow of 162 hm³ year⁻¹ (average for 1980–2002; Confederación Hidrográfica del Ebro, 2007a). The other small catchment (71 km²) is drained by the (32 km long) River Zamaca, which is a minor tributary of the River Ebro (Figs. 1 and 3). The upper and mid-sections of the River Zamaca are always dry, while the average flow in its lower course is 9 hm³ year⁻¹ (Confederación Hidrográfica del Ebro, 2007b). During spring and summer, the Oja–Tirón and the Zamaca catchments receive water from the adjacent River Najerilla catchment via the Najerilla irrigation channel (Fig. 1), which provides a maximum flow of 15 m³ s⁻¹ (Confederación Hidrográfica del Ebro, 2007b).

The Oja Alluvial Aquifer (Groundwater Mass 045, Hydrogeological Domain of the Depresión del Ebro) is an unconfined alluvial aquifer which is entirely located in the Community of La Rioja (Fig. 1). It is formed by highly permeable Quaternary deposits composed of coarse alluvial gravels, polygenic gravels and sands with a variable content of silt particles (Instituto Geológico y Minero de España, 1985b) which lie over a layer of conglomerates, sandstones and Miocene shales of variable permeability (Instituto Geológico y Minero de España, 1979, 1990a). The aquifer has an average thickness of 12 m, with resources from 48 to 57 hm³ year⁻¹ and total reserves of around 170 hm³ (Zeta Amaltea, 2005). Its average hydraulic conductivity is 200 m d⁻¹, the effective porosity is about 22% and the storage coefficient ranges from 0.50 to 0.12 (Instituto Geológico y Minero de España, 1985a, 1988). Recharge ranges from 0.0008 m d⁻¹, in the upper section of the aquifer, to 0.0002 m d⁻¹, in its lower section. The aquifer is used to supply water for irrigation and drinking (Confederación Hidrográfica del Ebro, 2007a). It is estimated that the amount of groundwater flow pumped for irrigation is about 10.2 hm³ year⁻¹, whereas a further 2.7 hm³ year⁻¹ is withdrawn for urban use (Instituto Geológico y Minero de España, 1987). This study was limited to the floodplains, alluvial fans and low terraces of the aquifer (113 km²; Fig. 1). The middle and upper terraces (located at the eastern edge of the main aquifer) were not included because they form part of a system of small independent aquifers that are not connected to the main aquifer (Zeta Amaltea, 2005).

The Tirón Alluvial Aquifer (Groundwater Mass 044, Hydrogeological Domain of the Depresión del Ebro) is an unconfined alluvial aquifer with an area of 30 km² (Fig. 1) that is also used to supply irrigation and drinking water (Confederación Hidrográfica del Ebro, 2007a). Almost 75% of the aquifer is located in the Community of Castilla y León, while the remaining 25% belongs to the Community of La Rioja. To date, these resources have yet to be assessed as this is considered an aquifer of little interest because of its small size (Zeta Amaltea, 2005). The narrow, elongated morphology of this aquifer was determined by the genesis of the valley and subsequent retrogressive erosion (Arauzo et al., 2006b). The aquifer is formed by highly permeable Quaternary deposits composed of...
poorly developed floodplains, alluvial fans and low terraces that
have formed on top of a layer of marls and Miocene gypsiums

The soils that have developed on the Oja and Tirón alluvial
deposits belong to the Calcaric Fluvisol, Skeletic Fluvisol and Cal-
caric Regosol types (Arauzo et al., 2006b; FAO, 2006). The soils in the
upper and middle alluvial areas contain large quantities of gravel
of varying sizes (2–230 mm diameter) which provides rapid infil-
tration paths for pollutants (Arauzo et al., 2010; Martínez-Bastida
et al., 2009, 2010a). The presence of coarse material in the lower
area of the Oja aquifer is limited; there is abundant silt, which
results in reduced drainage (Martínez-Bastida et al., 2010a).

According to the 2000–2009 crops and land use map of Spain
(Ministerio de Medio Ambiente y Medio Rural y Marino, 2010a),
about 57% of the surface area in the Oja–Tirón and Zamaca catch-
ments is used for agricultural purposes (middle–lower areas), 31%
conserved as mixed forest (upland areas) and the remaining 12%
corresponds to urban areas and other uses. The predominant land
use on the alluvial deposits is irrigated agriculture, which is
distributed uniformly across the alluvial surface. This includes
the production of sugar beet, potatoes, peas, green beans, cereals
and vineyards (Gobierno de La Rioja, 2010a), while the main eco-
nomic activity in non-alluvial areas is rainfed agriculture. With
respect to possible sources of nitrogen other than agriculture, mod-
erate to low livestock densities, of 6.7 LU km\(^{-2}\) and 4.5 LU km\(^{-2}\)
respectively, have been estimated on extensive and intensive pro-
duction units (Gobierno de La Rioja, 2010b; Instituto Nacional de
Estadística, 2010). Nitrogen contributions from urban sewage
effluents are also low, especially since 2002, when most of the
wastewaters were channelled to a central sewage treatment plant
at Haro (Fig. 1), which discharges into the River Ebro (Gobierno de
La Rioja, 2010c). The Confederação Hidrográficá del Ebro, 2007a,b
has established that the main pressures on water resources in this
area are diffuse nitrate pollution from fertilizers and groundwater
abstraction for irrigation.

In Spain, the implementation of the Nitrates Directive is respon-
sibility of Spain’s Autonomous Communities (Regional Administra-
tions – RD 261/1996). To date, the Community of Castilla y León

Fig. 1. Rivers and alluvial aquifers in the Oja–Tirón and the Zamaca catchments (La Rioja and Castilla y León, northern Spain). Locations of the sampling points on the Oja
(AO1–AO31) and Tirón (AT1–AT4) alluvial aquifers and the Rivers Oja (RO1–RO5), Tirón (RT1–RT3) and Zamaca (RZ1–RZ2). Locations of Nitrate Vulnerable Zones, drinking
water supply points (Confederação Hidrográficá del Ebro, 2007a) and the Najerilla irrigation channel.
has not made any designation of NVZs in the Oja–Tirón catchment, while the Community of La Rioja made designated 22.8 km² in 2001 (the lower area of the Zamaca catchment) and enlarged this to 94.3 km² in 2006 (including the lower alluvial area of the Oja–Tirón catchment; Gobierno de La Rioja, 2010a; Fig. 1). Until now, the NVZs designated in the area have only been associated with the Oja aquifer. Despite its high level of pollution, the Tirón aquifer has so far been considered of little interest due to its small volume (Zeta Amaltea, 2005). In this case, it seems that administrative factors have been put before environmental factors (the Tirón aquifer is shared by the two Autonomous Communities); it has not been taken into account that the Tirón and Oja aquifers belong to the same catchment and that the pollution of the former could affect the latter (Arauzo et al., 2006b).

2.2. Sampling campaigns and water analyses

From April 2005 to April 2009 an extensive hydrochemical characterisation was undertaken of the Rivers Oja, Tirón and Zamaca and groundwater of the Oja and Tirón alluvial aquifers.
Sampling campaigns were carried out on a 6-monthly basis during early April and October. These months correspond to when the depth of the water table usually reaches its minimum and maximum levels, respectively (Arauzo et al., 2006a). A total of 45 sampling stations were selected, of which 10 were located on rivers and 35 were groundwater stations. In the first campaign, altitude and UTM coordinates were measured, using a Garmin GPS 12 (Garmin Int., Olathe, Kansas, USA), at each sampling point. Five sampling stations on the River Oja were referred to as R01–R05, three on the River Tirón as RT1–RT3, and two on the River Zamaca as RZ1–RZ2 (Table 1, Fig. 1). Groundwater stations on the Oja aquifer were labelled AO1–AO31 and those on the Tirón aquifer were labelled AT1–AT4 (Table 1). Most of the groundwater stations corresponded to irrigation wells, but some springs were also sampled (Table 1).

During each sampling campaign, in situ simultaneous measurements of dissolved oxygen, pH, conductivity and temperature were performed in the water of each sampling station using a YSI 556 Multi-Probe System (YSI Inc., Yellow Springs, Ohio, USA). The depth of the water table at each groundwater station was measured using a Nordmeyer water level indicator (Nordmeyer, Overveen, The Netherlands). Water samples were collected for chemical analysis. Single subsurface water samples were taken from the river stations and wells. Water samples from wells were collected using a 2.5 l Wildco Beta Plus Horizontal Water Bottle (Forestry Suppliers, Inc., Jackson, Mississippi, USA).

Spectrophotometric determinations of total-N and nitrate (2,6-dimethylphenol method according to ISO 7890-1-2-1986), ammonium (indophenol blue method according to ISO 7150-1-1984), nitrite (sulphamic acid naphthylamine method according to DIN 38405-D10 1981) and chemical oxygen demand (COD; chromosulphuric oxidation method according to ISO 6060-1989) were performed on the water samples. The analyses were carried out using a DR 2800 portable spectrophotometer (Hach Lange GmbH, Düsseldorf, Germany; Hach Company, 2008). Organic nitrogen was estimated as the difference between total-N and the concentrations of nitrate, nitrite and ammonium, expressed as mg N L\(^{-1}\). It included forms of dissolved organic nitrogen (DON; aminoacids, proteins, urea and uncharacterised, complex, high molecular weight compounds) and, to a lesser extent, particulate organic nitrogen (PON; bacteria, microalgae, microfungi, detritus, etc.). Anions were determined by ionic chromatography and cations by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). A classification of the water samples according to their ionic contents was carried out using a Piper diagram (Piper, 1953).

### 2.3. Mapping and modelling

A descriptive map of the Oja–Tirón and Zamaca catchments and maps of groundwater flows, the seasonal fall in the water table and the distribution of nitrate in the Oja and the Tirón aquifers were generated using the Geographic Information System (GIS) software ArcGIS 9.2 [Environmental Systems Research Institute, 2006].

Groundwater flow velocities and directions within the alluvial aquifers were estimated using the three-dimensional finite-difference groundwater flow model MODFLOW-2000 (Harbaugh et al., 2000) coupled with the advective transport model PMPATH (Chiang and Kinzelbach, 1994, 1998). MODFLOW-2000 was required to simulate the distribution of the hydraulic head in the alluvial area. The conceptual model defined for the simulation consisted of one unconfined layer divided into a grid of 131 rows and 191 columns, in which the active cells were limited by the physical boundaries of the aquifers and by hydraulic boundaries, such as rivers. Calibration was carried out under steady-state conditions with the parameter estimator PEST (Doherty et al., 1994) and using the water table depth measured at the 35 groundwater stations during the study period. The input parameters of the model (hydraulic conductivity, effective porosity, storage coefficient and recharge) were adjusted until a good match was obtained. PMPATH was then used for calculating, through the distribution of the hydraulic head obtained from MODFLOW simulation, the average groundwater flow velocities at the centre of each cell of the grid.

A raster contour map of the seasonal fall of the water table in the Oja and the Tirón aquifers was generated using the values obtained for differences between mean water table depths (from 2005 to 2009) during the October and April campaigns (when the water table was respectively at its maximum and its minimum depths; see Table 1). A sequence of nine raster contour maps showing the groundwater nitrate distribution from April 2005 to April 2009, on a 6-monthly basis, were created using nitrate concentrations obtained at the 35 groundwater stations during each sampling campaign. Five classes of concentration were defined (0–25, >25–50, >50–75, >75–100 and >100 mg L\(^{-1}\)), using the limits established by European regulations as the guide (25 mg L\(^{-1}\) and permissible levels (50 mg L\(^{-1}\)). All the raster contour maps were generated using the Spline Interpolation Model supported by ArcGIS Spatial Analyst (Environmental Systems Research Institute, 2006).

### 2.4. Statistical analysis

Two-way repeated measures analyses of variance (RM ANOVAs) were performed (SPSS, 2007) to assess the effects of inter-annual (factor 1, four levels: 2005–2008) and intra-annual variability (factor 2, two levels: spring and autumn) on groundwater nitrate concentration in Zones 1, 2, 3 and 4 (Oja aquifer) and Zone 5 (Tirón aquifer) and on total-N in the Rivers Oja, Tirón and Zamaca. Bonferroni test was used as a post-hoc test. Student’s t test was used to compare the degree of nitrogen mineralisation in aquifers and rivers and to evaluate the differences between the upper and lower sections of the rivers (R02–R05; RT1–RT2–RT3; RZ1–RZ2) in relation to the total-N content. Pearson’s correlations were applied to examine relationships between the nitrate concentration and other environmental factors. Statistical analyses were made with SPSS 17.0 for Windows (SPSS Inc., Chicago, Illinois).

### 2.5. Nitrogen export

The annual nitrogen exports to the River Ebro from the Rivers Tirón and Zamaca and the Oja Alluvial Aquifer (via its two branches), were estimated from the annual flows of each in their respective areas of confluence with the River Ebro and the annual averages of total-N recorded in rivers and groundwaters in these areas. Annual flows for the River Tirón were obtained from the Confederación Hidrográfica del Ebro (2009). The approximate annual flow for the River Zamaca was obtained from the Confederación Hidrográfica del Ebro (2007b). The annual flows for the lower sections of the Oja aquifer (branches of the Oja–Tirón and Zamaca) were estimated from groundwater flow velocities (obtained by PMPATH) and cross-sectional areas of flow (using a digital hydro-geological map and GIS).

### 2.6. Additional information

The annual precipitation for the period 2005–2009 was recorded at five official weather stations located in the study area (Gobierno de La Rioja, 2010d; Ministerio de Medio Ambiente y Medio Rural y Marino, 2010b). The driest period was registered in 2005 (435 mm) while 2008 was the wettest year (751 mm). Annual N-inputs in La Rioja for the period 2005–2009 were obtained from the Ministerio de Agricultura, Pesca y Alimentación (2007) and the Ministerio de Medio Ambiente y Medio Rural y Gestión de los recursos hídricos (ARHID), and the Ministerio de Medio Ambiente y Medio Rural y Marino.
Table 1  
Characteristics of the sampling stations.

<table>
<thead>
<tr>
<th>Sampling stations</th>
<th>UTM coordinates</th>
<th>Altitude (m)</th>
<th>Name of the catchment</th>
<th>Name of the water body</th>
<th>Water table depth (m)</th>
<th>Type of sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>AO1</td>
<td>30T 501050</td>
<td>4691119</td>
<td>Oja–Tirón</td>
<td>Oja Alluvial Aquifer</td>
<td>2.5 ± 0.1</td>
<td>Groundwater (well)</td>
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<tr>
<td>AO2</td>
<td>30T 502132</td>
<td>4694253</td>
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<td>Oja Alluvial Aquifer</td>
<td>1.7 ± 0.0</td>
<td>Groundwater (well)</td>
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<td>30T 504989</td>
<td>4698370</td>
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<td>Oja Alluvial Aquifer</td>
<td>6.3 ± 0.2</td>
<td>Groundwater (well)</td>
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<tr>
<td>AO4</td>
<td>30T 503785</td>
<td>4699374</td>
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<td>Oja Alluvial Aquifer</td>
<td>3.1 ± 0.1</td>
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<td>AO5</td>
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<td>Oja Alluvial Aquifer</td>
<td>3.8 ± 0.8</td>
<td>Groundwater (well)</td>
</tr>
<tr>
<td>AO21</td>
<td>30T 512049</td>
<td>4709877</td>
<td>Zamaica</td>
<td>Oja Alluvial Aquifer</td>
<td>5.4 ± 0.8</td>
<td>Groundwater (well)</td>
</tr>
<tr>
<td>AO22</td>
<td>30T 512743</td>
<td>4712912</td>
<td>Oja–Tirón</td>
<td>Oja Alluvial Aquifer</td>
<td>2.8 ± 1.5</td>
<td>Groundwater (well)</td>
</tr>
<tr>
<td>AO23</td>
<td>30T 509487</td>
<td>4712403</td>
<td>Oja–Tirón</td>
<td>Oja Alluvial Aquifer</td>
<td>2.3 ± 0.3</td>
<td>Groundwater (well)</td>
</tr>
<tr>
<td>AO24</td>
<td>30T 503641</td>
<td>4712479</td>
<td>Oja–Tirón</td>
<td>Oja Alluvial Aquifer</td>
<td>10.6 ± 0.4</td>
<td>Groundwater (well)</td>
</tr>
<tr>
<td>AO25</td>
<td>30T 508723</td>
<td>4713413</td>
<td>Oja–Tirón</td>
<td>Oja Alluvial Aquifer</td>
<td>4.3 ± 0.7</td>
<td>Groundwater (well)</td>
</tr>
<tr>
<td>AO26</td>
<td>30T 504038</td>
<td>4710945</td>
<td>Oja–Tirón</td>
<td>Oja Alluvial Aquifer</td>
<td>6.0 ± 0.4</td>
<td>Groundwater (well)</td>
</tr>
<tr>
<td>AO27</td>
<td>30T 510468</td>
<td>4707745</td>
<td>Zamaica</td>
<td>Oja Alluvial Aquifer</td>
<td>0.0 ± 0.0</td>
<td>Groundwater (spring)</td>
</tr>
<tr>
<td>AO28</td>
<td>30T 512405</td>
<td>4713377</td>
<td>Oja–Tirón</td>
<td>Oja Alluvial Aquifer</td>
<td>2.8 ± 1.6</td>
<td>Groundwater (spring)</td>
</tr>
<tr>
<td>AO29</td>
<td>30T 506132</td>
<td>4698781</td>
<td>Oja–Tirón</td>
<td>Oja Alluvial Aquifer</td>
<td>0.0 ± 0.0</td>
<td>Groundwater (spring)</td>
</tr>
<tr>
<td>AO30</td>
<td>30T 506132</td>
<td>4698781</td>
<td>Oja–Tirón</td>
<td>Oja Alluvial Aquifer</td>
<td>0.0 ± 0.0</td>
<td>Groundwater (spring)</td>
</tr>
<tr>
<td>AO31</td>
<td>30T 507196</td>
<td>4701755</td>
<td>Oja–Tirón</td>
<td>Oja Alluvial Aquifer</td>
<td>1.4 ± 0.6</td>
<td>Groundwater (well)</td>
</tr>
<tr>
<td>AT1</td>
<td>30T 483771</td>
<td>4696246</td>
<td>Oja–Tirón</td>
<td>Tirón Alluvial Aquifer</td>
<td>4.0 ± 1.1</td>
<td>Groundwater (spring)</td>
</tr>
<tr>
<td>AT2</td>
<td>30T 489170</td>
<td>4703857</td>
<td>Oja–Tirón</td>
<td>Tirón Alluvial Aquifer</td>
<td>3.5 ± 0.3</td>
<td>Groundwater (well)</td>
</tr>
<tr>
<td>AT3</td>
<td>30T 496391</td>
<td>4705830</td>
<td>Oja–Tirón</td>
<td>Tirón Alluvial Aquifer</td>
<td>2.1 ± 0.3</td>
<td>Groundwater (well)</td>
</tr>
<tr>
<td>AT4</td>
<td>30T 492873</td>
<td>4704527</td>
<td>Oja–Tirón</td>
<td>Tirón Alluvial Aquifer</td>
<td>0.0 ± 0.0</td>
<td>Groundwater (spring)</td>
</tr>
<tr>
<td>RO1</td>
<td>30T 499300</td>
<td>4687373</td>
<td>Oja–Tirón</td>
<td>River Oja</td>
<td>-</td>
<td>Surface (river)</td>
</tr>
<tr>
<td>RO2</td>
<td>30T 499541</td>
<td>4687339</td>
<td>Oja–Tirón</td>
<td>River Oja</td>
<td>-</td>
<td>Surface (river)</td>
</tr>
<tr>
<td>RO3</td>
<td>30T 503289</td>
<td>4699294</td>
<td>Oja–Tirón</td>
<td>River Oja</td>
<td>-</td>
<td>Surface (river)</td>
</tr>
<tr>
<td>RO4</td>
<td>30T 503323</td>
<td>4699202</td>
<td>Oja–Tirón</td>
<td>River Oja</td>
<td>-</td>
<td>Surface (river)</td>
</tr>
<tr>
<td>RO5</td>
<td>30T 507069</td>
<td>4710818</td>
<td>Oja–Tirón</td>
<td>River Oja</td>
<td>-</td>
<td>Surface (river)</td>
</tr>
<tr>
<td>RT1</td>
<td>30T 483608</td>
<td>4696350</td>
<td>Oja–Tirón</td>
<td>Tirón River</td>
<td>-</td>
<td>Surface (river)</td>
</tr>
<tr>
<td>RT2</td>
<td>30T 496737</td>
<td>4706131</td>
<td>Oja–Tirón</td>
<td>River Tirón</td>
<td>-</td>
<td>Surface (river)</td>
</tr>
<tr>
<td>RT3</td>
<td>30T 512431</td>
<td>4714800</td>
<td>Oja–Tirón</td>
<td>River Tirón</td>
<td>-</td>
<td>Surface (river)</td>
</tr>
<tr>
<td>RZ1</td>
<td>30T 510539</td>
<td>4708540</td>
<td>Zamaca</td>
<td>River Zamaca</td>
<td>-</td>
<td>Surface (river)</td>
</tr>
<tr>
<td>RZ2</td>
<td>30T 512694</td>
<td>4710281</td>
<td>Zamaca</td>
<td>River Zamaca</td>
<td>-</td>
<td>Surface (river)</td>
</tr>
</tbody>
</table>

*a Mean values (±standard deviations) during April and October, from 2005 to 2009.*
Marino (2008, 2009, 2010c). From this information, the mean N-input in the agricultural areas of the Oja–Tirón and Zamaca catchments was estimated to be around 10.3 kt year\(^{-1}\).

3. Results and discussion

3.1. Hydrogeological characterisation

The natural recharge of the Oja Alluvial Aquifer mainly occurs from autumn to spring and comes from the direct infiltration of the precipitation that falls on the alluvial area and from runoff within the catchment. The main recharge area extends from the headwaters to Santo Domingo de la Calzada (Fig. 1), where the transmissivity ranges from 5000 to 2500 m\(^2\) d\(^{-1}\) (Instituto Geológico y Minero de España, 1988). From spring to autumn, irrigation returns contribute to aquifer recharge, also promoting nitrate leaching from fertilizers (Martínez-Bastida et al., 2009, 2010a and Arauzo et al., 2010). In the central (and widest) part of the Oja aquifer (Fig. 1) the Oja sub-catchment and the Zamaca catchment share the same underlying alluvial deposits. In this area the transmissivity is lower than 2500 m\(^2\) d\(^{-1}\) (Instituto Geológico y Minero de España, 1988). In the zone immediately below it, the Oja aquifer is divided into two narrower branches, with one corresponding to the River Oja and the other to the River Zamaca, which both drain into the River Ebro, albeit at different places (Fig. 1).

Groundwater flow in the Oja aquifer is conditioned by lithology, topography, climate and land uses. The highest flow velocities (10–20 m d\(^{-1}\)) were observed in the upper and mid-sections of the aquifer, along the longitudinal axis of the River Oja (this fact could be associated with a greater capacity of natural attenuation to groundwater pollution; Zone 1, Fig. 3). On the other hand, slower flows (0–10 m d\(^{-1}\)) and/or converging flows were found in three zones (in which there could be an increased tendency for contaminants to accumulate; Fig. 3): the eastern margin of the aquifer, including the branch of the River Zamaca (Zone 2); the left bank of the River Oja, in the mid-section of the aquifer (Zone 3); and the lower section of the Oja aquifer (Zone 4). Bekesi and McConchie (2002) assessed the vulnerability of alluvial aquifers based on the grain size of the aquifer medium and found that large grain sizes in the saturated zone (indicating high hydraulic conductivity) increase dilution, resulting in less concentration in the groundwater phase, whereas small grain sizes favour the accumulation of polluting agents.

The shallow water table in the Oja aquifer (from 0 to 13 m deep; Table 1) made it more vulnerable to pollution. Furthermore, the pumping of groundwater for irrigation combined with lower inputs from the tributary rivers and streams from April to October resulted in a fall in the level of the water table every summer (Fig. 4; Table 1). Groundwater depletion was more pronounced in the mid-section of the aquifer, where the largest concentration of groundwater pumping was located (Instituto Geológico y Minero de España, 1987), creating a zone of intermittent saturation of up to 5.2 m (Fig. 4; Table 1). As a result, the mid-section of the River Oja dried up every summer from RO2 to below RO4. This had serious ecological implications, such as the loss of streamside vegetation and the decline of many habitats that are important for maintaining freshwater biodiversity (Martínez-Bastida et al., 2006; Valladolid et al., 2006), although the river flow and piezometric levels recovered after the spring thaw in every year (Arauzo et al., 2006b). The upper and mid-sections of the River Zamaca remained dry during the study period. However, the lower sections of both rivers (points RO5 and R22) almost always maintained a certain flow, even during summer, as a result of the upwelling of groundwater. The topography and the reduction in size of the Oja aquifer in both of its branches may explain the exfiltration of groundwater to river water in these zones. These hydrological exchange processes (infiltration of river water to groundwater, and vice versa, exfiltration events) have been widely described by Abesser et al. (2008), Lewadowski et al. (2009) and Nützmann and Lewandowski (2009).

Recharge of the Tirón Alluvial Aquifer comes from the direct infiltration of precipitation falling on the alluvial area, runoff within the catchment area and returning irrigation water. The mid-section of the valley is asymmetrical; there is a sharp escarpment of gypsum facies along the left bank, a narrow encased alluvial plain and a large, first terrace on the right bank, which drains northwards (Fig. 3). This particular morphology determined flow velocities that ranged from 0 to 50 m d\(^{-1}\) (Fig. 3; Zone 5). The shallow water table (from 0 to 4 m deep: Table 1) made the aquifer more vulnerable to pollution. However, unlike the Oja aquifer, in the case of the Tirón aquifer, the seasonal fall in the level of the water table did not reach 1.5 m (Fig. 4; Table 1), probably as a result of lower pumping pressures and the greater extension of the catchment area (706 km\(^2\)). Due to its narrow morphology and limited depth, the Tirón aquifer probably drains into the Oja aquifer at a level very near to the surface and mainly through the Tirón riverbed itself.

3.2. Hydrochemical characterisation

From a hydrochemical point of view, the groundwater and surface water in each catchment were relatively similar with respect to the major ions present (Table 2); in the Oja sub-catchment the calcium-bicarbonate type was the most important, while in the Tirón sub-catchment and Zamaca catchment it was the calcium-sulphate type; these findings were in line with the distribution of the geochemical facies (Arauzo et al., 2006b). The good oxygenation and low values of COD observed in rivers and groundwaters throughout the study suggested the absence of any significant degradation processes of organic matter (Table 2; this also indicated that there were no major sources of urban pollution). The highest levels of electrical conductivity detected in the mid and lower sections of the River Tirón and its alluvial aquifer, as well as in the lower section of the Oja aquifer (Table 2), limited (in a slight to moderate degree) the suitability of using this water for irrigation (Ayers and Westcot, 1985). This increase in conductivity was explained by the high concentration of sulphates in the water, which was related to the presence of gypsum facies (Arauzo et al., 2006b). Furthermore, permanent high nitrate concentrations in large areas of aquifers, as found in the lower courses of their associated rivers (Figs. 5 and 6), mean that these waters cannot be recommended for drinking supplies and their use for irrigation should also be carefully considered (according the water quality standards laid out in Directive 91/676/EEC and the Hydrological Plan of the Ebro Basin, RD 1664/1998, Order of 13th August, 1999). At present, nitrate pollution poses a serious problem in this area, particularly given the wide distribution of wells used to supply drinking water (Fig. 1) and the predominant use of groundwater for irrigated agriculture (Gobierno de La Rioja, 2010a).

3.3. Patterns of nitrogen pollution

The main inorganic form of nitrogen present in rivers and alluvial aquifers was nitrate (Table 3); this is common in well-oxygenated waters with a low organic content (Table 2). Ammonium and nitrite levels were always below the limits of quantification (0.13 mg L\(^{-1}\) and 0.20 mg L\(^{-1}\), respectively). The remainder of the total-N found in the water corresponded to labile organic forms of nitrogen (DON + PON) that could be easily mineralised. Particularly in the rivers, the average percentage of NO\(_3\)-N with respect to total-N varied from 38%, in the upper courses, to 87%, in the lower
ones; the rest of the nitrogen detected was in organic forms. These findings were consistent with those of Kortelainen et al. (1997) and Willetts et al. (2004) in several European rivers. The degree of nitrogen mineralisation (percentage of NO$_3^-$-N out of total-N) in the aquifers was significantly higher when it was compared to that in rivers (Table 3) using the Student’s t test ($p \leq 0.01$). In this context, the natural exchange of water between rivers and alluvial aquifers (Abesser et al., 2008; Hubbs, 2004) could favour the rapid mineralisation of labile forms of organic nitrogen in surface waters, when rivers flow into aquifers, which represents an additional

Table 2
Characteristics of the water bodies (mean ± standard deviation, from 2005 to 2009).

<table>
<thead>
<tr>
<th>Water body</th>
<th>Temperature ($^\circ$C)</th>
<th>Conductivity ($\mu$S cm$^{-1}$)</th>
<th>pH</th>
<th>Dissolved oxygen (%)</th>
<th>COD (mg O$_2$ L$^{-1}$)</th>
<th>Piper’s classification of waters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oja alluvial aquifer</td>
<td>Upper section (AO1)</td>
<td>11.9 ± 2.0</td>
<td>225 ± 41</td>
<td>7.2 ± 0.6</td>
<td>83 ± 26</td>
<td>4 ± 1, Calcium-bicarbonate type</td>
</tr>
<tr>
<td></td>
<td>Mid-section (AO9)</td>
<td>13.9 ± 1.9</td>
<td>221 ± 39</td>
<td>7.1 ± 0.6</td>
<td>90 ± 21</td>
<td>4 ± 2, Calcium-bicarbonate type</td>
</tr>
<tr>
<td></td>
<td>Lower section (AO25)</td>
<td>14.6 ± 5.6</td>
<td>1154 ± 425</td>
<td>7.4 ± 2.9</td>
<td>82 ± 38</td>
<td>7 ± 6, Calcium-sulphate type</td>
</tr>
<tr>
<td>Tirón alluvial aquifer</td>
<td>Upper section (AT1)</td>
<td>12.8 ± 4.8</td>
<td>677 ± 268</td>
<td>7.4 ± 2.9</td>
<td>77 ± 29</td>
<td>8 ± 5, Calcium-sulphate type</td>
</tr>
<tr>
<td></td>
<td>Mid-section (AT2)</td>
<td>13.1 ± 4.6</td>
<td>1912 ± 710</td>
<td>7.3 ± 2.8</td>
<td>92 ± 40</td>
<td>5 ± 2, Calcium-sulphate type</td>
</tr>
<tr>
<td></td>
<td>Lower section (AT3)</td>
<td>13.0 ± 2.3</td>
<td>1625 ± 280</td>
<td>7.6 ± 0.3</td>
<td>94 ± 19</td>
<td>8 ± 3, Calcium-sulphate type</td>
</tr>
<tr>
<td>River Oja</td>
<td>Upper section (RO1)</td>
<td>7.6 ± 4.7</td>
<td>14 ± 7</td>
<td>6.6 ± 1.3</td>
<td>102 ± 4</td>
<td>3 ± 2, Calcium-bicarbonate-sulphate type</td>
</tr>
<tr>
<td></td>
<td>Mid-section (RO4)</td>
<td>12.7 ± 1.9</td>
<td>153 ± 46</td>
<td>7.9 ± 0.6</td>
<td>94 ± 18</td>
<td>5 ± 3, Calcium-bicarbonate type</td>
</tr>
<tr>
<td></td>
<td>Lower section (RO5)</td>
<td>14.1 ± 3.3</td>
<td>256 ± 62</td>
<td>7.7 ± 0.6</td>
<td>77 ± 24</td>
<td>8 ± 6, Calcium-bicarbonate type</td>
</tr>
<tr>
<td>River Tirón</td>
<td>Upper section (RT1)</td>
<td>12.4 ± 5.4</td>
<td>369 ± 160</td>
<td>8.1 ± 3.1</td>
<td>86 ± 37</td>
<td>8 ± 5, Calcium-sulphate type</td>
</tr>
<tr>
<td></td>
<td>Mid-section (RT2)</td>
<td>13.9 ± 5.2</td>
<td>1179 ± 463</td>
<td>8.3 ± 3.2</td>
<td>100 ± 40</td>
<td>10 ± 8, Calcium-sulphate type</td>
</tr>
<tr>
<td></td>
<td>Lower section (RT3)</td>
<td>14.4 ± 5.7</td>
<td>728 ± 275</td>
<td>8.3 ± 3.2</td>
<td>91 ± 40</td>
<td>9 ± 6, Calcium-sulphate type</td>
</tr>
<tr>
<td>River Zamaca</td>
<td>Upper section (dry)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Mid-section (dry)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Lower section (RZ2)</td>
<td>13.8 ± 5.3</td>
<td>688 ± 281</td>
<td>8.3 ± 3.1</td>
<td>98 ± 47</td>
<td>12 ± 6, Calcium-sulphate type</td>
</tr>
</tbody>
</table>

COD: chemical oxygen demand.
N-input that must be considered. However, when water flows from alluvial aquifers to rivers, nitrate is the principal form of N-input.

The nitrate concentrations in the rivers and alluvial aquifers showed a tendency to increase from the headwaters to the lower courses (Fig. 5). In the Oja and Tirón aquifers the threshold limit (50 mg L\(^{-1}\)) was exceeded at 66% of the sampling points. The Rivers Oja and Tirón exceeded the recommended limits for human consumption and eutrophication in freshwaters (25 mg L\(^{-1}\)) at the lower points (ROS, RT2 and RT3), while the level in the River Zamaca was above the recommended limit at RZ1 and above the threshold limit at RZ2 (Fig. 5). It should be noted, however, that forms of organic nitrogen, which were mainly found in rivers, significantly increased actual loads of the total-N (Table 3). This is often neglected when the standards required by the Nitrates Directive (based on nitrate contents) are applied. In fact, organic nitrogen is not determined in most routine European water quality monitoring programmes (Sutton et al., 2011). From a practical point of view, an approach based only on nitrate concentrations could be somewhat restrictive; it does not take into account the variety of forms of nitrogen present in some water bodies (Arauzo et al., 2008; Willett et al., 2004) and this could lead to an underestimation of actual nitrogen loads. Scheidleder et al. (2000) shared this approach when they observed the impact of ammonium on some groundwater bodies without exceeding the nitrate limits. Therefore, the standards required by the Nitrates Directive should refer to total-N (not only to nitrate contents), taking into account the variety of interchangeable forms of nitrogen present in water bodies, particularly in rivers.

The total-N contents in the Rivers Oja and Tirón presented significant intra-annual differences (lower concentrations in spring than in autumn) but inter-annual variability was not observed (Table 4). For both rivers, Student’s t tests (\(p < 0.01\)) separated the more polluted points, which were located in their lower courses (ROS in the River Oja, and RT2 and RT3 in the River Tirón), from the unpolluted points further upstream. This can be explained by the fact that the surface waters of the lower courses of the rivers were partly mixed with polluted groundwaters that had drained from the underlying aquifers. A higher incidence of pollution was observed at the lower points during the summer–autumn period, when there was either no surface flow, or very little flow, above these points. The total-N content in the River Zamaca did not show any significant differences, neither between spring and autumn, nor between different years (Table 4). However, significant differences were observed between points RZ1 and RZ2 (Student’s t test, \(p < 0.01\)). This could be explained by the fact that RZ1 only had water when it was received from the less polluted Najarilla irrigation channel, while the stream at RZ2 was mainly fed from the polluted underlying aquifer.

Maps of groundwater nitrate concentrations allowed us to analyse the spatio-temporal patterns of nitrate distribution from 2005 to 2009 on a 6-monthly basis (Fig. 6). In the Oja aquifer, three areas were identified that were either polluted by nitrate or at risk of being polluted (>50 mg L\(^{-1}\), 25–50 mg L\(^{-1}\)). This was consistent with the zoning established according the slow and/or covering flows shown in Fig. 3: the eastern margin of the aquifer, including the branch of the River Zamaca (Zone 2); the left bank of the River Oja in mid-section of the aquifer (Zone 3); and the lower section of the aquifer (Zone 4). The distribution of pollution in these areas showed great stability over time, with only minor variations. The only exception to this was Zone 3, where a seasonal dynamic was observed (with pollution increasing from spring to autumn and water quality recovering after each winter recharge). In contrast, the upper and mid-sections of the Oja aquifer, along the longitudinal axis of the River Oja (Zone 1 in Fig. 3, with higher flow velocities), generally showed levels of nitrate that remained below the recommended limit (Fig. 6). This was in line with the findings reported by Bekesi and McConchie (2002) who described a dilution effect in areas of high hydraulic conductivity. A discrepancy was observed in October 2005, when pollution temporarily extended to Zone 1. In the case of the Tirón aquifer (Zone 5 in Fig. 3), a continuously high level of nitrate extended across almost the whole of the alluvial area (excluding that corresponding to the station at AT1), exhibiting a certain variability over time (Fig. 6).

Since the mechanism by which mass transport of the pollutant occurs in aquifers largely depends on flow velocity (Martínez et al., 2006), advective transport was considered the predominant process in areas with faster flow (Zones 1 and 5) while molecular diffusion could become more relevant in those areas of Zones 2–4 where flow velocity was equal or close to zero (Fig. 3).

Nitrate distributions in the Oja and Tirón aquifers exhibited weak positive correlations with distance from the headwaters and negative correlations with altitude (Table 5); this can be explained by the accumulation process following the direction of flow. In accordance with Bekesi and McConchie (2002), significant
negative correlations were observed between nitrate and flow velocity and seasonal fall of the water table in the Oja aquifer (Table 5); this would seem to justify the zoning of nitrate polluted areas based on flow velocities. However, these correlations were not become significant for the Tirón aquifer, probably because of the small number of points used for the model. In contrast, water
RM ANOVAs to examine the effects of inter-annual (2005–2008) and intra-annual (spring and autumn) variability in groundwater nitrate concentrations in Zones 1–5 (Table 6) showed significant differences between years in Zones 1, 3 and 5. Zones 1 and 5, in which a certain regeneration capacity might be expected due to advective transport, showed decreasing trends in nitrate concentrations from 2005 to 2008 (Zone 1: 27–12 mg L$^{-1}$; Zone 5: 143–122 mg L$^{-1}$). This tendency could be related to inter-annual variations in precipitation (435 mm in 2005 and 751 mm in 2008) and to downward trends in N-inputs over the study period in La Rioja (20.4 kt year$^{-1}$ in 2005 and 12.9 kt year$^{-1}$ in 2008; Ministerio de Agricultura, Pesca y Alimentación, 2007; Ministerio de Medio Ambiente y Medio Rural y Marino, 2008, 2009, 2010c). The significant correlations between annual average nitrate levels throughout the alluvial area vs. annual N-input ($r = 0.76$; $p < 0.05$) and annual precipitation ($r = -0.73$; $p < 0.10$) would support this idea. No significant intra-annual variability in Zones 1 and 5 was found, however interactions between the two factors of analysis were observed. Similarly, RM ANOVAs showed significant differences between nitrate concentration in spring and autumn in Zone 3 of the Oja aquifer (Table 6), intermittently polluted, with higher concentrations during autumn (Fig. 6). This seasonal response could be explained by the rapid leaching of nitrate from fertilizers in the central area of the aquifer during the spring and summer watering (Arauzo et al., 2010; Martínez-Bastida et al., 2009). In Zones 2 and 4 no inter- or intra-annual responses were observed (Table 6).

### 3.4. Nitrogen exported to the River Ebro

The average quantity of nitrogen annually exported from the River Tirón, River Zamaca and two branches of the Oja aquifer to the River Ebro was estimated as 2.4 ± 0.2 kt year$^{-1}$ (mean ± standard deviation; Table 7), of which 49% was attributable to the River Tirón, 38% to the Oja–Tirón branch of the Oja aquifer, 7% to the River Zamaca and 6% to the Zamaca branch of the Oja aquifer. This quantity corresponded to a quarter of the estimated annual N-input into the agricultural areas of the Oja–Tirón and Zamaca catchments (Ministerio de Agricultura, Pesca y Alimentación, 2007; Ministerio de Medio Ambiente y Medio Rural y Marino, 2008, 2009, 2010c).

Nitrogen losses to the River Ebro (expressed in units related to catchment surface; 1779 kg N km$^{-2}$ year$^{-1}$) were in the medium to high range of emissions when compared with nitrogen losses to aquatic systems estimated for Europe (Sutton et al., 2011).

As previously noted, the River Tirón was the largest contributor to the total amount of nitrogen exported to the River Ebro. However, the nitrogen exported from this river was mainly composed of N-loads from the Rivers Oja and Tirón after their confluence. It is interesting to note that the N-load of the River Tirón immediately before it reaches the Oja aquifer was 0.7 ± 0.2 kt year$^{-1}$; this represents more than half of the total amount of nitrogen annually exported by the River Tirón (Table 7). As previously indicated, this can be explained by the fact that polluted groundwater from the Tirón aquifer drains into the River Tirón in the very narrow alluvial zone below RT2, significantly increasing the nitrate concentration in the river at this point (Fig. 5). These findings should lead us to reflect on the significance of considering river-alluvial aquifer systems as single units within the context of the natural boundaries of their catchment areas; this is also an important aspect to consider when designating NVZs.

### 4. NVZ designation: how and how much?

The implementation of the Nitrates Directive has been closely linked with the Common Agricultural Policy, both being related
using GIS and applying intrinsic vulnerability indexes (Aller et al., 1987; Foster and Hirata, 1991; Foster et al., 2002) and/or specific vulnerability indexes related to nitrate pollution (Martínez-Bastida et al., 1987; Foster and Hirata, 1991; Foster et al., 2002) and/or specific circumstances to the direct support to farmers and rural development. This means that the direct payments made to farmers and certain rural development payments are subject to cross compliance (European Commission, 2010). Since the WFD aims to achieve the “good status” of the waters by 2015, it would seem necessary to optimise the efficiency of the action programmes undertaken in the NVZs. If the direct payments made to farmers and certain rural development. This means the direct payments made to farmers and certain rural development payments are subject to cross compliance (European Commission, 2010). Hence, the current European map of NVZs (European Commission, 2010) reveals large discrepancies in the way that these zones are designated within the framework of the European Union and this may, in some cases, produce results that are either limited or difficult to interpret. For example, a recent investigation by Worrall et al. (2009) showed the lack of objective success in the majority of the 32 NVZs studied in the United Kingdom. This has called into doubt the use of input management as a means of limiting nitrate pollution, especially when the areas designated are small. At the regional scale, mapping the vulnerability of the territory using GIS and applying intrinsic vulnerability indexes (Aller et al., 1987; Foster and Hirata, 1991; Foster et al., 2002) and/or specific vulnerability indexes related to nitrate pollution (Martínez-Bastida et al., 2010b; Secunda et al., 1998) has proved a very useful tool for obtaining a more comprehensive view of the NVZs. However, at the catchment scale, the hydrogeological functioning of the catchments, and of the aquifers inside them, generates horizontal displacements of nitrogen compounds which condition the patterns of pollution in the water bodies. It is essential to understand that the NVZs (or pollutant input areas) and the areas with waters affected by nitrate pollution do not necessarily always coincide. In the case of the Oja–Tirón and Zamaca catchments, the designation of NVZs was restricted to part of the area in which the groundwater nitrate concentrations in Zones 1, 2, 3 and 4 (Oja aquifer) and Zone 5 (Tirón aquifer) were small. This has called into doubt the use of input management as a means of limiting nitrate pollution, especially when the areas designated are small. At the regional scale, mapping the vulnerability of the territory using GIS and applying intrinsic vulnerability indexes (Aller et al., 1987; Foster and Hirata, 1991; Foster et al., 2002) and/or specific vulnerability indexes related to nitrate pollution (Martínez-Bastida et al., 2010b; Secunda et al., 1998) has proved a very useful tool for obtaining a more comprehensive view of the NVZs. However, at the

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5. Conclusions

The main form of nitrogen present in the Oja and Tirón aquifers was nitrate. However, the percentage of NO$_3^-$–N with respect to total-N in their associated rivers varied from 38%, in the upper courses, to 87%, in the lower ones, with the rest of total-N being in organic forms. These results highlight the need to refer the standards required by the Nitrates Directive not only to nitrate content, but also to total-N.

The threshold limit of 50 mg L$^{-1}$ of nitrate (established by the Nitrates Directive) was exceeded at 66% of the sampling points on the Oja and Tirón alluvial aquifers. The Rivers Oja, Tirón and Zamaca were all above the recommended limit (25 mg L$^{-1}$) at their lowest points, with the River Zamaca exceeding the threshold limit. Pollution at these points was explained by the mixing of surface waters with polluted groundwaters which must have drained into the rivers from the underlying aquifers. These findings indicate the significance of considering the river–alluvial aquifer system as a whole functional unit, within the context of the natural boundaries of the catchment area; this is an important aspect to consider when designating NVZs. The nitrogen exported from these catchments to the River Ebro was estimated to be around 2.4 kt year$^{-1}$, which corresponded to a quarter of the annual N-input into the agricultural areas.

Five zones were analysed separately in order to describe the spatio-temporal patterns of nitrate in the alluvial areas: the upper and mid-sections of the Oja aquifer (Zone 1, unpolluted); the eastern margin of the Oja aquifer (Zone 2, very polluted); the left bank of the River Oja (Zone 3, intermittently polluted); the lower section of the Oja aquifer (Zone 4, very polluted); and the Tirón aquifer (Zone 5, very polluted). Zones 1 and 5 showed decreasing inter-annual trends in nitrate contents (high flow velocities favoured advective transport and dilution processes). This tendency was related to inter-annual variations in precipitation and to downward trends in N-inputs. In Zones 2 and 4 no inter- or intra-annual responses were observed (low flow favoured accumulation processes). Only Zone 3 showed seasonal responses.

This investigation shows that the entire alluvial surface in the study area should be included in the NVZ delimitation, due to its high vulnerability (the shallow water table, high permeability of the alluvial deposits, interconnections between the alluvial aquifers and surface waters, and intensive agricultural land use across the whole alluvial area). Our results highlight the need to include the alluvial area corresponding to the Tirón aquifer as a NVZ, particularly as the Tirón sub-catchment provides more than half of the nitrogen exported from the River Tirón to the River Ebro.

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References
