Importance of the vegetation-groundwater-stream continuum to understand transformation of biogenic carbon in aquatic systems – A case study based on a pine-maize comparison in a lowland sandy watershed (Landes de Gascogne, SW France)

Loris Deirmendjian a,e, Pierre Anschutz a, Christian Morel b, Alain Mollier b, Laurent Augusto b, Denis Loustau b, Luiz Carlos Cotovicz Jr a,c, Damien Buquet a, Katixa Lajaunie a,d, Gwenaelle Chaillou e, Baptiste Voltz a,d, Celine Charbonnier a, Dominique Poirier a, Gwenael Abril a,c,g

a Laboratoire Environnements et Paléoenvironnements Océaniques et Continentaux (EPOC), CNRS, Université de Bordeaux, Allée Geoffroy Saint-Hilaire, 33615 Pessac Cedex, France
b UMR 1391 ISPA, INRA, Bordeaux Sciences Agro, Villenave d’Ornon, 33883, France
c Programma de pos-graduação em Geoquímica, Universidade Federal Fluminense, Outeiro São João Batista s/n, 24020015 Niterói, RJ, Brazil
d Aix Marseille Université, CNRS/INSU, Université de Toulon, Mediterranean Institute of Oceanography (MIO) UM 110, France
e Département Biologie, Chimie, Géographie, Université du Québec à Rimouski, Québec, Canada
f Univ. Lille, CNRS, Univ. Littoral Côte d’Opale, UMR 8187, LOC, Laboratoire d’Océanologie et de Géosciences, F-62 930 Wimereux, France
g Biologie des Organismes et Ecosystèmes Aquatiques (BOREA), Muséum National d’Histoire Naturelle, CNRS, IBDR, UPMC, UCBN, UAG. 61 rue Buffon, 75231 Paris cedex 05, France

HIGHLIGHTS

• Forest groundwater was in anoxic conditions whereas crop groundwater was in oxic conditions.
• Leaching of soil DOC occurred mostly in forest groundwater during high flow period.
• CO₂ and CH₄ were higher in forest groundwater than in crop groundwater.
• CH₄ was higher in crop streams compared to forest streams.
• CO₂ was not different between crop streams and forest streams.

ABSTRACT

During land-aquatic transfer, carbon (C) and inorganic nutrients (IN) are transformed in soils, groundwater, and at the groundwater-surface water interface as well as in stream channels and stream sediments. However, processes and factors controlling these transfers and transformations are not well constrained, particularly with respect to land use effect. We compared C and IN concentrations in shallow groundwater and first-order streams of a sandy lowland catchment dominated by two types of land use: pine forest and maize cropland. Contrary to forest groundwater, crop groundwater exhibited oxic conditions all-year round as a result of higher evapotranspiration and better lateral drainage that decreased the water table below the organic-rich soil horizon, prevented the leaching of soil-generated dissolved organic carbon (DOC) in groundwater, and thus limited consumption of dissolved oxygen (O₂). In crop groundwater, oxic conditions inhibited denitrification and methanogenesis resulting in high nitrate (NO₃⁻; on average...
1. Introduction

Despite their small surface area worldwide (Downing et al., 2012), inland waters have been recognized as key component of the global carbon (C) cycle, constituting a preferential pathway of dissolved and particulate C transport from terrestrial ecosystems to the coastal ocean (Cole et al., 2007; Meybeck, 1982; Ludwig et al., 1996a; 1996b; Meybeck, 1987). Inland waters act as significant sources of carbon dioxide (CO₂) and methane (CH₄) to the atmosphere because inland waters are generally supersaturated with CO₂ and CH₄ compared to the overlying atmosphere (Abril et al., 2014; Bastviken et al., 2011; Borges et al., 2015; Lauverwald et al., 2015; Raymond et al., 2013; Stanley et al., 2016).

Inland waters and specifically small streams are tightly connected to their catchment characteristics such as hydrology and land use, as they receive large inputs of C from land (mainly from soils and groundwater), which in turn control the stream biogeochemical processes and the water composition (Aitkenhead et al., 1999; Deirmendjian and Abril, 2018; Hotchkiss et al., 2015; Johnson et al., 2006; Jones and Mulholland, 1998; McClain et al., 2003; Polsenaere and Abril, 2012; Bodmer et al., 2016; Findlay et al., 2001; Lehrter, 2006). Groundwater discharge has been recognized as an important source of CO₂ in riverine systems, especially in small streams and headwaters (Deirmendjian and Abril, 2018; Hotchkiss et al., 2015; Johnson et al., 2008; Kokic et al., 2015; Marx et al., 2017; Raymond et al., 2013; Wallin et al., 2013). On the contrary to riverine CO₂, riverine CH₄ is likely to originate from wetlands that generally combine a strong hydrological connectivity with riverine waters and a high productivity (Abril et al., 2014; Abril and Borges, 2018). Although some studies found low CH₄ concentrations in the groundwater of Belgium (up to 1.1 μmol L⁻¹; Borges et al., 2018; Jurado et al., 2017), other studies found high CH₄ concentrations in the groundwater of Great Britain (up to 295 μmol L⁻¹; Bell et al., 2017) and in the Appalachian basin of the USA (up to 28,000 μmol L⁻¹; Molofsky et al., 2016). Actually, soil moisture, which controls oxic/anoxic conditions in soil, is the main determinant of terrestrial CO₂ or CH₄ production in soil. As a consequence, CH₄ emissions from soils are high under strictly anaerobic conditions in waterlogged soils whereas CO₂ emissions from soils are high under aerobic conditions in drier soils (Christensen et al., 2003; Moore and Knowles, 1989). Crop-lands affect water mass balance at the plot scale, especially through irrigation and extraction of groundwater, which results in declining water table in many regions worldwide (Foley et al., 2005; Gleick, 2003; Jackson et al., 2001; Postel, 1999; Rosegrant et al., 2002). Investigating spatial dynamics of CO₂ and CH₄ in groundwater in relation with land use is critical better understanding processes governing their terrestrial production and leaching to groundwater.

Croplands cover about 40% of the terrestrial ice-free surface and are often associated with degradation of both ground and surface water quality (Asner et al., 2004; Clague et al., 2015; Foley et al., 2005; Hiscock et al., 1991; Ramankutty and Foley, 1999). Intensive agriculture led to an increase of nitrate (NO₃⁻) entering ground and surface water environments that has fueled aquatic primary production in surface waters and led to low CO₂ and high CH₄ concentrations, the latter being related to enhanced organic matter delivery in sediments (Borges et al., 2018; Carpenter et al., 1999; Clague et al., 2015; Crawford et al., 2016; Jordan and Weller, 1996; Smith, 2003; Zhou et al., 2017). Additionally, aquatic primary production in crop streams is enhanced as a result of low light limitation (clearing of riparian vegetation), and the excessive transport of sediment-bound organic matter and nutrients to surface waters (Berner et al., 2010; Lamba et al., 2015; Ramos et al., 2015; Young and Hurny, 1999). Soil erosion rates in agricultural landscapes are one to two times larger than those in areas with native vegetation (Montgomery, 2007; Quinton et al., 2010). Indeed, riparian forest is usually considered stream buffer zones that attenuate stream bank erosion and NO₃⁻ inputs from croplands (Balestrini et al., 2016; Cey et al., 1999; Christensen et al., 2013; Stott, 2005; Wynn and Mostaghimi, 2006). Denitrification represents a permanent removal pathway that limits the extent and impact of NO₃⁻ contamination by transforming NO₃⁻ to inert dinitrogen (N₂). However, incomplete denitrification can produce nitrous oxide (N₂O), a major anthropogenic ozone-depleting substance (Ravishankara et al., 2009). On the contrary to croplands, forests are known to export fewer nutrients by limiting runoff and leakage of nutrients (Canton et al., 2012; Onderka et al., 2010).

Land use effects on both water composition and biogeochemical processes have been studied in streams and groundwater (Barnes and Raymond, 2010, 2009; Bernot et al., 2010; Bodmer et al., 2016; Jeong, 2001; Lehrter, 2006; Masese et al., 2017; Raymond and Cole, 2003; Rodrigues et al., 2018; Salvia-Castelli et al., 2005; Vidon et al., 2008; Wilson and Xenopoulos, 2009; Young and Hurny, 1999; Zhang et al., 2018), but land use studies with simultaneous groundwater and stream sampling are more scarce (Bass et al., 2014; Borges et al., 2018; Hu et al., 2014).
The objective of this study was to understand how two contrasting types of land use (pine forest and maize cropland) affected C and inorganic nutrient (IN) concentrations in shallow groundwater and in first-order streams of a sandy lowland catchment. We hypothesized that the biogeochemical variability between crop groundwater and forest groundwater was due to agricultural practices that affect N inputs (fertilizer) and water mass balance (irrigation and drainage). We hypothesized that the biogeochemical variability between crop and forest streams originate from differential lateral export of C and IN from two distinct sources (i.e., crop groundwater and forest groundwater) because of a strong hydrological connection between groundwater and streams in the studied catchment.

2. Materials and methods

2.1. Study site

The Leyre catchment (2100 km$^2$) is located in the southwestern part of France. This is a flat coastal plain with a mean slope lower than 0.125% and a mean altitude lower than 50 m (Jolivet et al., 2007). The lithology is relatively homogeneous and composed of sandy permeable surface layers dating from the Plio-Quaternary period (Legigan, 1979; Bertran et al., 2009, 2011). The soils are podzols characterized by a low pH (≈4), low nutrient availability, low cationic exchange capacity, and high organic C content that can reach 50 g per kg of soil (Augusto et al., 2010; Lundström et al., 2000). In Leyre sandy podzols, the low clay and silt content causes a low soil water retention (Augusto et al., 2010).

The study area was a vast wetland until the 19th century, when a wide forest of maritime pine was sown following a landscape drainage campaign resulting from an imperial decree of Napoleon III in 1857 (Jolivet et al., 2007). Currently, the catchment is mainly occupied by C$_3$ pine forest (approximately 85%), with a modest proportion of C$_4$ maize cropland (approximately 15%) (Fig. 1; Jolivet et al., 2007). Following catastrophic forest wildfires, the maize croplands were installed during the second half of the 20th century. Consequently, their spatial distribution was not based on soil properties, as confirmed by the similar mean values of soil texture in local croplands and forests (Augusto et al., 2010; Jolivet et al., 2003). During the maize cropping season (usually May to November), farmers irrigate the plots by pumping shallow groundwater (~1–5 m deep) almost daily to maintain adequate soil moisture status, whereas maritime pine stands are never irrigated (Govind et al., 2012). As N is not limiting for tree growth in our study region (Trichet et al., 2009), forests are never fertilized with N. Conversely, croplands generally receive two N fertilizer applications annually, a first at the beginning of May (30–50 kg N ha$^{-1}$), and second at the beginning of June with 200–250 kg N ha$^{-1}$ (Canton et al., 2012; Jambert et al., 1997; Ulrich et al., 2002). Additionally, in order to maintain soil pH in the 5.5–6.0 range, local maize croplands are limed with crushed limestone (CaCO$_3$) containing a small portion of dolomite (CaMg(CO$_3$)$_2$) (10 t ha$^{-1}$ right after forest conversion and then 0.5 t ha$^{-1}$ an$^{-1}$; Jolivet et al., 2003).

The climate is oceanic with a mean annual air temperature of 13 °C and a mean annual precipitation of 930 mm (Moreaux et al., 2011). Owing to the low slope, the low soil water retention and the high permeability of the soil (i.e., hydraulic conductivity is approximately 40 cm h$^{-1}$; Corbier et al., 2010), the percolation of rain water is fast (55 cm h$^{-1}$ on average, Vernier and Castro, 2010). Consequently, surface runoff does not occur as the excess of rainfall percolates into the soil and recharges the shallow groundwater, causing the water table to rise. The sandy permeable surface layers contain a free and continuous water table that is strongly interconnected with the superficial river network. This is facilitated by a dense network of drainage ditches, initiated in the 19th century and currently maintained by forest managers in order to enhance tree regeneration and growth (Thivolle-Cazat and Najar, 2001). During the sampling period, channels of some crop streams were dredged before they began to flow again. This was done to optimize local cropland drainage and to feed croplands with IN and organic residuals found in the stream sediments. To increase soil permeability and to optimize lateral drainage in local maize
croplands, farmers practice subsoiling and agricultural ditches are generally deeper (2.0–2.5 m) than forest ditches (1.0 m).

2.2. Sampling strategy

We defined order 0 as groundwater and order 1 as streams and ditches either having no tributaries or being seasonally dry (from June to December during our sampling period). We selected 17 sampling stations (5 shallow groundwater and 12 first-order streams) within the Leyre catchment (Table 1; Fig. 1). The groundwater sampling stations were located in maize cropland (n = 2), pine forest (n = 2; one is the Bilos station (FR-Bil) of the ICOS Research infrastructure) and in a riparian forest adjacent to a maize cropland (n = 1; Table 1; Fig. 1). The stream sampling stations were chosen based on the different proportions of croplands in their respective catchments (Table 1; Fig. 1).

Groundwater was sampled for temperature, electrical conductivity (EC), pH, dissolved oxygen (O₂), dissolved iron (Fe²⁺), nitrate (NO₃⁻), total alkalinity (TA), dissolved inorganic carbon (DIC), particulate organic carbon (POC) and the POC content of the TSM (POCs). The pCO₂ in groundwater and streams was measured directly using an equilibrator (Frankignoulle and Borges, 2001; Polsenaaere et al., 2013) following the procedure of Deirmendjian and Abril (2018).

We stored the total alkalinity (TA) samples in polypropylene bottles after filtration using a syringe equipped with glass fiber filters (GF/F; 0.7 μm). TA was then analyzed on filtered samples by automated electro-titration on 50 mL samples with 0.1 N HCl as the titrant. The equivalence point was determined from pH between 4 and 3 with the Gran method (Gran, 1952). Precision based on replicate analyses was better than ±5 μmol L⁻¹. For samples with a very low pH (<4.5), we bubbled the water with atmospheric air in order to degas the CO₂. Consequently, the initial pH increased above 5, and the TA titration was then performed (Abril et al., 2015).

We calculated DIC from pCO₂, TA, and temperature measurements using the carbonic acid dissociation constants of Millero (1979) and the CO₂ solubility from Weiss (1974), using the CO₂SYS software (Lewis et al., 1998). The δ¹³C-DIC samples were collected using 120 mL glass serum bottles sealed with a rubber stopper and treated with 0.3 mL of HgCl₂ at 20 g L⁻¹ to avoid any microbial respiration during storage. Vials were carefully sealed such that no air remained in contact with samples and were stored in the dark to prevent photodissolution. The δ¹³C-DIC measurements were performed with the headspace technique using an isotope ratio mass spectrometer coupled to an elemental analyzer (EA-IRMS, Micromass Isoprime) equipped with a manual gas injection port as described in Gillikin and Bouillon (2007).

CH₄ was also measured using a headspace technique in 60 mL glass serum bottles. The headspace was created with 10 mL of N₂ gas. We then injected 0.5 mL of the headspace in a gas chromatograph equipped with a flame ionization detector (GC-FID).

DOC samples were obtained after filtration in the field through pre-combusted GF/F (0.7 μm). DOC filtrates were stored in pre-combusted Pyrex vials (25 mL), acidified with 50 μL of 37% HCl to reach pH 2, and kept at 4 °C in the laboratory before analysis. The DOC concentrations were measured with a SHIMADZU TOC 500 analyzer (in TOC-IC mode), using a technique based on thermal oxidation after a DIC removal step (Sharp, 1993). The repeatability was better than 10 μmol L⁻¹.

2.3. Field measurements and laboratory analyses

Groundwater and streams were sampled at approximately monthly time intervals between Jan. 2014 and Jul. 2015 (Table S1). In total, throughout the sampling period, we sampled 55 groundwaters and 137 stream waters.

Table 1

<table>
<thead>
<tr>
<th>Stream order</th>
<th>Description</th>
<th>Catchment area (km²)</th>
<th>Crop (%)</th>
<th>Forest (%)</th>
<th>Urban (%)</th>
<th>During high flow</th>
<th>During base flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ditch</td>
<td>1.0</td>
<td>86.5</td>
<td>13.5</td>
<td>0.0</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>Ditch</td>
<td>1.3</td>
<td>53.8</td>
<td>46.2</td>
<td>0.0</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>Ditch</td>
<td>11.3</td>
<td>44.2</td>
<td>55.8</td>
<td>0.0</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>Ditch</td>
<td>13.4</td>
<td>42.5</td>
<td>57.5</td>
<td>0.0</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>Stream</td>
<td>57.0</td>
<td>30.7</td>
<td>69.3</td>
<td>0.0</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>Stream</td>
<td>16.8</td>
<td>7.8</td>
<td>92.2</td>
<td>0.0</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>1</td>
<td>Ditch</td>
<td>7.0</td>
<td>5.8</td>
<td>94.2</td>
<td>0.0</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>1</td>
<td>Ditch</td>
<td>2.3</td>
<td>5.2</td>
<td>94.8</td>
<td>0.0</td>
<td>F</td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>Stream</td>
<td>16.0</td>
<td>4.6</td>
<td>93.8</td>
<td>1.6</td>
<td>C</td>
<td>F</td>
</tr>
<tr>
<td>1</td>
<td>Stream</td>
<td>34.0</td>
<td>3.8</td>
<td>96.2</td>
<td>0.0</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>1</td>
<td>Stream</td>
<td>31.0</td>
<td>2.3</td>
<td>97.7</td>
<td>0.0</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>1</td>
<td>Headwater</td>
<td>0.3</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>0</td>
<td>Groundwater in a riparian forest but very near (5 m) a maize cropland (P1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>0</td>
<td>Groundwater in maize cropland (P2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>0</td>
<td>Groundwater in maize cropland (P3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>0</td>
<td>Groundwater in pine forest (P4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>0</td>
<td>Groundwater in pine forest (P5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F</td>
<td>F</td>
</tr>
</tbody>
</table>
The water for TSM and POC measurements was filtered through preweighed and pre-combusted GF/F glass fiber filters (0.7 μm). The filters were dried at 60 °C and stored in the dark, and subsequently, TSM was determined by gravimetry. POC was measured using the same filter. The filters were acidified in crucibles with 2 N HCl to remove carbonates and were then dried at 60 °C to remove inorganic carbon and most of the remaining acid and water (Etcheber et al., 2007). POC content was measured by combustion (1500 °C) using a LECO CS 200 analyzer and the CO2 formed was determined quantitatively by infrared absorption. POC in μmol L−1 and POC% were then calculated. The uncertainty was ±0.05% of TSM.

For IN determination, water was filtered through a 0.20 μm cellulose acetate syringe membrane. Subsamples for Fe2+ were acidified with 37% HCl to prevent precipitation of iron oxide, whereas subsamples for NH4+ and NO3− were not acidified but kept frozen until later analyses. Then, NH4+, NO3−, and Fe2+ were analyzed by colorimetry according to standard techniques. NH4+ was analyzed following the procedure of Harwood and Kühn (1970). NO3− was analyzed by flow injection analysis following the procedure of Anderson (1979). Fe2+ was analyzed using the ferrozine method (Stookney, 1970). Precision was ±10% for NH4+ and NO3−, and ±5% for Fe2+.

EC, temperature, O2, and pH were measured using portable probes (WTW®). Before each field trip, the pH probe was calibrated using two NBS buffer solutions (4 and 7), the oxygen polarographic probe was calibrated to 100% in a humid atmosphere and the conductivity probe was calibrated using a salinity standard.

2.4. Statistical analyses

K-means clustering analysis (MacQueen, 1967) was used to classify waters either as forest-dominated or as cropland-affected (Table 1). Indeed, K-means clustering analysis allows partitioning a dataset into k groups (i.e., clusters) pre-specified by the analyst (MacQueen, 1967). Contrary to forest waters at our study site, crop waters exhibit disproportionately higher NO3− concentration as a result of N fertilizer use on maize cropland (Canton et al., 2012; De Wit et al., 2005; Jambert et al., 1997, 1999). Consequently, in the K-means clustering analysis we used NO3− concentration data as a proxy to establish a statistical distinction between forest and crop waters (Table 1). K-means clustering analysis was performed one time with the groundwater dataset (but excluding the riparian groundwater) and a second time with the first-order streams dataset. We excluded data from riparian groundwater because we have considered riparian groundwater as a cluster itself (Table 1).

Principal component analysis (PCA) was used to condense multivariate information on correlated biogeochemical parameters to a set of uncorrelated variables called principal components (further referred to as dimensions). PCA was performed one time with a dataset consisting of each measured parameter in groundwater (but excluding the riparian groundwater) and a second time with the corresponding first-order streams dataset. PCA was performed separately for groundwater and streams because particulate parameters were not present in groundwater. If PCA were not performed separately for groundwater and streams, all data from groundwater would have been removed from the analysis (indeed, if one parameter is missing for a given sampling station, the sampling station is entirely deleted from the PCA). In addition, performing the PCA separately for groundwater and streams led to information that was more robust with respect to the biogeochemical variability induced by land use, in either groundwater or streams. However, to observe whether the two groundwater (crop and forest) and two streams (crop and forest) sources could be distinguished mathematically in one PCA, we performed an additional PCA with data from both groundwater and streams that excluded particulate parameters from the analysis. All concentrations data were log-transformed prior to PCA. The PCAs showed the biogeochemical variability across forest, cropland, and hydrological seasons in either groundwater or first-order streams.

Later, non-parametric bivariate analyses (Mann-Whitney statistical tests) were used to estimate if hydrological seasons or increasing stream order significantly influenced the concentration of a biogeochemical parameter. Linear regressions were performed to model the relationships between two variables by fitting a linear equation to observed data.

K-means clustering analysis (package Stats) and PCA analysis (package FactoMineR for analysis and package factoextra for visualization; Kassamba and Mundt, 2017; Lê et al., 2008) were performed with R software version 3.1.4 (R Core Team, 2018). Mann-Whitney tests and linear regressions were performed with Graph Pad Prism version 7 software.

3. Results

3.1. Hydrology

In previous work based on the same dataset, but excluding cropland sampling stations, we identified two major hydrological seasons (Deirmendjian and Abril, 2018). One defined a high flow period as two relatively short flood events that occurred in Jan. 2014–Mar. 2014 and in Feb. 2015–Mar. 2015, whereas we defined the base flow period as two longer periods of low flow occurring in Apr. 2014–Jan. 2015 and Apr. 2015–Jul. 2015. During high flow, the average and the maximum river flows were 50 m3 s−1 and 119 m3 s−1, respectively. During base flow, the average and the minimum river flow were 10 m3 s−1 and 5 m3 s−1, respectively. The water tables in the forest, riparian forest, and cropland exhibited similar temporal fluctuations but with a different intensity, and the forest had an overall higher water table depth than the cropland (Fig. 2). The water table in the riparian area exhibited intermediate depth between the forest and cropland sites (Fig. 2). As surface runoff was negligible in the studied sandy and flat catchment, most of the stream water likely originated from groundwater discharge.

To investigate the temporal variability of the studied biogeochemical parameters, we chose to rely on hydrological regimes (high flow and base flow periods) rather than on temperature periods (seasons). At our study site climate was oceanic (by definition very temperate) and the amplitude of the water temperature was not as high as the amplitude of the river flow. As an example, Leyre River (main stem) flow could be up to 119 m3 s−1 and could be down to 5 m3 s−1, whereas the highest water temperature amplitude occurred in forest streams and was 6.4–25.8 °C (Table 2). Additionally, most of the lateral export

Fig. 2. Water table depth during the sampling period (Jan. 2014–Jul. 2015) across land use in the Leyre catchment. The water table in riparian area is the water table at P1 (Table 1). The water table in crop plot is the average ± standard deviations of water tables at P2 and P3 (Table 1). The water table in forest plot is the average ± standard deviations of water tables at P4 and P5 (Table 1).
occurred during the short periods of high flow (up to 90% for DOC, Deirmendjian et al., 2018). Thus, characterizing biogeochemical variability and biogeochemical processes in relation with land use during this hydrological period was important. Furthermore, the seasonality induced by water temperature was to a certain extent included in the defined hydrological regimes since the high flow period was associated

### Table 2

Values of carbon and ancillary parameters throughout sampling period (Jan. 2014-Jul. 2015) in crop and forest continuums and in riparian groundwater. Numbers between brackets are corresponding to the sampling size. For each parameter, the table showed average ± standard deviations and the range.

<table>
<thead>
<tr>
<th>Groundwaters (22)</th>
<th>Streams (59)</th>
<th>Forest_HF (16)</th>
<th>Riparian_HF (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.5 ± 0.2</td>
<td>6.0 ± 0.3</td>
<td>4.5 ± 0.3</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>14.5 ± 1.8</td>
<td>13.6 ± 4.2</td>
<td>12.8 ± 1.8</td>
</tr>
<tr>
<td>EC (µS cm⁻¹)</td>
<td>360 ± 70</td>
<td>6.4-25.8</td>
<td>8.5-15.1</td>
</tr>
<tr>
<td>NO₃ (µmol L⁻¹)</td>
<td>1140 ± 485</td>
<td>340 ± 200</td>
<td>25 ± 4.0</td>
</tr>
<tr>
<td>NH₄⁺ (µmol L⁻¹)</td>
<td>0.4 ± 0.8</td>
<td>6.1 ± 7.0</td>
<td>4.5 ± 7.0</td>
</tr>
<tr>
<td>O₂ (µmol L⁻¹)</td>
<td>0.3-3.5</td>
<td>0-40</td>
<td>0.3-30</td>
</tr>
<tr>
<td>CH₄ (nmol L⁻¹)</td>
<td>220 ± 465</td>
<td>25-730</td>
<td>75-115</td>
</tr>
<tr>
<td>pCO₂ (ppmv)</td>
<td>30,650 ± 11,590</td>
<td>4480 ± 2680</td>
<td>50,630 ± 26,070</td>
</tr>
<tr>
<td>TA (µmol L⁻¹)</td>
<td>290 ± 45</td>
<td>110-400</td>
<td>20-30</td>
</tr>
<tr>
<td>DIC (µmol L⁻¹)</td>
<td>370 ± 60</td>
<td>360 ± 70</td>
<td>90 ± 15</td>
</tr>
<tr>
<td>DOC (µmol L⁻¹)</td>
<td>275-880</td>
<td>220-2290</td>
<td>310-3670</td>
</tr>
<tr>
<td>TSM (mg L⁻¹)</td>
<td>5.6 ± 8.6</td>
<td>0.1-50.5</td>
<td>2.3 ± 1.7</td>
</tr>
<tr>
<td>POC (%)</td>
<td>28 ± 10</td>
<td>28 ± 10</td>
<td>50 ± 35</td>
</tr>
<tr>
<td>POC (µmol L⁻¹)</td>
<td>120 ± 180</td>
<td>17.5 ± 10</td>
<td>25.5 ± 10</td>
</tr>
</tbody>
</table>

### Table 3

Values of carbon and ancillary parameters throughout sampling period (Jan. 2014-Jul. 2015) in different types of groundwater across hydrological seasons. Numbers between brackets are corresponding to the sampling size. For each parameter, the table showed the average ± standard deviations and the range. We defined six groups that are Cropland_HF/Cropland_BF, Forest_HF/Forest_BF and Riparian_HF/Riparian_BF corresponding to groundwaters during high flow (HF) or base flow (BF); in either cropland, forest or riparian forest.

<table>
<thead>
<tr>
<th>Groundwater</th>
<th>Cropland_HF (4)</th>
<th>Cropland_BF (18)</th>
<th>Forest_HF (6)</th>
<th>Forest_BF (16)</th>
<th>Riparian_HF (2)</th>
<th>Riparian_BF (9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.6 ± 0.3</td>
<td>4.5 ± 0.2</td>
<td>4.4 ± 0.3</td>
<td>4.5 ± 0.3</td>
<td>4.7 ± 0.1</td>
<td>4.6 ± 0.1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>12.8 ± 1.7</td>
<td>14.9 ± 2.4</td>
<td>10.7-14.5</td>
<td>11.1-15.7</td>
<td>11.5 ± 1.5</td>
<td>12.2 ± 0.6</td>
</tr>
<tr>
<td>EC (µS cm⁻¹)</td>
<td>370 ± 60</td>
<td>360 ± 70</td>
<td>90 ± 15</td>
<td>90 ± 10</td>
<td>185-215</td>
<td>115 ± 50</td>
</tr>
<tr>
<td>NO₃ (µmol L⁻¹)</td>
<td>1140 ± 485</td>
<td>340 ± 200</td>
<td>25 ± 4.0</td>
<td>75 ± 70</td>
<td>280 ± 50</td>
<td>100 ± 70</td>
</tr>
<tr>
<td>NH₄⁺ (µmol L⁻¹)</td>
<td>0.4 ± 0.8</td>
<td>6.1 ± 7.0</td>
<td>4.5 ± 7.0</td>
<td>1.8 ± 1.7</td>
<td>0.4 ± 0.4</td>
<td>0 ± 1.5</td>
</tr>
<tr>
<td>O₂ (µmol L⁻¹)</td>
<td>0.3-3.5</td>
<td>0-40</td>
<td>0.3-30</td>
<td>0-8-7</td>
<td>0.3-1.5</td>
<td>0-1.5</td>
</tr>
<tr>
<td>CH₄ (nmol L⁻¹)</td>
<td>220 ± 465</td>
<td>25-730</td>
<td>75-115</td>
<td>70-200</td>
<td>170 ± 100</td>
<td>100 ± 80</td>
</tr>
<tr>
<td>pCO₂ (ppmv)</td>
<td>32,050 ± 12,000</td>
<td>32,560 ± 12,000</td>
<td>28,100-11,580</td>
<td>59,080 ± 25,060</td>
<td>21,530 ± 5950</td>
<td>47,700 ± 29,590</td>
</tr>
<tr>
<td>TA (µmol L⁻¹)</td>
<td>204 ± 70</td>
<td>210 ± 70</td>
<td>190 ± 10</td>
<td>170 ± 10</td>
<td>170-170</td>
<td>170-170</td>
</tr>
<tr>
<td>DIC (µmol L⁻¹)</td>
<td>1140 ± 485</td>
<td>340 ± 200</td>
<td>25 ± 4.0</td>
<td>75 ± 70</td>
<td>280 ± 50</td>
<td>100 ± 70</td>
</tr>
<tr>
<td>DOC (µmol L⁻¹)</td>
<td>320-590</td>
<td>340-880</td>
<td>575-3670</td>
<td>310-1720</td>
<td>275-350</td>
<td>310-620</td>
</tr>
</tbody>
</table>
with lower water temperatures while the base flow period was associated with higher water temperatures (Tables 2–4).

3.2. K-means clustering analysis

For both hydrological seasons (i.e., high and base flow), we partitioned each sampling stations (except riparian groundwater), into either cropland-affected or forest-dominated waters (Table 1). K-means clustering analysis produced satisfactory results. Logically, groundwater located in cropland was classified as crop water whereas groundwater located in forest was classified as forest water (Table 1). Stream sampling stations having >30% of croplands in their respective catchment were always classified as crop waters (Table 1). Stream sampling stations having ~8% of croplands in their respective catchment were always classified as forest waters excepting two times (Table 1). These two stream sampling stations were located a few kilometers downstream from important maize croplands. Specifically, one station was a ditch strongly vegetated during the base flow period that showed signs of N fertilizer uptake from upstream cropland and, therefore, this ditch was logically classified as a crop station during base flow (Table 1). One station was a stream that exhibited a high water flow during the high flow period, which probably increased the upstream cropland influences during this hydrological period and, therefore, this stream was logically classified as a crop station during high flow (Table 1).

Excepting one strictly forested headwater, the other sampled streams were not strictly forested or cropped (Table 1). Consequently, as explained further, some biogeochemical variability between forest and crop streams was introduced by simple water mixing from two distinct sources: forest groundwater and crop groundwater. We used the term crop stream to indicate a stream classified as a crop-affected one, although such stream was a forest stream affected by cropland rather that a strictly crop stream.

3.3. Land use influence on water composition of shallow groundwater

PCA on the groundwater dataset revealed that groundwater biogeochemical variability was strongly dependent on land use (maize cropland vs. pine forest) and hydrological seasons (base flow vs. high flow) (Fig. 3a, b). The first three PCA dimensions covered 44%, 17.5% and 10.5% of the total variance within the dataset, respectively (Fig. 3a, b).

PCA dimension 1 clearly separated forest groundwater from crop groundwater based on two groups of variables negatively correlated with one another (Fig. 3a). One group of variables was characterized crop groundwater and was composed of EC, NO\textsubscript{3}, \textsuperscript{\delta}{C-DIC}, and O\textsubscript{2}, whereas the second group of variables was characterized forest groundwater and was composed of DIC, pCO\textsubscript{2}, CH\textsubscript{4}, Fe\textsuperscript{3+}, and NH\textsubscript{4}\textsuperscript{+} (Fig. 3a). Indeed, we observed that the yearly average of EC (+270 µmol cm\textsuperscript{-2}), NO\textsubscript{3} (+1115 µmol L\textsuperscript{-1}), \textsuperscript{\delta}{C-DIC} (+6.9%), and O\textsubscript{2} (+200 µmol L\textsuperscript{-1}) were higher in crop groundwater than in forest groundwater and were significantly and positively affected by cropland cover (Table 2; Fig. 4b, c, f, j). Conversely, we observed higher DIC (+1010 µmol L\textsuperscript{-1}), pCO\textsubscript{2} (+1985 ppmv), CH\textsubscript{4} (+1730 µmol L\textsuperscript{-1}), Fe\textsuperscript{3+} (+14.1 µmol L\textsuperscript{-1}), and NH\textsubscript{4}\textsuperscript{+} (+4.1 µmol L\textsuperscript{-1}) in forest groundwater than in crop groundwater; these were significantly and positively affected by forest cover (Table 2; Fig. 4d, e, g, h, k). In riparian groundwater, EC, NO\textsubscript{3}, \textsuperscript{\delta}{C-DIC}, O\textsubscript{2}, DIC, pCO\textsubscript{2}, and CH\textsubscript{4} exhibited intermediate values between the groundwater of forest and crop sites, whereas Fe\textsuperscript{3+} and NH\textsubscript{4}\textsuperscript{+} were low and close to those found in crop groundwater (Table 2; Fig. 4b, c, d, e, f, g, h, j).

In crop groundwater, EC, NO\textsubscript{3}, \textsuperscript{\delta}{C-DIC}, and O\textsubscript{2} were not significantly affected by hydrological seasons (Fig. 3a, 3c, h, j, k). However, \textsuperscript{\delta}{C-DIC} (+1.1%), NO\textsubscript{3} (+120 µmol L\textsuperscript{-1}), and DO (+130 µmol L\textsuperscript{-1}) were slightly higher (but not significantly) during base flow compared to high flow (Table 3; Fig. 5c, h, j, k, l). In forest groundwater, pCO\textsubscript{2}, DIC, CH\textsubscript{4}, and DO were significantly affected by hydrological seasons (Table 3; Fig. 5g, h, i, k, l). DO (+1490 µmol L\textsuperscript{-1}) was significantly higher during high flow, whereas pCO\textsubscript{2} (+30,980 ppmv), DIC (+1330 µmol L\textsuperscript{-1}) and CH\textsubscript{4} (+1780 nmol L\textsuperscript{-1}) were significantly higher during base flow (Table 3; Fig. 52 and 54g, h, i, l). In crop and riparian groundwater, we also observed higher pCO\textsubscript{2} and DIC values during base flow, but with lower intensities than in forest groundwater (Table 3; Fig. 52h, j, k).

3.4. Land use influence on water composition of first-order streams

Fig. 3c–d present PCA based on first-order streams data set. The first three PCA dimensions covered 28.6%, 18.5% and 13.8% of the total variance within the dataset, respectively (Fig. 3c, d).

Interestingly, the PCA based on the first-order streams dataset did not clearly separate crop streams from forest streams as it did for groundwater dataset (Fig. 3a–d). This implied lower spatial variability in streams in relation to land use in than in groundwater (Tables 2–4; Fig. 4). Nevertheless, a land use gradient was observed on PCA dimension 2 (Fig. 3c, d). PCA dimension 2 was best defined by a group of variables composed of EC, CH\textsubscript{4}, NO\textsubscript{3}, NH\textsubscript{4}\textsuperscript{+}, DIC, TSM, and POC, which collectively characterized crop streams (Fig. 3c, d). On a yearly average basis, significantly higher EC (+105 µmol cm\textsuperscript{-2}), CH\textsubscript{4} (+220 µmol L\textsuperscript{-1}), NO\textsubscript{3} (+265 µmol L\textsuperscript{-1}), NH\textsubscript{4}\textsuperscript{+} (+4.3 µmol L\textsuperscript{-1}), DO (+135 µmol L\textsuperscript{-1}), TSM (+3.3 mg L\textsuperscript{-1}), and POC (+70 µmol L\textsuperscript{-1}) were observed in crop streams compared to forest streams (Table 2; Fig. 4b, c, d, g, l, m, o). High CH\textsubscript{4}, NH\textsubscript{4}\textsuperscript{+}, and DOC...
concentrations were characteristics of forest groundwater, but in streams, these parameters were characteristic of crop streams (Fig. 3a–d). In addition, pCO$_2$, DIC, $\delta^{13}$C-DIC and O$_2$ were not able to separate crop streams from forest streams as they did for groundwaters (Fig. 3a–d). On a yearly average basis, no significant differences were observed between crop and forest streams for these four parameters (Fig. 3f, h, j, k).

The relatively low temporal variability between high and base flow periods observed in both crop and forest streams for the studied parameters did not allow the PCA based on stream data set to clearly separate base flow samples from high flow samples (Table 4; Figs. 3c–d, S3, S4). Nevertheless, in crop streams, pH (+0.2) and $\delta^{13}$C-DIC (+3.8‰) were significantly higher during base flow while pCO$_2$ (−1160 ppmv), NO$_3$ (−130 μmol L$^{-1}$) and DOC (−230 μmol L$^{-1}$) were significantly lower.

Fig. 3. Principal component analysis (PCA) of shallow groundwater dataset (a–b) and first-order streams dataset (c–d). We represented only the first three dimensions. Numbers between brackets are corresponding to the sampling size. The sampling size in the PCAs did not correspond exactly to the sampling size in Tables 3 and 4 because R software deletes stations from the analysis with a missing value for one parameter. In these PCAs, we used all the quantitative variables measured in this study. In each PCA, we plotted as well the individuals separated in four groups. The first group corresponds to cropland-affected samples during high flow (Crop_HF), the second group corresponds to cropland-affected samples during base flow (Crop_BF), the third group corresponds to forest-dominated samples during high flow (Forest_HF) and the fourth group corresponds to forest-dominated samples during base flow (Forest_BF). The mean value of each qualitative group has 95% chance to be within the corresponding confidence ellipse.

Fig. 4. Values of carbon and ancillary parameters throughout the sampling period (Jan. 2014–Jul. 2015) in groundwater and streams across land use. Histograms represent the mean with standard deviations of a given parameter. We defined four groups that are GW_Forest/GW_Crop and I_Forest/I_crop corresponding to groundwaters and streams order 1 either dominated by forests or croplands. A fifth group is GW_Riparian and corresponding to riparian groundwater. Then, based on Mann-Whitney statistical analysis, we compared GW_Crop VS I_Crop, GW_Forest VS I_Forest, GW_Crop VS GW_Forest, I_Crop VS I_Forest. Three red stars (****) indicate that data were significantly different with \( p < 0.001 \). One blue star (*) indicates that data were significantly different with \( p < 0.05 \). No stars indicate that data were not significantly different (\( p > 0.05 \)). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
during the same period (Table 4; Fig. S3a, j, c, h, l, m, o). In streams, TSM and POC were significantly higher during high flow but with a higher intensity in crop streams than in forest streams (Table 4; Fig. S3m, o). Interestingly, in both forest and crop streams, POC% was not significantly affected by hydrological regime (Table 4; Fig. S3n).

3.5. Upstream-downstream distribution of biogeochemical parameters

To explore the influence of land use on water composition at the groundwater-stream continuum, we observed the upstream-downstream (groundwater-stream) distribution of biogeochemical parameters along forest and crop continuums (Table 2; Fig. 4). Along both types of continuum, some parameters (i.e., pCO$_2$, TA, DIC, δ$^{13}$C-DIC, pH, O$_2$) exhibited the same upstream-downstream distribution, whereas other parameters (i.e., EC, NO$_3^-$, NH$_4^+$, Fe$^{2+}$, CH$_4$, DOC) exhibited a different upstream-downstream distribution (Table 2; Fig. 4).

In crop and forest continuums, we observed strong spatial patterns for pCO$_2$, TA, DIC, δ$^{13}$C-DIC, and pH: pCO$_2$ and DIC decreased while TA remained more or less constant, and δ$^{13}$C-DIC and pH increased (Table 2; Fig. 4a, h, i, j, k). However, a larger decrease in pCO$_2$ levels in the forest continuum suggested a more intense degassing in forest streams (Table 2; Fig. 4h). We also observed an increase in O$_2$ in both types of continuum, which could result from stream ventilation, although with a higher intensity in forest continuum (Table 2; Fig. 4f, h).

EC decreased downstream in the crop continuum, but did not in the forest continuum where EC remained very stable and much lower than in the crop continuum (Table 2; Fig. 4b). NO$_2^-$ decreased downstream between groundwater and streams in croplands, and in contrast, in forests NO$_2^-$ increased downstream between groundwater and streams (Table 2; Fig. 4c). NH$_4^+$, Fe$^{2+}$, and CH$_4$ decreased in the forest continuum but they increased in the crop continuum (Table 2; Fig. 4d, e, g). DOC significantly decreased in the forest continuum but remained stable in the crop continuum (Table 2; Fig. 4i). TSM and POC were significantly higher in crop relative to forest streams; however, similarly high POC% (28%) was observed in both types of streams (Table 2; Fig. 4m, n, o).

3.6. Biogeochemistry dynamics in the groundwater-stream continuum

PCA with groundwater and streams datasets indicated mathematically that streams were fed with two distinct sources: forest groundwater mostly characterized by high pCO$_2$, DIC, and CH$_4$ concentrations and crop groundwater mostly characterized by high NO$_3^-$ concentrations (Fig. 5). Forest and crop streams were characterized by higher O$_2$, δ$^{13}$C-DIC and pH values than in groundwater (Fig. 5). In this PCA, the distinction between forest and crop streams was primarily a function of NO$_3^-$, crop streams points were moved upward along dimension 2 (Fig. 5). Throughout the sampling period, we observed a negative linear relationship ($R^2 = 0.6$, $p < 0.001$, $n = 192$) between CO$_2$ and O$_2$ for all sampled groundwater and streams (Fig. 6a). On the one side, stream samples were mostly characterized by high O$_2$ (mean was 290 μmol L$^{-1}$) and low CO$_2$ (mean was 4480 ppmv), excepting some forest streams during summer that were characterized by low O$_2$ (down to 110 μmol L$^{-1}$) and high CO$_2$ (up to 27,200 ppmv) (Table 2; Fig. 6a, S4f, h). On the other side, anoxic conditions associated with high CO$_2$ (mean was 50,630 ppmv) were characteristic of forest groundwater, whereas crop groundwater exhibited O$_2$ (mean was 220 μmol L$^{-1}$) and CO$_2$ (mean was 30,650 ppmv) intermediate between streams and forest groundwater (Table 2; Fig. 6a). In forest groundwater, DOC was negatively and linearly correlated with CO$_2$ ($R^2 = 0.4$, $p < 0.001$, $n = 22$) suggesting that part of groundwater CO$_2$ came from degradation.

![Fig. 5. Principal component analysis (PCA) of shallow groundwater and stream datasets. We represented only the first three dimensions. Numbers between brackets are corresponding to the sampling size. The sampling size in the PCA did not correspond exactly to the sampling size in Table 2 because R software deletes stations from the analysis with a missing value for one parameter. In these multivariate statistical analyses, we used all the quantitative variables measured in this study. We defined four groups that are Crop_GW/Forest_GW and Crop_stream/Forest_stream, which are corresponding to groundwater and streams order 1, either dominated by forests or croplands. The mean value of each qualitative group has 95% chance to be within the corresponding confidence ellipse.](image-url)
of groundwater DOC (Fig. 6b). A comparison of CO₂ and CH₄ for all sampled groundwaters and streams showed that a large portion of the CO₂ and CH₄ in forest streams could come from forest groundwater discharge (Table 2; Fig. 6e). In crop streams, CH₄, NH₄⁺, and Fe²⁺ could not originate from crop groundwater discharge since they had much lower CH₄, NH₄⁺, and Fe²⁺ concentrations than crop streams (Table 2; Fig. 6c, 7d, f). We observed a positive linear relationship between CH₄ and NH₄⁺ (R² = 0.4, p < 0.001, n = 53) in crop streams, demonstrating that these two compounds may come from the same source (Fig. 7c). Conversely, a comparison of O₂ and NH₄⁺ or Fe²⁺ in forest streams indicated that NH₄⁺ and Fe²⁺ were mostly discharged through forest groundwater (Fig. 7b, f). In forest streams, the negative linear relationship between O₂ and NH₄⁺ (R² = 0.1, p-value < 0.05, n = 70), Fe²⁺ (R² = 0.5, p-value < 0.001, n = 77), or CH₄ (R² = 0.1, p-value < 0.001, n = 77) suggested oxidation of these reduced compounds in the stream water column (Fig. 6c, 7b, f). We observed a gradient of NO₃⁻ concentration, from high values to low values, between crop groundwater (mean was 1140 µmol L⁻¹), to riparian groundwater and crop streams (310 and 340 µmol L⁻¹, respectively), to forest streams (75 µmol L⁻¹) and to forest groundwater (25 µmol L⁻¹) (Table 2; Fig. 7a, c, e). In crop streams, a large share of riverine NO₃⁻ could be discharged through crop groundwater. Conversely, NO₃⁻ concentration in forest streams could not be explained by NO₃⁻ concentration in forest groundwater (Table 2; Fig. 7a, c, e). In crop groundwater, high NO₃⁻ concentrations were associated with low CH₄ concentrations. In crop streams, high NO₃⁻ concentrations could be related to high CH₄ concentrations (Fig. 7c).

4. Discussion

4.1. Water table depth in relation to land use

At the studied catchment scale, lithology, topography, soils, and precipitation are more or less uniform (Augusto et al., 2010; Jolivet et al., 2003). At the plot scale, spatial variability of water table depth in relation to land use was thus necessarily dependent on how water outputs (drainage, evapotranspiration or groundwater storage) of the water mass balance were human-affected (Govind et al., 2012; Stella et al., 2009). Local forests are never irrigated, conversely, irrigation with extraction of groundwater (that decreases groundwater storage) in local croplands could strongly bias the water mass balance at the plot scale since about half of the water diverted for irrigation is rapidly consumed through evapotranspiration (e.g., Jackson et al., 2001). Additionally, evapotranspiration in maize croplands is typically higher than in forests owing to the larger stomatal conductance that makes the exchange of C and water between the biosphere and the atmosphere much easier (Govind et al., 2012; Stella et al., 2009). Other studies have shown that the combination of subsiding practices (increasing soil permeability) with deep agricultural ditches in croplands also affected water mass balance at the plot scale by enhancing lateral drainage of groundwater (Evans et al., 1996; Robinson et al., 1985). From an 8 year survey of local cropland, Juste et al. (1982) showed that lateral drainage strongly affected the water mass balance at the plot scale as it represented an annual mean of 637 mm (70% of the amount of precipitation), whereas precipitation was estimated at 922 mm. At the forest plot scale, lateral
drainage represented an annual mean of 182 mm (20% of the amount of precipitation), whereas precipitation was estimated at 895 mm (Deirmendjian et al., 2018). At the study site, deeper water table in croplands was thus a consequence of a higher evapotranspiration and more lateral drainage than in forest. As explained further, water table depth is an important determinant for understanding the biogeochemical variability in groundwater in relation to land use.

4.2 Dynamic of $O_2$, DOC, DIC and $\delta^{13}C$-DIC in groundwater: A combination of hydrological, physical and metabolic processes

In other aquifer systems worldwide, several studies have observed a significant positive correlation between groundwater $O_2$ concentration and depth to water (Datry et al., 2004; Foulquier et al., 2010; Goldscheider et al., 2006; McMahon and Chapelle, 2008; Pabich et al., 2001). Where the water table is close to the soil surface, groundwater $O_2$ consumption is likely rapid because of incomplete degradation of soil-generated labile DOC in the unsaturated zone. On the contrary, where the water table is far from the soil surface, strong oxygen depletion in the vicinity of the water table does not occur since the higher residence time of infiltrating water results in almost complete degradation of soil-generated DOC in the unsaturated zone (Malar and Herrant, 1999; Starr and Gillham, 1993). A regional study in forest soils of Switzerland (Hageron et al., 2000) and a study compiling a global database of soil carbon (Camino-Serrano et al., 2014) both found that soil-generated DOC was preferentially mobilized under reducing conditions in soils because of dissolution of Fe oxides. Deeper water tables in croplands do not reach topsoil that exhibits high labile organic C content. Thus, reducing conditions in topsoil and the leaching of soil-generated DOC are prevented as is the consumption of the groundwater $O_2$ stock, as occurs in forests during high flow stages (Table 3; Fig. S2l; Deirmendjian et al., 2018). Therefore, groundwater pCO$_2$ was higher in the forest during high flow than it was in cropland and riparian sites (Table 3; Fig. 4h, S2l, h). This also explains the negative correlation between DOC and CO$_2$ observed only in forest groundwater (Fig. 6b). During base flow, we observed a clear land use spatial pattern among cropland, riparian forest, and forest sites (Table 3; Fig. S2h). We hypothesize that this difference was a consequence of a less intense soil respiration in croplands during summer. From simultaneous eddy covariance measurements over pine forests and maize croplands of the study area, Stella et al. (2009) confirmed that ecosystem respiration was lower in cropland than in forests over the whole year. However, Stella et al. (2009) also showed that ecosystem respiration was larger during the growing season of the maize, because of increased soil respiration in response to the higher soil water content caused by irrigation. In forest sites, groundwater pCO$_2$ increases during the summer because soil CO$_2$ diffuses downward and then is dissolved into the water table (Deirmendjian et al., 2018; Tsypin and Macpherson, 2012). A deeper water table in cropland suggests a less efficient CO$_2$ transfer from soil air to water table. Higher soil moisture in croplands due to irrigation probably delays soil CO$_2$ diffusion to groundwater.

Fig. 7. Scatter plots of (a) $O_2$ (µmol L$^{-1}$) vs. NO$_3^-$ (µmol L$^{-1}$), (b) $O_2$ (µmol L$^{-1}$) vs. $NH_4^+$ (µmol L$^{-1}$), (c) CH$_4$ (µmol L$^{-1}$) vs. NO$_3^-$ (µmol L$^{-1}$), (d) CH$_4$ (µmol L$^{-1}$) vs. NO$_2^-$ (µmol L$^{-1}$), (e) DOC (µmol L$^{-1}$) vs. NO$_3^-$ (µmol L$^{-1}$), and (f) $O_2$ (µmol L$^{-1}$) vs. Fe$^{2+}$ (µmol L$^{-1}$), in all sampled groundwater and streams.
The δ¹³C-DIC signature of forest groundwater was typical of a signature that originated from respiration of soil organic matter derived from C₃ plants (O’Leary, 1988; Vogel et al., 1993). The studied forest soils have no natural carbonate minerals (Augusto et al., 2010) and DIC originating from silicate weathering has the same isotopic signature as DIC originating from soil respiration (Das et al., 2005; Polsenaere and Abril, 2012; Wachniew, 2006). Crop groundwater had a heavier δ¹³C-DIC signature than forest groundwater and this discrepancy resulted from distinct processes. Liming in croplands brings artificial carbonates into crop soil and DIC originating from carbonate weathering produced DIC with a δ¹³C value of approximately half of that of soil CO₂ as carbonate rocks have a δ¹³C of approximately 0‰, making δ¹³C-DIC less negative (Clark and Fritz, 1997; Salomons and Mook, 1986). Irrigation with extraction of groundwater could also increase the δ¹³C-DIC signature by enhancing the degassing rate of ¹³C relative to ¹²C (Deirmendjian and Abril, 2018; Polsenaere and Abril, 2012). Changes in the δ¹³C-DIC signature could also originate from respiration of soil organic matter derived from maize, a C₄ plant with a heavier δ¹³C signature than C₃ forest plants (O’Leary, 1988; Vogel et al., 1993), as observed in the study region (Quéénéa et al., 2006). Indeed, after three decades of cultivation, the remaining carbon from the forest pool was mostly recalcitrant and its degradation probably did not affect the δ¹³C-DIC pool (Jolivet et al., 1997).

4.3. Dynamics of IN and CH₄ in groundwater: The influence of groundwater O₂

Subsurface and groundwater redox zonation is driven by the spatial and temporal distribution of O₂ that serves as the primary terminal electron acceptor during the degradation of organic C. In crop groundwater, high O₂ concentrations inhibited methanogenesis, as this process is strictly anaerobic and thus resulted in very low CH₄ concentrations (Table 2; Fig. 4f, g; Borges et al., 2018; Cais et al., 2010; Jurado et al., 2017; Klüber and Conrad, 1998). Conversely, forest and riparian groundwater exhibited anoxic conditions that allowed methanogenesis to occur and created higher CH₄ concentrations in forest sites compared to cropland sites (Table 2; Fig. 4f, g). High water table stages in forested areas cause anoxia in soils, forcing plants and microorganisms to switch to anaerobic metabolism (Naumburg et al., 2005; Bakker et al., 2006, 2009). Thus, in riparian and forest areas, we expected a positive relationship between water table and groundwater CH₄ but, to the contrary, we observed a negative relationship between these two parameters (R² = 0.25, p < 0.05; data not shown). This implies that methanogenesis primarily occurs in deeper layers of forest soils, especially in summer. Fe³⁺ and NH₄⁺ accumulates in forest groundwater because anoxic conditions inhibit nitrification and iron oxidation (Table 2; Fig. 4d, e; Jambert et al., 1994; Widdel et al., 1993).

In groundwater, anoxic conditions enable heterotrophic denitrification, whereas an O₃₄ threshold of 30–60 μmol L⁻¹ completely inhibits heterotrophic denitrification (Balestrini et al., 2016; Cey et al., 1999; Christensen et al., 2013; Jambert et al., 1994; Kolbjørn Jensen et al., 2017; Korom, 1992). In strictly forest sites, denitrification in groundwater is usually limited by the scarcity of NO₃⁻, whereas in strictly crop sites denitrification is often limited by organic C availability (Table 2; Jambert et al., 1994; Starr and Gillham, 1993). Thus, N fertilizer application associated with different groundwater denitrification rates in the different plots creates the observed spatial pattern of groundwater NO₃⁻ concentration in crop, riparian and forest sites (Table 2; Fig. 4c).

In local maize croplands, Jambert et al. (1997) found that 13% of the N fertilizers inputs were converted to N₂ gas, demonstrating that denitrification could occur in these oxic cropl soils and groundwater. Although oxic conditions are not favorable for groundwater denitrification, some studies in agricultural catchments do describe this process at relatively high O₂ (150 μmol L⁻¹) levels (McAleer et al., 2017; Otero et al., 2009). In crop soils, Rubol et al. (2016) investigated the spatio-temporal dynamics in oxidative microbial activity and the development of anoxic micro zones (i.e., anoxic hot-spots) at the microscopic level (µm to cm). They found that labile C addition resulted in maximum rates of local metabolic activity within a few minutes and led to the subsequent formation of anoxic hotspots and thus, both oxic and anoxic conditions coexisted closely within a small volume of crop soils. Consequently, denitrification probably occurs in anoxic microsites in waterlogged soil during irrigation as higher soil moisture results in lower soil oxygen concentration, lower redox potential and higher leaching of soil DOC (Hagedorn et al., 2000; Jambert et al., 1997; Rubol et al., 2012; Silver et al., 1999).

N fertilizer load in local croplands is 25 g N m⁻² yr⁻¹ (Jambert et al., 1997), whereas export (using drainage of 637 mm yr⁻¹ and the average NO₃⁻ concentration in crop groundwater) of NO₃⁻ through crop groundwater was estimated at 10 g N m⁻² yr⁻¹ (40% of the annual N fertilizer load), and export (using same drainage and the average NO₃⁻ concentration in riparian groundwater) of NO₃⁻ through riparian groundwater was estimated at 2.8 g N m⁻² yr⁻¹ (8% of the annual N fertilizer load). This shows the importance of riparian groundwater to attenuate N inputs from adjacent croplands to streams, otherwise a large portion of the annual N fertilizer load would have been leached into adjacent streams rather than being denitrified or used by plants. In riparian groundwater adjacent to a farm in the New York state (USA), Anderson et al. (2014) found that total groundwater denitrification was equivalent to 32% of manure N spread on the adjacent upland field. Melaka et al. (2017) simulated the transport and dynamics of N in an agricultural soil under flooded conditions and concluded that relatively shallow aquifers with sandy soil are vulnerable to NO₃⁻ contamination at around 10 days if continuous irrigation is practiced. They also stated that NO₃⁻ had higher leaching potential than NH₄⁺ or DOC. At our study site, irrigation and associated desorption of DOC and NO₃⁻ could explain their slight increase in crop groundwater during base flow (Table 3, Fig. 1, S2c). In a storm infiltration basin in Florida (USA), O’Reilly et al. (2012) found that concomitant peaks in groundwater O₂ and NO₃⁻ concentrations after storm rainfall were a consequence of organic N leaching, indicating that there were short periods of ammonification and nitrification. In crop groundwater of Wallonia (Belgium), when groundwater O₂ levels are higher than 125 μmol L⁻¹ (as at the study site), nitrification rather than denitrification promotes the accumulation of N₂O in groundwater (Jurado et al., 2017).

4.4. Stream biogeochemical functioning: Mostly a function of groundwater composition

NO₃⁻ inputs to streams cause stream eutrophication (Carpenter et al., 1998; Jordan and Weller, 1996; Smith, 2003; Zhou et al., 2017). This is consistent with our field observations where we observed that crop streams were highly vegetated with macrophytes during base flow stages. Compared to high flow conditions, crop stream eutrophication was accompanied by higher pH and δ¹³C-DIC, and lower pCO₂ caused by preferential ¹²CO₂ uptake during the macrophyte plant photosynthesis (Table 4; Fig. S3a, h, j; De Carvalho et al., 2009; Raven et al., 2002). The development of macrophytes in crop streams modifies flow and can cause a significant drop in water velocity, which in turn, gives rise to extensive deposition and retention of sediment beneath the macrophytes (Cotton et al., 2006; Sand-Jensen and Pedersen, 1999). This leads to seasonal accumulation of organic matter, a predominance of anoxic conditions in stream sediments, and thus the occurrence of methanogenesis as evidenced by peaks in dissolved CH₄ during base flow (Table 4; Fig. S3g; Borges et al., 2018; Crawford et al., 2016; Sanders et al., 2007). Crop stream CH₄ concentration was 390 nmol L⁻¹ during base flow (Table 2), a concentration significantly lower (1430 nmol L⁻¹) than chalk streams impacted by macrophyte vegetation in England (Sanders et al., 2007). This discrepancy probably resulted from the increased in silt and clay fraction during summer of the underlying sediment in chalk streams (Sanders et al., 2007). This would suggest that the permeability of chalk stream sediment became
lower than that of sandy stream sediment and created stronger reduc-
ing conditions in chalk stream sediments, which likely increased the po-
tential for methanogenesis (Baker et al., 1999; Findlay, 1995; Kankaala et al., 2005; Morrice et al., 1997). Sanders et al. (2007) also showed that the chalk streams’ emissions of CH₄ to the atmosphere were ap-
proximately 50 times lower than the CH₄ production in stream sedi-
ments, illustrating the high potential for CH₄ oxidation in the water column of crop stream. During base flow, a second explanation for higher CH₄ (and NH₄⁺) concentrations in crop streams relative to forest streams could be differential hydrology. Drainage plot is a function of the water table height (hydraulic gradient, Darcy’s law). During base flow, the water table in cropland was deeper than in forest (e.g., 4 m deeper in Sep. 2014; Fig. 2), and so during this period, potentially more forest groundwater was drained into crop streams. However, in forest streams we usually did not observe CH₄ (or NH₄⁺) concentrations as high as in crop streams (Table 2; Fig. 7d) indicating that CH₄ (or NH₄⁺) in crop streams primarily originated from crop stream sediments rather than from higher discharge of forest groundwater. In crop streams, CH₄ was correlated with NH₄⁺ but not correlated with NO₃⁻ or DOC (Figs. 6d, 7c, d). Such relationships were also observed in the Meuse river basin (Belgium) (Borges et al., 2018) and in a global meta-analysis of riverine CH₄ (Stanley et al., 2016). In contrast, this does not fit the conceptual model of Schade et al. (2016) developed from data in New Hampshire streams, whereby the CH₄ was positively correlated with DOC, while negatively related to NO₃⁻.

Sandy sediments of low order stream beds impacted by eutrophi-
cation are significant areas of NO₃⁻ reduction over the spring and summer, lowering DOC and NO₃⁻ concentrations in stream water (Table 4; Figs. 3c, f; Böhlke et al., 2009; Mulholland et al., 2008; Sanders et al., 2007). Additionally, the decreased of stream velocity during base flow increased residence times of NO₃⁻ in the hyporheic zone and the time for denitrification (Bardini et al., 2012). In a small stream dominated by maize cropland in the USA, Böhlke et al. (2009) demonstrated that denitrification mainly occurred in sediments and not in the water column since integrated rates of pore-water denitrification derived from ¹⁵N tracer profiles within the hyporheic zone were similar to the reach-scale rates derived from measurements in the stream. In crop streams, a portion of the NO₃⁻ variability between the two hydrological periods could also result from higher drainage of forest groundwater during base flow, which would dilute the NO₃⁻ signal from crop groundwater.

Considering the flat catchment topography, a minor portion of TSM and POC in streams originates from soil erosion and surface runoff. The most frequent effects of dredging on aquatic ecosystems are changes in the concentration of suspended solids, turbidity and light penetration (Lewis et al., 2001; Newell et al., 1998). Higher concentra-
tions of POC (and TSM) observed in crop streams were also caused by macrophyte biomass developed in summer became a sediment trap. When stream discharge was sufficiently energetic, it re-suspended all the accumulated sediment and removed this litter. Moreover, we ob-
served peaks of CH₄ and NH₄⁺ in crop streams during high flow (Table 4; Fig. 3d, g), suggesting that dredging or streambed erosion of crop streams also release CH₄ and NH₄⁺ from the sediment.

In forest streams, we observed significantly lower concentrations of Fe²⁺, NH₄⁺, and CH₄ than in forest groundwater and significant negative linear relationships between O₂ on the one side and Fe²⁺, NH₄⁺, or CH₄ (Table 2; Figs. 4d, e, g, 7d, f). This suggests there were low O₂ concentra-
tions in forest streams, NH₄⁺ inputs with high concentrations of reduced com-
pounds and that the stream water was gradually oxygenated, which induced Fe²⁺ and CH₄ oxidations and nitrification. Mulholland et al. (2000) studied N cycling by adding ¹⁵N-labeled NH₄⁺ into a forest stream in eastern Tennessee (USA). They concluded that the residence time of NH₄⁺ in the water column was low (5 min) and that nitrification was an important sink for NH₄⁺, accounting for 19% of total ammonium uptake. In forest streams, the NH₄⁺ concentration was approximately 3 μmol L⁻¹ lower than in forest groundwater and thus did not explained the NO₃⁻ increase of 50 μmol L⁻¹ (Table 2; Figs. 3c, d). Up to 76% of N ex-
ports from local forest are in organic forms but these N exports are very low (≤0.2 g N m⁻² yr⁻¹; De Wit et al., 2005; Rimmelin, 1998; Vernier et al., 2003), so in-stream mineralization of organic N coupled to nitrifi-
cation could not explain NO₃⁻ concentrations in forest streams. Since the sampled forest streams are not strictly forested, NO₃⁻ concentration are explained by simple hydrological mixing between crop and forest groundwater (Table 2).

In streams, pCO₂ was lower and O₂ was higher than in groundwater (Table 2; Figs. 3f, h, 6a). This shows that gas exchange between stream water and the atmosphere occurs quickly, favoring low stream depth and strong concentration gradients between the two compartments. Some authors (e.g., Bodmer et al., 2016; Borges et al., 2018) found elevated pCO₂ in crop streams rather than in forest streams, due to higher levels of dissolved and particulate organic matter in crop dominated systems compared to the forested ones that facilitated the in-stream degradation of organic matter. Moreover, land uses are expected to change the composition of terrestrial soil organic matter leached to streams, shifting from vegetation- to microbe-derived organic matter with greater agricultural land use and potentially higher emissions in crop streams (Fuss et al., 2017; Graeber et al., 2015; Wilson and Xenopoulos, 2009). Those results contrasted with ours because we found no difference in pCO₂ between crop and forest streams. Forest groundwater did have higher pCO₂ than crop groundwater, indicating a more intense degassing in forest streams. The similar δ¹³C-DIC signa-
tures in forest and crop streams despite the strong difference between crop and forest groundwater suggests faster isotopic equilibration of DIC resulting from degassing. The greater gas transfer velocity in forest streams is a consequence of the abundance of coarse woody debris which generates higher levels of water turbulence (e.g., Bodmer et al., 2016), and is consistent with our field observations. A lower gas transfer velocity lower in crop streams results from stream calibration reducing turbulent flow, and macrophyte vegetation that protects the water surface from wind shear.

5. Conclusion

The present study demonstrates that C and IN concentrations in shallow groundwater and in first-order streams are strongly sensitive to land use. In sandy lowland catchments, simultaneous measurements of biogeochemical parameters in groundwater and streams are crucial for identifying and quantifying biogeochemical processes involved at the groundwater-stream interface. We also show that a statistical clus-
tering analysis based on NO₃⁻ dataset enables partitioning of groundwa-
ter and streams into crop-affected or forest-dominated waters. Such a classification could be useful to river managers and policy makers. The water table had greater depth in croplands and was a crucial parameter necessary for understanding groundwater biogeochemical variability in relation to land use. Higher water table stages in forests created anoxic conditions and increased soil leaching. Conversely, in croplands, the deeper water table prevented anoxic conditions, creating different groundwater compositions from forest groundwater and inhibiting the denitrification of the N fertilizers, which led to groundwater NO₃⁻ accumulation. Despite the occurrence of groundwater denitrification in riparian and forest sites, N fertilizers inputs in crop streams were still high enough to generate eutrophic conditions in these streams. Eu-
trophication resulted in a biogeochemical cascading effect, which sustained high CH₄ concentration and lowered NO₃⁻. High CO₂ and CH₄ production occurs in forest soils and groundwater, but these two gases exhibit lower concentrations in forest streams, indicating intense degassing or oxidation.

The groundwater-stream interface is a biogeochemical hotspot and hot moment for C emissions and N removal processes (McClain et al., 2003). Future studies focusing on the groundwater-stream interface in relation to land use are needed to better understand C and N dynamics.