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## 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, Pierre Anschutz, Christian Morel, Alain Mollier, Laurent Augusto, Denis Loustau, Luiz Carlos Cotovicz, Damien Buquet, Katixa Lajaunie, Gwénaëlle Chaillou, et al.

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

4  
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23

24 **Abstract**

25 During land-aquatic transfer, carbon (C) and inorganic nutrients (IN) are transformed in soils,  
26 groundwater, and at the groundwater-surface water interface as well as in stream channels and stream  
27 sediments. However, processes and factors controlling these transfers and transformations are not well  
28 constrained, particularly with respect to land use effect. We compared C and IN concentrations in shallow  
29 groundwater and first-order streams of a sandy lowland catchment dominated by two types of land use:  
30 pine forest and maize cropland. Contrary to forest groundwater, crop groundwater exhibited oxic

31 conditions all-year round as a result of higher evapotranspiration and better lateral drainage that decreased  
32 the water table below the organic-rich soil horizon, prevented the leaching of soil-generated dissolved  
33 organic carbon (DOC) in groundwater, and thus limited consumption of dissolved oxygen ( $O_2$ ). In crop  
34 groundwater, oxic conditions inhibited denitrification and methanogenesis resulting in high nitrate ( $NO_3^-$ ;  
35 on average  $1,140 \pm 485 \mu\text{mol L}^{-1}$ ) and low methane ( $CH_4$ ;  $40 \pm 25 \text{ nmol L}^{-1}$ ) concentrations. Conversely,  
36 anoxic conditions in forest groundwater led to lower  $NO_3^-$  ( $25 \pm 40 \mu\text{mol L}^{-1}$ ) and higher  $CH_4$  ( $1,770 \pm$   
37  $1,830 \text{ nmol L}^{-1}$ ) concentrations. The partial pressure of carbon dioxide ( $pCO_2$ ;  $30,650 \pm 11,590 \text{ ppmv}$ ) in  
38 crop groundwater was significantly lower than in forest groundwater ( $50,630 \pm 26,070 \text{ ppmv}$ ), and was  
39 apparently caused by the deeper water table delaying downward diffusion of soil  $CO_2$  to the water table. In  
40 contrast,  $pCO_2$  was not significantly different in crop ( $4,480 \pm 2,680 \text{ ppmv}$ ) and forest ( $4,900 \pm 4,500$   
41  $\text{ppmv}$ ) streams, suggesting faster degassing in forest streams resulting from greater water turbulence.  
42 Although  $NO_3^-$  concentrations indicated that denitrification occurred in riparian-forest groundwater, crop  
43 streams nevertheless exhibited important signs of spring and summer eutrophication such as the  
44 development of macrophytes. Stream eutrophication favored development of anaerobic conditions in crop  
45 stream sediments, as evidenced by increased ammonia ( $NH_4^+$ ) and  $CH_4$  in stream waters and concomitant  
46 decreased in  $NO_3^-$  concentrations as a result of sediment denitrification. In crop streams, dredging and  
47 erosion of streambed sediments during winter sustained high concentration of particulate organic C,  $NH_4^+$   
48 and  $CH_4$ . In forest streams, dissolved iron ( $Fe^{2+}$ ),  $NH_4^+$  and  $CH_4$  were negatively correlated with  $O_2$   
49 reflecting the gradual oxygenation of stream water and associated oxidations of  $Fe^{2+}$ ,  $NH_4^+$  and  $CH_4$ . The  
50 results overall showed that forest groundwater behaved as source of  $CO_2$  and  $CH_4$  to streams, the intensity  
51 depending on the hydrological connectivity among soils, groundwater, and streams.  $CH_4$  production was  
52 prevented in cropland in soils and groundwater, however crop groundwater acted as a source of  $CO_2$  to  
53 streams (but less so than forest groundwater). Conversely, in streams,  $pCO_2$  was not significantly affected  
54 by land use while  $CH_4$  production was enhanced by cropland. At the catchment scale, this study found  
55 substantial biogeochemical heterogeneity in C and IN concentrations between forest and crop waters,  
56 demonstrating the importance of including the full vegetation-groundwater-stream continuum when

57 estimating land-water fluxes of C (and nitrogen) and attempting to understand their spatial and temporal  
58 dynamics.

59 Keywords: carbon dioxide, methane, groundwater, stream, land use, pine, maize

60

## 61 **1. Introduction**

62 Despite their small surface area worldwide (Downing et al., 2012), inland waters have been recognized as  
63 key component of the global carbon (C) cycle, constituting a preferential pathway of dissolved and  
64 particulate C transport from terrestrial ecosystems to the coastal ocean (Cole et al., 2007; Meybeck, 1982;  
65 Ludwig et al., 1996b, 1996a; Meybeck, 1987). Inland waters act as significant sources of carbon dioxide  
66 (CO<sub>2</sub>) and methane (CH<sub>4</sub>) to the atmosphere because inland waters are generally supersaturated by CO<sub>2</sub>  
67 and CH<sub>4</sub> compared to the overlying atmosphere (Abril et al., 2014; Bastviken et al., 2011; Borges et al.,  
68 2015; Lauerwald et al., 2015; Raymond et al., 2013; Stanley et al., 2016).

69 Inland waters and specifically small streams are tightly connected to their catchment characteristics such  
70 as hydrology and land use, as they receive large inputs of C from land (mainly from soils and  
71 groundwater), which in turn control the stream biogeochemical processes and the water composition  
72 (Aitkenhead et al., 1999; Deirmendjian and Abril, 2018; Hotchkiss et al., 2015; Johnson et al., 2006; Jones  
73 and Mulholland, 1998; McClain et al., 2003; Polsenaeere and Abril, 2012; Bodmer et al., 2016; Findlay et  
74 al., 2001; Lehrter, 2006). Groundwater discharge has been recognized as an important source of CO<sub>2</sub> in  
75 riverine systems, especially in small streams and headwaters (Deirmendjian and Abril, 2018; Hotchkiss et  
76 al., 2015; Johnson et al., 2008; Kokic et al., 2015; Marx et al., 2017; Raymond et al., 2013; Wallin et al.,  
77 2013). On the contrary to riverine CO<sub>2</sub>, riverine CH<sub>4</sub> is likely to originate from wetlands that generally  
78 combine a strong hydrological connectivity with riverine waters and a high productivity (Abril et al.,  
79 2014; Abril and Borges, 2018). Although some studies found low CH<sub>4</sub> concentrations in the groundwater  
80 of Belgium (up to 1.1 μmol L<sup>-1</sup>; Borges et al., 2018; Jurado et al., 2017), other studies found high CH<sub>4</sub>

81 concentrations in the groundwater of Great Britain (up to 295  $\mu\text{mol L}^{-1}$ ; Bell et al., 2017) and in the  
82 Appalachian basin of the USA (up to 2,8000  $\mu\text{mol L}^{-1}$ ; Molofsky et al., 2016). Actually, soil moisture,  
83 which controls oxic/anoxic conditions in soil, is the main determinant of terrestrial  $\text{CO}_2$  or  $\text{CH}_4$  production  
84 in soil. As a consequence,  $\text{CH}_4$  emissions from soils are high under strictly anaerobic conditions in  
85 waterlogged soils whereas  $\text{CO}_2$  emissions from soils are high under aerobic conditions in drier soils  
86 (Christensen et al., 2003; Moore and Knowles, 1989). Croplands affect water mass balance at the plot  
87 scale, especially through irrigation and extraction of groundwater, which results in declining water table in  
88 many regions worldwide (Foley et al., 2005; Gleick, 2003; Jackson et al., 2001; Postel, 1999; Rosegrant et  
89 al., 2002). Investigating spatial dynamics of  $\text{CO}_2$  and  $\text{CH}_4$  in groundwater in relation with land use is  
90 critical better understanding processes governing their terrestrial production and leaching to groundwater.

91 Croplands cover about 40% of the terrestrial ice-free surface and are often associated with degradation of  
92 both ground and surface water quality (Asner et al., 2004; Clague et al., 2015; Foley et al., 2005; Hiscock  
93 et al., 1991; Ramankutty and Foley, 1999). Intensive agriculture led to an increase of nitrate ( $\text{NO}_3^-$ )  
94 entering ground and surface water environments that has fueled aquatic primary production in surface  
95 waters and led to low  $\text{CO}_2$  and high  $\text{CH}_4$  concentrations, the latter being related to enhanced organic  
96 matter delivery in sediments (Borges et al., 2018; Carpenter et al., 1998; Clague et al., 2015; Crawford et  
97 al., 2016; Jordan and Weller, 1996; Smith, 2003; Zhou et al., 2017). Additionally, aquatic primary  
98 production in crop streams is enhanced as a result of low light limitation (clearing of riparian vegetation),  
99 and the excessive transport of sediment-bound organic matter and nutrients to surface waters (Bernot et  
100 al., 2010; Lamba et al., 2015; Ramos et al., 2015; Young and Huryn, 1999). Soil erosion rates in  
101 agricultural landscapes are one to two times larger than those in areas with native vegetation  
102 (Montgomery, 2007; Quinton et al., 2010). Indeed, riparian forest is usually considered stream buffer  
103 zones that attenuate stream bank erosion and  $\text{NO}_3^-$  inputs from croplands (Balestrini et al., 2016; Cey et  
104 al., 1999; Christensen et al., 2013; Stott, 2005; Wynn and Mostaghimi, 2006). Denitrification represents a  
105 permanent removal pathway that limits the extent and impact of  $\text{NO}_3^-$  contamination by transforming  $\text{NO}_3^-$

106 to inert dinitrogen (N<sub>2</sub>). However, incomplete denitrification can produced nitrous oxide (N<sub>2</sub>O), a major  
107 anthropogenic ozone-depleting substance (Ravishankara et al., 2009). On the contrary to croplands, forests  
108 are known to export fewer nutrients by limiting runoff and leakage of nutrients (Canton et al., 2012;  
109 Onderka et al., 2010).

110 Land use effects on both water composition and biogeochemical processes have been studied in streams  
111 and groundwater (Barnes and Raymond, 2010, 2009; Bernot et al., 2010; Bodmer et al., 2016; Jeong,  
112 2001; Lehrter, 2006; Masese et al., 2017; Raymond and Cole, 2003; Rodrigues et al., 2018; Salvia-  
113 Castellví et al., 2005; Vidon et al., 2008; Wilson and Xenopoulos, 2009; Young and Huryn, 1999; Zhang  
114 et al., 2018), but land use studies with simultaneous groundwater and stream sampling are more scarce  
115 (Bass et al., 2014; Borges et al., 2018; Hu et al., 2016). The objective of this study was to understand how  
116 two contrasting types of land use (pine forest and maize cropland) affected C and inorganic nutrient (IN)  
117 concentrations in shallow groundwater and in first-order streams of a sandy lowland catchment. We  
118 hypothesized that the biogeochemical variability between crop groundwater and forest groundwater was  
119 due to agricultural practices that affect N inputs (fertilizer) and water mass balance (irrigation and  
120 drainage). We hypothesized that the biogeochemical variability between crop and forest streams originate  
121 from differential lateral export of C and IN from two distinct sources (i.e., crop groundwater and forest  
122 groundwater) because of a strong hydrological connection between groundwater and streams in the  
123 studied catchment.

124

## 125 **2. Materials and Methods**

### 126 **2.1. Study site**

127 The Leyre catchment (2,100 km<sup>2</sup>) is located in the southwestern part of France. This is a flat coastal plain  
128 with a mean slope lower than 0.125% and a mean altitude lower than 50 m (Jolivet et al., 2007). The  
129 lithology is relatively homogeneous and composed of sandy permeable surface layers dating from the

130 Plio-Quaternary period (Legigan, 1979; Bertran et al., 2009, 2011). The soils are podzols characterized by  
131 a low pH ( $\approx 4$ ), low nutrient availability, low cationic exchange capacity, and high organic C content that  
132 can reach 50 g per kg of soil (Augusto et al., 2010; Lundström et al., 2000). In Leyre sandy podzols, the  
133 low clay and silt content causes a low soil water retention (Augusto et al., 2010).

134 The study area was a vast wetland until the 19<sup>th</sup> century, when a wide forest of maritime pine was sown  
135 following a landscape drainage campaign resulting from an imperial decree of Napoleon III in 1857  
136 (Jolivet et al., 2007). Currently, the catchment is mainly occupied by C<sub>3</sub> pine forest (approximately 85%),  
137 with a modest proportion of C<sub>4</sub> maize cropland (approximately 15%) (Fig. 1; Jolivet et al., 2007).  
138 Following catastrophic forest wildfires, the maize croplands were installed during the second half of the  
139 20<sup>th</sup> century. Consequently, their spatial distribution was not based on soil properties, as confirmed by the  
140 similar mean values of soil texture in local croplands and forests (Augusto et al., 2010; Jolivet et al.,  
141 2003). During the maize cropping season (usually May to November), farmers irrigate the plots by  
142 pumping shallow groundwater ( $\sim 1$ -5 m deep) almost daily to maintain adequate soil moisture status,  
143 whereas maritime pine stands are never irrigated (Govind et al., 2012). As N is not limiting for tree growth  
144 in our study region (Trichet et al., 2009), forests are never fertilized with N. Conversely, croplands  
145 generally receive two N fertilizer applications annually, a first at the beginning of May (30–50 kg N ha<sup>-1</sup>),  
146 and second at the beginning of June with 200–250 kg N ha<sup>-1</sup> (Canton et al., 2012; Jambert et al., 1997;  
147 Ulrich et al., 2002). Additionally, in order to maintain soil pH in the 5.5–6.0 range, local maize croplands  
148 are limed with crushed limestone (CaCO<sub>3</sub>) containing a small portion of dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) (10 t ha<sup>-1</sup>  
149 right after forest conversion and then 0.5 t ha<sup>-1</sup> an<sup>-1</sup>; Jolivet et al., 2003).

150 The climate is oceanic with a mean annual air temperature of 13°C and a mean annual precipitation of 930  
151 mm (Moreaux et al., 2011). Owing to the low slope, the low soil water retention and the high permeability  
152 of the soil (i.e., hydraulic conductivity is approximately 40 cm h<sup>-1</sup>, Corbier et al., 2010), the percolation of  
153 rain water is fast (55 cm h<sup>-1</sup> on average, Vernier and Castro, 2010). Consequently, surface runoff does not  
154 occur as the excess of rainfall percolates into the soil and recharges the shallow groundwater, causing the

155 water table to rise. The sandy permeable surface layers contain a free and continuous water table that is  
156 strongly interconnected with the superficial river network. This is facilitated by a dense network of  
157 drainage ditches, initiated in the 19<sup>th</sup> century and currently maintained by forest managers in order to  
158 enhance tree regeneration and growth (Thivolle-Cazat and Najjar, 2001). During the sampling period,  
159 channels of some crop streams were dredged before they began to flow again. This was done to optimize  
160 local cropland drainage and to feed croplands with IN and organic residuals found in the stream  
161 sediments. To increase soil permeability and to optimize lateral drainage in local maize croplands, farmers  
162 practice subsoiling and agricultural ditches are generally deeper (2.0–2.5m) than forest ditches (1.0m).

163

## 164 **2.2. Sampling strategy**

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

172 Groundwater was sampled for temperature, electrical conductivity (EC), pH, dissolved oxygen (O<sub>2</sub>),  
173 methane (CH<sub>4</sub>), partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>), total alkalinity (TA), dissolved inorganic carbon (DIC),  
174 stable isotope composition of the dissolved inorganic carbon ( $\delta^{13}\text{C-DIC}$ ), dissolved organic carbon  
175 (DOC), ammonia (NH<sub>4</sub><sup>+</sup>), nitrate (NO<sub>3</sub><sup>-</sup>) and dissolved iron (Fe<sup>2+</sup>). For groundwater, we took the  
176 precaution to renew the water in the piezometers by pumping with a submersible pump before sampling.  
177 Groundwater was then sampled once the stabilization (approximately 10 min) of groundwater  
178 temperature, pH, EC and O<sub>2</sub> monitored with portable probes was observed. Streams were sampled for the



179 same parameters, plus total suspended matter (TSM), particulate organic carbon (POC) and the POC  
180 content of the TSM (POC%).

181

### 182 **2.3. Field measurements and laboratory analyses**

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

186 The pCO<sub>2</sub> in groundwater and streams was measured directly using an equilibrator (Frankignoulle and  
187 Borges, 2001; Polsenaere et al., 2013) following the procedure of Deirmendjian and Abril (2018).

188 We stored the total alkalinity (TA) samples in polypropylene bottles after filtration using a syringe  
189 equipped with glass fiber filters (GF/F; 0.7 μm). TA was then analyzed on filtered samples by automated  
190 electro-titration on 50 mL samples with 0.1N HCl as the titrant. The equivalence point was determined  
191 from pH between 4 and 3 with the Gran method (Gran, 1952). Precision based on replicate analyses was  
192 better than ±5 μmol L<sup>-1</sup>. For samples with a very low pH (<4.5), we bubbled the water with atmospheric  
193 air in order to degas the CO<sub>2</sub>. Consequently, the initial pH increased above 5, and the TA titration was  
194 then performed (Abril et al., 2015).

195 We calculated DIC from pCO<sub>2</sub>, TA, and temperature measurements using the carbonic acid dissociation  
196 constants of Millero (1979) and the CO<sub>2</sub> solubility from Weiss (1974), using the CO<sub>2</sub>SYS software (Lewis  
197 et al., 1998). The δ<sup>13</sup>C-DIC samples were collected using 120 mL glass serum bottles sealed with a rubber  
198 stopper and treated with 0.3 mL of HgCl<sub>2</sub> at 20 g L<sup>-1</sup> to avoid any microbial respiration during storage.

199 Vials were carefully sealed such that no air remained in contact with samples and were stored in the dark  
200 to prevent photo-oxidation. The δ<sup>13</sup>C-DIC measurements were performed with the headspace technique  
201 using an isotope ratio mass spectrometer coupled to an elemental analyser (EA-IRMS, Micromass  
202 IsoPrime) equipped with a manual gas injection port as described in Gillikin and Bouillon (2007).

203 CH<sub>4</sub> was also measured using a headspace technique in 60 mL glass serum bottles. The headspace was  
204 created with 10 mL of N<sub>2</sub> gas. We then injected 0.5 mL of the headspace in a gas chromatograph equipped  
205 with a flame ionization detector (GC-FID).

206 DOC samples were obtained after filtration in the field through pre-combusted GF/F (0.7 μm). DOC  
207 filtrates were stored in pre-combusted Pyrex vials (25 mL), acidified with 50 μL of 37% HCl to reach pH  
208 2, and kept at 4 °C in the laboratory before analysis. The DOC concentrations were measured with a  
209 SHIMADZU TOC 500 analyzer (in TOC-IC mode), using a technique based on thermal oxidation after a  
210 DIC removal step (Sharp, 1993). The repeatability was better than 0.1 mg L<sup>-1</sup>.

211 The water for TSM and POC measurements was filtered through pre-weighed and pre-combusted GF/F  
212 glass fiber filters (0.7 μm). The filters were dried at 60 °C and stored in the dark, and subsequently, TSM  
213 was determined by gravimetry. POC was measured using the same filter. The filters were acidified in  
214 crucibles with 2N HCl to remove carbonates and were then dried at 60 °C to remove inorganic carbon and  
215 most of the remaining acid and water (Etcheber et al., 2007). POC content was measured by combustion  
216 (1500 °C) using a LECO CS 200 analyzer and the CO<sub>2</sub> formed was determined quantitatively by infrared  
217 absorption. POC in μmol L<sup>-1</sup> and POC% were then calculated. The uncertainty was ±0.05% of TSM.

218 For IN determination, water was filtered through a 0.20 μm cellulose acetate syringe membrane.  
219 Subsamples for Fe<sup>2+</sup> were acidified with 37% HCl to prevent precipitation of iron oxide, whereas  
220 subsamples for NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were not acidified but kept frozen until later analyses. Then, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>,  
221 and Fe<sup>2+</sup> were analyzed by colorimetry according to standard techniques. NH<sub>4</sub><sup>+</sup> was analyzed following the  
222 procedure of Harwood and Kühn (1970). NO<sub>3</sub><sup>-</sup> was analyzed by flow injection analysis following the  
223 procedure of Anderson (1979). Fe<sup>2+</sup> was analyzed using the ferrozine method (Stookey, 1970). Precision  
224 was ±10% for NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub>, and was ±5% for Fe<sup>2+</sup>.

225 EC, temperature, O<sub>2</sub>, and pH were measured using portable probes (WTW®). Before each field trip, the  
226 pH probe was calibrated using two NBS buffer solutions (4 and 7), the oxygen polarographic probe was

227 calibrated to 100% in a humid atmosphere and the conductivity probe was calibrated using a salinity  
228 standard.

229

#### 230 **2.4. Statistical analyses**

231 K-means clustering analysis (MacQueen, 1967) was used to classify waters either as forest-dominated or  
232 as cropland-affected (Tab. 1). Indeed, K-means clustering analysis allows partitioning a dataset into k  
233 groups (i.e., clusters) pre-specified by the analyst (MacQueen, 1967). Contrary to forest waters at our  
234 study site, crop waters exhibit disproportionately higher  $\text{NO}_3^-$  concentration as a result of N fertilizer use  
235 on maize cropland (Canton et al., 2012; De Wit et al., 2005; Jambert et al., 1997, 1994). Consequently, in  
236 the K-means clustering analysis we used  $\text{NO}_3^-$  concentration data as a proxy to establish a statistical  
237 distinction between forest and crop waters (Tab. 1). K-means clustering analysis was performed one time  
238 with the groundwater dataset (but excluding the riparian groundwater) and a second time with the first-  
239 order streams dataset. We excluded data from riparian groundwater because we have considered riparian  
240 groundwater as a cluster itself (Tab. 1).

241 Principal component analysis (PCA) was used to condense multivariate information on correlated  
242 biogeochemical parameters to a set of uncorrelated variables called principal components (further referred  
243 to as dimensions). PCA was performed one time with a dataset consisting of each measured parameter in  
244 groundwater (but excluding the riparian groundwater) and a second time with the corresponding first-  
245 order streams dataset. PCA was performed separately for groundwater and streams because particulate  
246 parameters were not present in groundwater. If PCA were not performed separately for groundwater and  
247 streams, all data from groundwater would have been removed from the analysis (indeed, if one parameter  
248 is missing for a given sampling station, the sampling station is entirely deleted from the PCA). In addition,  
249 performing the PCA separately for groundwater and streams led to information that was more robust with  
250 respect to the biogeochemical variability induced by land use, in either groundwater or streams. However,

251 to observe whether the two groundwater (crop and forest) and two streams (crop and forest) sources could  
252 be distinguished mathematically in one PCA, we performed an additional PCA with data from both  
253 groundwater and streams that excluded particulate parameters from the analysis. All concentrations data  
254 were log-transformed prior to PCA. The PCAs showed the biogeochemical variability across forest,  
255 cropland, and hydrological seasons in either groundwater or first-order streams.

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

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

264

## 265 **3. Results**

### 266 **3.1. Hydrology**

267 In previous work based on the same dataset, but excluding cropland sampling stations, we identified two  
268 major hydrological seasons (Deirmendjian and Abril, 2018). One defined a high flow period as two  
269 relatively short flood events that occurred in Jan. 2014–Mar. 2014 and in Feb. 2015–Mar. 2015, whereas  
270 we defined the base flow period as two longer periods of low flow occurring in Apr. 2014–Jan. 2015 and  
271 Apr. 2015–Jul. 2015. During high flow, the average and the maximum river flows were  $50 \text{ m}^3 \text{ s}^{-1}$  and  $119$   
272  $\text{m}^3 \text{ s}^{-1}$ , respectively. During base flow, the average and the minimum river flow were  $10 \text{ m}^3 \text{ s}^{-1}$  and  $5 \text{ m}^3 \text{ s}^{-1}$ ,  
273 respectively. The water tables in the forest, riparian forest, and cropland exhibited similar temporal  
274 fluctuations but with a different intensity, and the forest had an overall higher water table depth than the

275 cropland (Fig. 2). The water table in the riparian area exhibited intermediate depth between the forest and  
276 cropland sites (Fig. 2). As surface runoff was negligible in the studied sandy and flat catchment, most of  
277 the stream water likely originated from groundwater discharge.

278 To investigate the temporal variability of the studied biogeochemical parameters, we chose to rely on  
279 hydrological regimes (high flow and base flow periods) rather than on temperature periods (seasons). At  
280 our study site climate was oceanic (by definition very temperate) and the amplitude of the water  
281 temperature was not as high as the amplitude of the river flow. As an example, Leyre River (main stem)  
282 flow could be up to  $119 \text{ m}^3 \text{ s}^{-1}$  and could be down to  $5 \text{ m}^3 \text{ s}^{-1}$ , whereas the highest water temperature  
283 amplitude occurred in forest streams and was  $6.4\text{--}25.8 \text{ }^\circ\text{C}$  (Tab. 2). Additionally, most of the lateral export  
284 occurred during the short periods of high flow (up to 90% for DOC, Deirmendjian et al., 2018). Thus,  
285 characterizing biogeochemical variability and biogeochemical processes in relation with land use during  
286 this hydrological period was important. Furthermore, the seasonality induced by water temperature was to  
287 a certain extent included in the defined hydrological regimes since the high flow period was associated  
288 with lower water temperatures while the base flow period was associated with higher water temperatures  
289 (Tabs. 2-4).

290

### 291 **3.2. K-means clustering analysis**

292 For both hydrological seasons (i.e., high and base flow), we partitioned each sampling stations (excepting  
293 riparian groundwater), into either cropland-affected or forest-dominated waters (Tab. 1). K-means  
294 clustering analysis produced satisfactory results. Logically, groundwater located in cropland was classified  
295 as crop water whereas groundwater located in forest was classified as forest water (Tab. 1). Stream  
296 sampling stations having more than 30% of croplands in their respective catchment were always classified  
297 as crop waters (Tab. 1). Stream sampling stations having less than 8% of croplands in their respective  
298 catchment were always classified as forest waters excepting two times (Tab. 1). These two stream

299 sampling stations were located a few kilometers downstream from important maize croplands.  
300 Specifically, one station was a ditch strongly vegetated during the base flow period that showed signs of N  
301 fertilizer uptake from upstream cropland and, therefore, this ditch was logically classified as a crop station  
302 during base flow (Tab. 1). One station was a stream that exhibited a high water flow during the high flow  
303 period, which probably increased the upstream cropland influences during this hydrological period and,  
304 therefore, this stream was logically classified as a crop station during high flow (Tab. 1).

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

310

### 311 **3.3. Land use influence on water composition of shallow groundwater**

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

316 PCA dimension 1 clearly separated forest groundwater from crop groundwater based on two groups of  
317 variables negatively correlated with one another (Fig. 3a). One group of variables was characterized crop  
318 groundwater and was composed of EC,  $\text{NO}_3^-$ ,  $\delta^{13}\text{C-DIC}$ , and  $\text{O}_2$ , whereas the second group of variables  
319 was characterized forest groundwater and was composed of DIC,  $\text{pCO}_2$ ,  $\text{CH}_4$ ,  $\text{Fe}^{2+}$ , and  $\text{NH}_4^+$  (Fig. 3a).  
320 Indeed, we observed that the yearly average of EC ( $+270 \mu\text{S cm}^{-1}$ ),  $\text{NO}_3^-$  ( $+1,115 \mu\text{mol L}^{-1}$ ),  $\delta^{13}\text{C-DIC}$   
321 ( $+6.9\%$ ), and  $\text{O}_2$  ( $+200 \mu\text{mol L}^{-1}$ ) were higher in crop groundwater than in forest groundwater and were  
322 significantly and positively affected by cropland cover (Tab. 2; Figs. 4b, c, f, j). Conversely, we observed

323 higher DIC (+1,010  $\mu\text{mol L}^{-1}$ ),  $\text{pCO}_2$  (+19,985 ppmv),  $\text{CH}_4$  (+1,730  $\mu\text{mol L}^{-1}$ ),  $\text{Fe}^{2+}$  (+14.1  $\mu\text{mol L}^{-1}$ ), and  
324  $\text{NH}_4^+$  (+4.1  $\mu\text{mol L}^{-1}$ ) in forest groundwater than in crop groundwater; these were significantly and  
325 positively affected by forest cover (Tab. 2; Figs. 4d, e, g, h, k). In riparian groundwater, EC,  $\text{NO}_3^-$ ,  $\delta^{13}\text{C}$ -  
326 DIC,  $\text{O}_2$ , DIC,  $\text{pCO}_2$ , and  $\text{CH}_4$  exhibited intermediate values between the groundwater of forest and crop  
327 sites, whereas  $\text{Fe}^{2+}$  and  $\text{NH}_4^+$  were low and close to those found in crop groundwater (Tab. 2; Figs. 4b, c,  
328 d, e, f, g, h, j, k).

329 In crop groundwater, EC,  $\text{NO}_3^-$ ,  $\delta^{13}\text{C}$ -DIC, and  $\text{O}_2$  were not significantly affected by hydrological seasons  
330 (Figs. 3a, S2c, h, j, k, l). However,  $\delta^{13}\text{C}$ -DIC (+1.1‰),  $\text{NO}_3^-$  (+120  $\mu\text{mol L}^{-1}$ ), and DOC (+130  $\mu\text{mol L}^{-1}$ )  
331 were slightly higher (but not significantly) during base flow compared to high flow (Tab. 3; Figs. S2c, h, j,  
332 k, l). In forest groundwater,  $\text{pCO}_2$ , DIC,  $\text{CH}_4$ , and DOC were significantly affected by hydrological  
333 seasons (Tab. 3; Figs. S2g, h, k, l). DOC (+1,490  $\mu\text{mol L}^{-1}$ ) was significantly higher during high flow,  
334 whereas  $\text{pCO}_2$  (+30,980 ppmv), DIC (+1,330  $\mu\text{mol L}^{-1}$ ) and  $\text{CH}_4$  (+1,780  $\text{nmol L}^{-1}$ ) were significantly  
335 higher during base flow (Tab. 3; Figs. S2 and S4g, h, k, l). In crop and riparian groundwater, we also  
336 observed higher  $\text{pCO}_2$  and DIC values during base flow, but with lower intensities than in forest  
337 groundwater (Tab. 3; Figs. S2h, k).

338

### 339 **3.4. Land use influence on water composition of first-order streams**

340 Figures 3c-d present PCA based on first-order streams data set. The first three PCA dimensions covered  
341 28.6%, 18.5% and 13.8% of the total variance within the dataset, respectively (Figs. 3c, d).

342 Interestingly, the PCA based on the first-order streams dataset did not clearly separate crop streams from  
343 forest streams as it did for groundwater dataset (Figs. 3a-d). This implied lower spatial variability in  
344 streams in relation to land use in than in groundwater (Tabs. 2-4; Fig. 4). Nevertheless, a land use gradient  
345 was observed on PCA dimension 2 (Figs. 3c, d). PCA dimension 2 was best defined by a group of  
346 variables composed of EC,  $\text{CH}_4$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , DOC, TSM, and POC, which collectively characterized crop

347 streams (Figs. 3c, d). On a yearly average basis, significantly higher EC (+105  $\mu\text{S cm}^{-1}$ ),  $\text{CH}_4$  (+220  $\mu\text{mol}$   
348  $\text{L}^{-1}$ ),  $\text{NO}_3^-$  (+265  $\mu\text{mol L}^{-1}$ ),  $\text{NH}_4^+$  (+4.3  $\mu\text{mol L}^{-1}$ ), DOC (+135  $\mu\text{mol L}^{-1}$ ), TSM (+3.3  $\text{mg L}^{-1}$ ), and POC  
349 (+70  $\mu\text{mol L}^{-1}$ ) were observed in crop streams compared to forest streams (Tab. 2; Figs. 4b, c, d, g, l, m,  
350 o). High  $\text{CH}_4$ ,  $\text{NH}_4^+$ , and DOC concentrations were characteristics of forest groundwater, but in streams,  
351 these parameters were characteristic of crop streams (Figs. 3a-d). In addition,  $\text{pCO}_2$ , DIC,  $\delta^{13}\text{C-DIC}$  and  
352  $\text{O}_2$  were not able to separate crop streams from forest streams as they did for groundwaters (Figs. 3a-d).  
353 On a yearly average basis, no significant differences were observed between crop and forest streams for  
354 these four parameters (Figs. 3f, h, j, k).

355 The relatively low temporal variability between high and base flow periods observed in both crop and  
356 forest streams for the studied parameters did not allow the PCA based on stream data set to clearly  
357 separate base flow samples from high flow samples (Tab. 4; Figs. 3c-d, S3, S4). Nevertheless, in crop  
358 streams, pH (+0.2) and  $\delta^{13}\text{C-DIC}$  (+3.8‰) were significantly higher during base flow while  $\text{pCO}_2$  (-1,160  
359 ppmv),  $\text{NO}_3^-$  (-130  $\mu\text{mol L}^{-1}$ ) and DOC (-230  $\mu\text{mol L}^{-1}$ ) were significantly lower during the same period  
360 (Tab. 4; Figs. S3a, j, c, h, l, m, o). In streams, TSM and POC were significantly higher during high flow  
361 but with a higher intensity in crop streams than in forest streams (Tab. 4; Fig. S3m, o). Interestingly, in  
362 both forest and crop streams, POC% was not significantly affected by hydrological regime (Tab. 4; Fig.  
363 S3n).

364

### 365 **3.5. Upstream-downstream distribution of biogeochemical parameters**

366 To explore the influence of land use on water composition at the groundwater-stream continuum, we  
367 observed the upstream-downstream (groundwater-stream) distribution of biogeochemical parameters  
368 along forest and crop continuums (Tab. 2; Fig. 4). Along both types of continuum, some parameters (i.e.,  
369  $\text{pCO}_2$ , TA, DIC,  $\delta^{13}\text{C-DIC}$ , pH,  $\text{O}_2$ ) exhibited the same upstream-downstream distribution, whereas other



370 parameters (i.e., EC,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Fe}^{2+}$ ,  $\text{CH}_4$ , DOC) exhibited a different upstream-downstream distribution  
371 (Tab. 2; Fig. 4).

372 In crop and forest continuums, we observed strong spatial patterns for  $\text{pCO}_2$ , TA, DIC,  $\delta^{13}\text{C-DIC}$ , and pH:  
373  $\text{pCO}_2$  and DIC decreased while TA remained more or less constant, and  $\delta^{13}\text{C-DIC}$  and pH increased (Tab.  
374 2; Figs. 4a, h, i, j, k). However, a larger decrease in  $\text{pCO}_2$  levels in the forest continuum suggested a more  
375 intense degassing in forest streams (Tab. 2; Fig. 4h). We also observed an increase in  $\text{O}_2$  in both types of  
376 continuum, which could result from stream ventilation, although with a higher intensity in forest  
377 continuum (Tab. 2; Figs. 4f, h).

378 EC decreased downstream in the crop continuum, but did not in the forest continuum where EC remained  
379 very stable and much lower than in the crop continuum (Tab. 2; Fig. 4b).  $\text{NO}_3^-$  decreased downstream  
380 between groundwater and streams in croplands, and in contrast, in forests  $\text{NO}_3^-$  increased downstream  
381 between groundwaters and streams (Tab. 2; Fig. 4c).  $\text{NH}_4^+$ ,  $\text{Fe}^{2+}$ , and  $\text{CH}_4$  decreased in the forest  
382 continuum but they increased in the crop continuum (Tab. 2; Figs. 4d, e, g). DOC significantly decreased  
383 in the forest continuum but remained stable in the crop continuum (Tab. 2; Fig. 4l). TSM and POC were  
384 significantly higher in crop relative to forest streams; however, similarly high POC% (28%) was observed  
385 in both types of streams (Tab. 2; Fig. 4m, n, o).

386

### 387 **3.6. Biogeochemistry dynamics in the groundwater-stream continuum**

388 PCA with groundwater and streams datasets indicated mathematically that streams were fed with two  
389 distinct sources: forest groundwater mostly characterized by high  $\text{pCO}_2$ , DIC, and  $\text{CH}_4$  concentrations and  
390 crop groundwater mostly characterized by high  $\text{NO}_3^-$  concentrations (Figs. 5). Forest and crop streams  
391 were characterized by higher  $\text{O}_2$ ,  $\delta^{13}\text{C-DIC}$  and pH values than in groundwater (Figs. 5). In this PCA, the  
392 distinction between forest and crop streams was primarily a function of  $\text{NO}_3^-$ , crop streams points were  
393 moved upward along dimension 2 (Figs. 5). Throughout the sampling period, we observed a negative

394 linear relationship ( $R^2=0.6$ ,  $p<0.001$ ,  $n=192$ ) between  $\text{CO}_2$  and  $\text{O}_2$  for all sampled groundwater and  
395 streams (Fig. 6a). On the one side, stream samples were mostly characterized by high  $\text{O}_2$  (mean was 290  
396  $\mu\text{mol L}^{-1}$ ) and low  $\text{CO}_2$  (mean was 4,480 ppmv), excepting some forest streams during summer that were  
397 characterized by low  $\text{O}_2$  (down to 110  $\mu\text{mol L}^{-1}$ ) and high  $\text{CO}_2$  (up to 27,200 ppmv) (Tab. 2; Figs. 6a, S4f,  
398 h). On the other side, anoxic conditions associated with high  $\text{CO}_2$  (mean was 50,630 ppmv) were  
399 characteristic of forest groundwater, whereas crop groundwater exhibited  $\text{O}_2$  (mean was 220  $\mu\text{mol L}^{-1}$ ) and  
400  $\text{CO}_2$  (mean was 30,650 ppmv) intermediate between streams and forest groundwater (Tab. 2; Fig. 6a). In  
401 forest groundwater, DOC was negatively and linearly correlated with  $\text{CO}_2$  ( $R^2=0.4$ ,  $p < 0.001$ ,  $n=22$ )  
402 suggesting that part of groundwater  $\text{CO}_2$  came from degradation of groundwater DOC (Fig. 6b). A  
403 comparison of  $\text{CO}_2$  and  $\text{CH}_4$  for all sampled groundwaters and streams showed that a large portion of the  
404  $\text{CO}_2$  and  $\text{CH}_4$  in forest streams could come from forest groundwater discharge (Tab. 2; Fig. 6e). In crop  
405 streams,  $\text{CH}_4$ ,  $\text{NH}_4^+$ , and  $\text{Fe}^{2+}$  could not originate from crop groundwater discharge since they had much  
406 lower  $\text{CH}_4$ ,  $\text{NH}_4^+$ , and  $\text{Fe}^{2+}$  concentrations than crop streams (Tab. 2; Fig. 6e, 7e, 7f). We observed a  
407 positive linear relationship between  $\text{CH}_4$  and  $\text{NH}_4^+$  ( $R^2=0.4$ ,  $p<0.001$ ,  $n=53$ ) in crop streams,  
408 demonstrating that these two compounds may come from the same source (Fig. 7d). Conversely, a  
409 comparison of  $\text{O}_2$  and  $\text{NH}_4^+$  or  $\text{Fe}^{2+}$  in forest streams indicated that  $\text{NH}_4^+$  and  $\text{Fe}^{2+}$  were mostly discharged  
410 through forest groundwater (Fig. 7e, f). In forest streams, the negative linear relationship between  $\text{O}_2$  and  
411  $\text{NH}_4^+$  ( $R^2=0.1$ ,  $p\text{-value}<0.05$ ,  $n=70$ ),  $\text{Fe}^{2+}$  ( $R^2=0.5$ ,  $p\text{-value}<0.001$ ,  $n=77$ ), or  $\text{CH}_4$  ( $R^2=0.1$ ,  $p\text{-value}<0.001$ ,  
412  $n=77$ ) suggested oxidation of these reduced compounds in the stream water column (Fig. 7e, f). We  
413 observed a gradient of  $\text{NO}_3^-$  concentration, from high values to low values, between crop groundwater  
414 (mean was 1,140  $\mu\text{mol L}^{-1}$ ), to riparian groundwater and crop streams (310 and 340  $\mu\text{mol L}^{-1}$ ,  
415 respectively), to forest streams (75  $\mu\text{mol L}^{-1}$ ) and to forest groundwater (25  $\mu\text{mol L}^{-1}$ ) (Tab. 2; Fig. 7a, b,  
416 c). In crop streams, a large share of riverine  $\text{NO}_3^-$  could be discharged through crop groundwater.  
417 Conversely,  $\text{NO}_3^-$  concentration in forest streams could not be explained by  $\text{NO}_3^-$  concentration in forest  
418 groundwater (Tab. 2; Fig. 7a, b, c, d). In crop groundwater, high  $\text{NO}_3^-$  concentrations were associated with

419 low CH<sub>4</sub> concentrations. In crop streams, high NO<sub>3</sub><sup>-</sup> concentrations could be related to high CH<sub>4</sub>  
420 concentrations (Fig. 7c).

421

## 422 **4. Discussion**

### 423 **4.1. Water table depth in relation to land use**

424 At the studied catchment scale, lithology, topography, soils, and precipitation are more or less uniform  
425 (Augusto et al., 2010; Jolivet et al., 2003). At the plot scale, spatial variability of water table depth in  
426 relation to land use was thus necessarily dependent on how water outputs (drainage, evapotranspiration or  
427 groundwater storage) of the water mass balance were human-affected (Govind et al., 2012; Stella et al.,  
428 2009). Local forests are never irrigated, conversely, irrigation with extraction of groundwater (that  
429 decreases groundwater storage) in local croplands could strongly bias the water mass balance at the plot  
430 scale since about half of the water diverted for irrigation is rapidly consumed through evapotranspiration  
431 (e.g., Jackson et al; 2001). Additionally, evapotranspiration in maize croplands is typically higher than in  
432 forests owing to the larger stomatal conductance that makes the exchange of C and water between the  
433 biosphere and the atmosphere much easier (Govind et al., 2012; Stella et al., 2009). Other studies have  
434 shown that the combination of subsoiling practices (increasing soil permeability) with deep agricultural  
435 ditches in croplands also affected water mass balance at the plot scale by enhancing lateral drainage of  
436 groundwater (Evans et al., 1996; Robinson et al., 1985). From an 8 year survey of local cropland, Juste et  
437 al (1982) showed that lateral drainage strongly affected the water mass balance at the plot scale as it  
438 represented an annual mean of 637 mm (70% of the amount of precipitation), whereas precipitation was  
439 estimated at 922 mm. At the forest plot scale, lateral drainage represented an annual mean of 182 mm  
440 (20% of the amount of precipitation), whereas precipitation was estimated at 895mm (Deirmendjian et al,  
441 2018). At the study site, deeper water table in croplands was thus a consequence of a higher  
442 evapotranspiration and more lateral drainage than in forest. As explained further, water table depth is an

443 important determinant for understanding the biogeochemical variability in groundwater in relation to land  
444 use.

445

446 **4.2. Dynamic of O<sub>2</sub>, DOC, DIC and δ<sup>13</sup>C-DIC in groundwater: a combination of hydrological,**  
447 **physical and metabolic processes**

448 In other aquifer systems worldwide, several studies have observed a significant positive correlation  
449 between groundwater O<sub>2</sub> concentration and depth to water (Datry et al., 2004; Foulquier et al., 2010;  
450 Goldscheider et al., 2006; McMahon and Chapelle, 2008; Pabich et al., 2001). Where the water table is  
451 close to the soil surface, groundwater O<sub>2</sub> consumption is likely rapid because of incomplete degradation of  
452 soil-generated labile DOC in the unsaturated zone. On the contrary, where the water table is far from the  
453 soil surface, strong oxygen depletion in the vicinity of the water table does not occur since the higher  
454 residence time of infiltrating water results in almost complete degradation of soil-generated DOC in the  
455 unsaturated zone (Malard and Hervant, 1999; Starr and Gillham, 1993). A regional study in forest soils of  
456 Switzerland (Hagerdon et al., 2000) and a study compiling a global database of soil carbon (Camino-  
457 Serrano et al., 2014) both found that soil-generated DOC was preferentially mobilized under reducing  
458 conditions in soils because of dissolution of Fe oxides. Deeper water tables in croplands do not reach  
459 topsoil that exhibits high labile organic C content. Thus, reducing conditions in topsoil and the leaching of  
460 soil-generated DOC are prevented as is the consumption of the groundwater O<sub>2</sub> stock, as occurs in forests  
461 during high flow stages (Tab. 3; Fig. S21; Deirmendjian et al. 2018). Therefore, groundwater pCO<sub>2</sub> was  
462 higher in the forest during high flow than it was in cropland and riparian sites (Tab.3; Figs. 4h, S21, h).  
463 This also explains the negative correlation between DOC and CO<sub>2</sub> observed only in forest groundwater  
464 (Fig. 6b). During base flow, we observed a clear land use spatial pattern among cropland, riparian forest,  
465 and forest sites (Tab. 3; Fig. S2h). We hypothesize that this difference was a consequence of a less intense  
466 soil respiration in croplands during summer. From simultaneous eddy covariance measurements over pine  
467 forests and maize croplands of the study area, Stella et al (2009) confirmed that ecosystem respiration was

468 lower in croplands than in forests over the whole year. However, Stella et al (2009) also showed that  
469 ecosystem respiration was larger during the growing season of the maize, because of increased of soil  
470 respiration in response to the higher soil water content caused by irrigation. In forest sites, groundwater  
471 pCO<sub>2</sub> increases during the summer because soil CO<sub>2</sub> diffuses downward and then is dissolved into the  
472 water table (Deirmendjian et al., 2018; Tsy-pin and Macpherson, 2012). A deeper water table in cropland  
473 suggests a less efficient CO<sub>2</sub> transfer from soil air to water table. Higher soil moisture in croplands due to  
474 irrigation probably delays soil CO<sub>2</sub> diffusion to groundwater.

475 The δ<sup>13</sup>C-DIC signature of forest groundwater was typical of a signature that originated from respiration  
476 of soil organic matter derived from C<sub>3</sub> plants (O'Leary, 1988; Vogel et al., 1993). The studied forest soils  
477 have no natural carbonate minerals (Augusto et al., 2010) and DIC originating from silicate weathering  
478 has the same isotopic signature as DIC originating from soil respiration (Das et al., 2005; Polsenaere and  
479 Abril, 2012; Wachniew, 2006). Crop groundwater had a heavier δ<sup>13</sup>C-DIC signature than forest  
480 groundwater and this discrepancy resulted from distinct processes. Liming in cropland brings artificial  
481 carbonates into crop soil and DIC originating from carbonate weathering produced DIC with a δ<sup>13</sup>C value  
482 of approximately half of that of soil CO<sub>2</sub> as carbonate rocks have a δ<sup>13</sup>C of approximately 0 ‰, making  
483 δ<sup>13</sup>C-DIC less negative (Clark and Fritz, 1997; Salomons and Mook, 1986). Irrigation with extraction of  
484 groundwater could also increase the δ<sup>13</sup>C-DIC signature by enhancing the degassing rate of <sup>12</sup>CO<sub>2</sub> relative  
485 to <sup>13</sup>CO<sub>2</sub> (Deirmendjian and Abril, 2018; Polsenaere and Abril, 2012). Changes in the δ<sup>13</sup>C-DIC signature  
486 could also originate from respiration of soil organic matter derived from maize, a C<sub>4</sub> plant with a heavier  
487 δ<sup>13</sup>C signature than C<sub>3</sub> forest plants (O'Leary, 1988; Vogel et al., 1993), as observed in the study region  
488 (Quénéa et al., 2006). Indeed, after three decades of cultivation, the remaining carbon from the forest pool  
489 was mostly recalcitrant and its degradation probably did not affect the δ<sup>13</sup>C-DIC pool (Jolivet et al., 1997).

490

#### 491 **4.3. Dynamics of IN and CH<sub>4</sub> in groundwater: the influence of groundwater O<sub>2</sub>**

492 Subsurface and groundwater redox zonation is driven by the spatial and temporal distribution of O<sub>2</sub> that  
493 serves as the primary terminal electron acceptor during the degradation of organic C. In crop groundwater,  
494 high O<sub>2</sub> concentrations inhibited methanogenesis, as this process is strictly anaerobic and thus resulted in  
495 very low CH<sub>4</sub> concentrations (Tab. 2; Figs. 4f, g; Borges et al., 2018; Ciais et al., 2010; Jurado et al.,  
496 2017; Klüber and Conrad, 1998). Conversely, forest and riparian groundwater exhibited anoxic conditions  
497 that allowed methanogenesis to occur and created higher CH<sub>4</sub> concentration in forest sites compared to  
498 cropland sites (Tab. 2; Figs. 4f, g). High water table stages in forested areas cause anoxia in soils, forcing  
499 plants and microorganisms to switch to anaerobic metabolism (Naumburg et al., 2005; Bakker et al., 2006,  
500 2009). Thus, in riparian and forest areas, we expected a positive relationship between water table and  
501 groundwater CH<sub>4</sub> but, to the contrary, we observed a negative relationship between these two parameters  
502 ( $R^2 = 0.25$ ,  $p < 0.05$ ; data not shown). This implies that methanogenesis primarily occurs in deeper layers of  
503 forest soils, especially in summer. Fe<sup>2+</sup> and NH<sub>4</sub><sup>+</sup> accumulates in forest groundwater because anoxic  
504 conditions inhibit nitrification and iron oxidation (Tab. 2; Figs. 4d, e; Jambert et al., 1994; Widdel et al.,  
505 1993).

506 In groundwater, anoxic conditions enable heterotrophic denitrification, whereas an O<sub>2</sub> threshold of 30–60  
507  $\mu\text{mol L}^{-1}$  completely inhibits heterotrophic denitrification (Balestrini et al., 2016; Cey et al., 1999;  
508 Christensen et al., 2013; Jambert et al., 1994; Kolbjørn Jensen et al., 2017; Korom, 1992). In strictly forest  
509 sites, denitrification in groundwater is usually limited by the scarcity of NO<sub>3</sub><sup>-</sup>, whereas in strictly crop sites  
510 denitrification is often limited by organic C availability (Tab. 2; Jambert et al., 1994; Starr and Gillham,  
511 1993). Thus, N fertilizer application associated with different groundwater denitrification rates in the  
512 different plots creates the observed spatial pattern of groundwater NO<sub>3</sub><sup>-</sup> concentration in crop, riparian and  
513 forest sites (Tab. 2; Fig. 4c). In local maize croplands, Jambert et al (1997) found that 13% of the N  
514 fertilizers inputs were converted to N<sub>2</sub> gas, demonstrating that denitrification could occur in these oxic  
515 crop soils and groundwater. Although oxic conditions are not favorable for groundwater denitrification,  
516 some studies in agricultural catchments do describe this process at relatively high O<sub>2</sub> (150  $\mu\text{mol L}^{-1}$ )

517 levels (McAleer et al., 2017; Otero et al., 2009). In crop soils, Rubol et al. (2016) investigated the spatio-  
518 temporal dynamics in oxidative microbial activity and the development of anoxic micro zones (i.e., anoxic  
519 hot-spots) at the microscopic level ( $\mu\text{m}$  to  $\text{cm}$ ). They found that labile C addition resulted in maximum  
520 rates of local metabolic activity within a few minutes and led to the subsequent formation of anoxic  
521 hotspots and thus, both oxic and anoxic conditions coexisted closely within a small volume of crop soils.  
522 Consequently, denitrification probably occurs in anoxic microsites in waterlogged soil during irrigation as  
523 higher soil moisture results in lower soil oxygen concentration, lower redox potential and higher leaching  
524 of soil DOC (Hagedorn et al., 2000; Jambert et al., 1997; Rubol et al., 2012; Silver et al., 1999).

525 N fertilizer load in local croplands is  $25 \text{ g N m}^{-2} \text{ yr}^{-1}$  (Jambert et al., 1997), whereas export (using drainage  
526 of  $637 \text{ mm yr}^{-1}$  and the average  $\text{NO}_3^-$  concentration in crop groundwater) of  $\text{NO}_3^-$  through crop  
527 groundwater was estimated at  $10 \text{ g N m}^{-2} \text{ yr}^{-1}$  (40% of the annual N fertilizer load), and export (using same  
528 drainage and the average  $\text{NO}_3^-$  concentration in riparian groundwater) of  $\text{NO}_3^-$  through riparian  
529 groundwater was estimated at  $2.8 \text{ g N m}^{-2} \text{ yr}^{-1}$  (8% of the annual N fertilizer load). This shows the  
530 importance of riparian groundwater to attenuate N inputs from adjacent croplands to streams, otherwise a  
531 large portion of the annual N fertilizer load would have been leached into adjacent streams rather than  
532 being denitrified or used by plants. In riparian groundwater adjacent to a farm in the New York state  
533 (USA), Anderson et al. (2014) found that total groundwater denitrification was equivalent to 32% of  
534 manure N spread on the adjacent upland field. (Mekala et al., 2017) simulated the transport and dynamics  
535 of N in an agricultural soil under flooded conditions and concluded that relatively shallow aquifers with  
536 sandy soil are vulnerable to  $\text{NO}_3^-$  contamination at around 10 days if continuous irrigation is practiced.  
537 They also stated that  $\text{NO}_3^-$  had higher leaching potential than  $\text{NH}_4^+$  or DOC. At our study site, irrigation  
538 and associated desorption of DOC and  $\text{NO}_3^-$  could explain their slight increase in crop groundwater during  
539 base flow (Tab. 3, Figs. 1, S2c). In a storm infiltration basin in Florida (USA), O'Reilly et al. (2012)  
540 found that concomitant peaks in groundwater  $\text{O}_2$  and  $\text{NO}_3^-$  concentrations after storm rainfall were a  
541 consequence of organic N leaching, indicating that there were short periods of ammonification and

542 nitrification. In crop groundwater of Wallonia (Belgium), when groundwater O<sub>2</sub> levels are higher than 125  
543 μmol L<sup>-1</sup> (as at the study site), nitrification rather than denitrification promotes the accumulation of N<sub>2</sub>O in  
544 groundwater (Jurado et al., 2017).

545

#### 546 **4.4. Stream biogeochemical functioning: mostly a function of groundwater composition**

547 NO<sub>3</sub><sup>-</sup> inputs to streams cause stream eutrophication (Carpenter et al., 1998; Jordan and Weller, 1996;  
548 Smith, 2003; Zhou et al., 2017). This is consistent with our field observations where we observed that crop  
549 streams were highly vegetated with macrophytes during base flow stages. Compared to high flow  
550 conditions, crop stream eutrophication was accompanied by higher pH and δ<sup>13</sup>C-DIC, and lower  
551 pCO<sub>2</sub> caused by preferential <sup>12</sup>CO<sub>2</sub> uptake during the macrophyte plant photosynthesis (Tab. 4; Figs. S3a,  
552 h, j; De Carvalho et al., 2009; Raven et al., 2002). The development of macrophytes in crop streams  
553 modifies flow and can cause a significant drop in water velocity, which in turn, gives rise to extensive  
554 deposition and retention of sediment beneath the macrophytes (Cotton et al., 2006; Sand-Jensen and  
555 Pedersen, 1999). This leads to seasonal accumulation of organic matter, a predominance of anoxic  
556 conditions in stream sediments, and thus the occurrence of methanogenesis as evidenced by peaks in  
557 dissolved CH<sub>4</sub> during base flow (Tab. 4; Figs. S3g; Borges et al., 2018; Crawford et al., 2016; Sanders et  
558 al., 2007). Crop stream CH<sub>4</sub> concentration was 390 nmol L<sup>-1</sup> during base flow (Tab. 2), a concentration  
559 significantly lower (1,430 nmol L<sup>-1</sup>) than chalk streams impacted by macrophyte vegetation in England  
560 (Sanders et al., 2007). This discrepancy probably resulted from the increased in silt and clay fraction  
561 during summer of the underlying sediment in chalk streams (Sanders et al., 2007). This would suggest that  
562 the permeability of chalk stream sediment became lower than that of sandy stream sediment and created  
563 stronger reducing conditions in chalk stream sediments, which likely increased the potential for  
564 methanogenesis (Baker et al., 1999; Findlay, 1995; Kankaala et al., 2005; Morrice et al., 1997). Sanders et  
565 al. (2007) also showed that the chalk streams' emissions of CH<sub>4</sub> to the atmosphere were approximately 50  
566 times lower than the CH<sub>4</sub> production in stream sediments, illustrating the high potential for CH<sub>4</sub> oxidation



567 in the water column of crop stream. During base flow, a second explanation for higher  $\text{CH}_4$  (and  $\text{NH}_4^+$ )  
568 concentrations in crop streams relative to forest streams could be differential hydrology. Drainage plot is a  
569 function of the water table height (hydraulic gradient, Darcy's law). During base flow, the water table in  
570 cropland was deeper than in forest (e.g., 4 m deeper in Sep. 2014; Fig. 2), and so during this period,  
571 potentially more forest groundwater was drained into crop streams. However, in forest streams we usually  
572 did not observe  $\text{CH}_4$  (or  $\text{NH}_4^+$ ) concentrations as high as in crop streams (Tab. 2; Fig. 7d) indicating that  
573  $\text{CH}_4$  (or  $\text{NH}_4^+$ ) in crop streams primarily originated from crop stream sediments rather than from higher  
574 discharge of forest groundwater. In crop streams,  $\text{CH}_4$  was correlated with  $\text{NH}_4^+$  but not correlated with  
575  $\text{NO}_3^-$  or DOC (Figs. 6d, 7c, d). Such relationships were also observed in the Meuse river basin (Belgium)  
576 (Borges et al., 2018) and in a global meta-analysis of riverine  $\text{CH}_4$  (Stanley et al., 2016). In contrast, this  
577 does not fit the conceptual model of Schade et al (2016) developed from data in New Hampshire streams,  
578 whereby the  $\text{CH}_4$  was positively correlated with DOC, while negatively related to  $\text{NO}_3^-$ .

579 Sandy sediments of low order stream beds impacted by eutrophication are significant areas of  $\text{NO}_3^-$   
580 reduction over the spring and summer, lowering DOC and  $\text{NO}_3^-$  concentrations in stream water (Tab. 4;  
581 Figs. S3c, l; Böhlke et al., 2009; Mulholland et al., 2008; Sanders et al., 2007). Additionally, the decreased  
582 of stream velocity during base flow increased residence times of  $\text{NO}_3^-$  in the hyporheic zone and the time  
583 for denitrification (Bardini et al., 2012). In a small stream dominated by maize cropland in the USA,  
584 Böhlke et al. (2009) demonstrated that denitrification mainly occurred in sediments and not in the water  
585 column since integrated rates of pore-water denitrification derived from  $^{15}\text{N}$  tracer profiles within the  
586 hyporheic zone were similar to the reach-scale rates derived from measurements in the stream. In crop  
587 streams, a portion of the  $\text{NO}_3^-$  variability between the two hydrological periods could also result from  
588 higher drainage of forest groundwater during base flow, which would dilute the  $\text{NO}_3^-$  signal from crop  
589 groundwater.

590 Considering the flat catchment topography, a minor portion of TSM and POC in streams originates from  
591 soil erosion and surface runoff. The most frequent effects of dredging on aquatic ecosystems are changes

592 in the concentration of suspended solids, turbidity and light penetration (Lewis et al., 2001; Newell et al.,  
593 1998). Higher concentrations of POC (and TSM) observed in crop streams were also caused by  
594 macrophyte biomass developed in summer became a sediment trap. When stream discharge was  
595 sufficiently energetic, it re-suspended all the accumulated sediment and removed this litter. Moreover, we  
596 observed peaks of  $\text{CH}_4$  and  $\text{NH}_4^+$  in crop streams during high flow (Tab. 4; Figs. S3d, g), suggesting that  
597 dredging or streambed erosion of crop streams also release  $\text{CH}_4$  and  $\text{NH}_4^+$  from the sediment.

598 In forest streams, we observed significantly lower concentrations of  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{CH}_4$  than in forest  
599 groundwater and significant negative linear relationships between  $\text{O}_2$  on the one side and  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$ , or  
600  $\text{CH}_4$  (Tab. 2; Figs. 4d, e, g, 7e, f). This suggests there were low  $\text{O}_2$  concentration groundwater inputs with  
601 high concentrations of reduced compounds and that the stream water was gradually oxygenated, which  
602 induced  $\text{Fe}^{2+}$  and  $\text{CH}_4$  oxidations and nitrification. Mulholland et al. (2000) studied N cycling by adding  
603  $^{15}\text{N}$ -labeled  $\text{NH}_4^+$  into a forest stream in eastern Tennessee (USA). They concluded that the residence time  
604 of  $\text{NH}_4^+$  in the water column was low (5 min) and that nitrification was an important sink for  $\text{NH}_4^+$ ,  
605 accounting for 19% of total ammonium uptake. In forest streams, the  $\text{NH}_4^+$  concentration was  
606 approximately  $3 \mu\text{mol L}^{-1}$  lower than in forest groundwater and thus did not explained the  $\text{NO}_3^-$  increase of  
607  $50 \mu\text{mol L}^{-1}$  (Tab. 2; Figs. 3c, d). Up to 76% of N exports from local forest are in organic forms but these  
608 N exports are very low ( $< 0.2 \text{ g N m}^{-2} \text{ yr}^{-1}$ ; De Wit et al., 2005; Rimmelin, 1998; Vernier et al., 2003), so  
609 in-stream mineralization of organic N coupled to nitrification could not explain  $\text{NO}_3^-$  concentrations in  
610 forest streams. Since the sampled forest streams are not strictly forested,  $\text{NO}_3^-$  concentration are explained  
611 by simple hydrological mixing between crop and forest groundwater (Tab. 2).

612 In streams,  $\text{pCO}_2$  was lower and  $\text{O}_2$  was higher than in groundwater (Tab. 2; Figs. 3f, h, 5a). This shows  
613 that gas exchange between stream water and the atmosphere occurs quickly, favored by low stream depth  
614 and strong concentration gradients between the two compartments. Some authors (e.g., Bodmer et al.  
615 2016; Borges et al., 2018) found elevated  $\text{pCO}_2$  in crop streams rather than in forest streams, due to higher  
616 levels of dissolved and particulate organic matter in crop dominated systems compared to the forested

617 ones that facilitated the in-stream degradation of organic matter. Moreover, land uses are expected to  
618 change the composition of terrestrial soil organic matter leached to streams, shifting from vegetation- to  
619 microbe-derived organic matter with greater agricultural land use and potentially higher emissions in crop  
620 streams (Fuss et al., 2017; Graeber et al., 2015; Wilson and Xenopoulos, 2009). Those results contrasted  
621 with ours because we found no difference in pCO<sub>2</sub> between crop and forest streams. Forest groundwater  
622 did have higher pCO<sub>2</sub> than crop groundwater, indicating a more intense degassing in forest streams. The  
623 similar δ<sup>13</sup>C-DIC signatures in forest and crop streams despite the strong difference between crop and  
624 forest groundwater suggests faster isotopic equilibration of DIC resulting from degassing. The greater gas  
625 transfer velocity in forest streams is a consequence of the abundance of coarse woody debris which  
626 generates higher levels of water turbulence (e.g., Bodmer et al. 2016), and is consistent with our field  
627 observations. A lower gas transfer velocity lower in crop streams results from stream calibration reducing  
628 turbulent flow, and macrophyte vegetation that protects the water surface from wind shear.

629

## 630 **5. Conclusion**

631 The present study demonstrates that C and IN concentrations in shallow groundwater and in first-order  
632 streams are strongly sensitive to land use. In sandy lowland catchments, simultaneous measurements of  
633 biogeochemical parameters in groundwater and streams are crucial for identifying and quantifying  
634 biogeochemical processes involved at the groundwater-stream interface. We also show that a statistical  
635 clustering analysis based on NO<sub>3</sub><sup>-</sup> dataset enables partitioning of groundwater and streams into crop-  
636 affected or forest-dominated waters. Such a classification could be useful to river managers and policy  
637 makers. The water table had greater depth in croplands and was a crucial parameter necessary for  
638 understanding groundwater biogeochemical variability in relation to land use. Higher water table stages in  
639 forests created anoxic conditions and increased soil leaching. Conversely, in croplands, the deeper water  
640 table prevented anoxic conditions, creating different groundwater compositions from forest groundwater  
641 and inhibiting the denitrification of the N fertilizers, which led to groundwater NO<sub>3</sub><sup>-</sup> accumulation. Despite

642 the occurrence of groundwater denitrification in riparian and forest sites, N fertilizers inputs in crop  
643 streams were still high enough to generate eutrophic conditions in these streams. Eutrophication resulted  
644 in a biogeochemical cascading effect, which sustained high CH<sub>4</sub> concentration and lowered NO<sub>3</sub><sup>-</sup>. High  
645 CO<sub>2</sub> and CH<sub>4</sub> production occurs in forest soils and groundwater, but these two gases exhibit lower  
646 concentrations in forest streams, indicating intense degassing or oxidation.

647 The groundwater-stream interface is a biogeochemical hotspot and hot moment for C emissions and N  
648 removal processes (McClain et al., 2003). Future studies focusing on the groundwater-stream interface in  
649 relation to land use are needed to better understand C and N dynamics in aquatic systems in order to  
650 correctly close C and N budgets at regional and global scales.

651

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655

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Stream Order	Description	Catchment area (km <sup>2</sup> ) <sup>a</sup>	Crop (%) <sup>b</sup>	Forest (%) <sup>b</sup>	Urban (%) <sup>b</sup>	During High Flow <sup>c</sup>	During Base Flow <sup>c</sup>
1	Ditch	1.0	86.5	13.5	0.0	C	C
1	Ditch	1.3	53.8	46.2	0.0	C	C
1	Ditch	11.3	44.2	55.8	0.0	C	C
1	Ditch	13.4	42.5	57.5	0.0	C	C
1	Stream	57.0	30.7	69.3	0.0	C	C
1	Stream	16.8	7.8	92.2	0.0	F	F
1	Ditch	7.9	5.8	94.2	0.0	F	F
1	Ditch	2.3	5.2	94.8	0.0	F	C
1	Stream	16.0	4.6	93.8	1.6	C	F
1	Stream	34.0	3.8	96.2	0.0	F	F
1	Stream	31.0	2.3	97.7	0.0	F	F
1	Headwater	0.3	0.0	100.0	0.0	F	F
0	Groundwater in a riparian forest but very near (5m) a maize cropland (P1)					R	R
0	Groundwater in maize cropland (P2)					C	C
0	Groundwater in maize cropland (P3)					C	C
0	Groundwater in pine forest (P4)					F	F
0	Groundwater in pine forest (P5)					F	F

1086 Table 1. Characteristics of groundwater and stream sampling stations, ranked in decreasing order of cropland percentage in their respective sub-  
1087 catchments. <sup>a</sup> delimited with a geographic information system software (ArcGIS 10.5®) using an hydrological database in a polyline form (BD  
1088 CARTHAGE®) and a digital elevation model (BD ALTI®, resolution of 25m), which both have been made available by the national geographic  
1089 institute of France (<http://www.ign.fr/>). <sup>b</sup> retrieved with the CORINE land cover 2006 database (EEA, 2014) using a geographic information system  
1090 software (ArcGIS 10.5®). <sup>c</sup> C, F, R corresponding to crop, forest and riparian waters, respectively, either during high or base flow. Piezometer 1  
1091 (P1) is located in a riparian mixed pine and oak forest near a first-order stream and near a maize cropland, which where P2 is located. P2 and P3  
1092 are located in the middle of two different maize croplands of 0.6 km<sup>2</sup> and 6 km<sup>2</sup>, respectively. P5 is located in an 11-years old pine plot of 0.6 km<sup>2</sup>  
1093 and is part of the ICOS (name is FR-Bil) research infrastructure (<http://icos-ri.eu>), whereas P4 is located in another pine forest (approximately  
1094 same age as P5 pine forest). The depth of piezometers (from the soil surface to the bottom of the piezometer) is 5.3m for P1, 4.9m for P2, 9.1m for  
1095 P3, 5m for P4 and P5.

1096

	Crop continuum		Forest continuum		Riparian groundwater
	Groundwaters (22)	Streams (59)	Groundwaters (22)	Streams (78)	Groundwaters (11)
pH	4.5±0.2 4.3-5.0	6.0±0.3 5.4-7.0	4.5±0.3 3.7-4.8	5.8±0.5 4.2-6.9	4.7±0.1 4.4-4.8
Temperature (°C)	14.5±1.8 10.7-17.5	13.6±4.2 6.4-25.8	12.8±1.8 8.5-15.1	12.9±3.9 4.8-22.1	14.9±2.4 11.8-17.9
EC (µS cm <sup>-1</sup> )	360±70 220-465	220±55 75-370	90±10 65-115	115±30 70-200	160±50 95-270
NO <sub>3</sub> <sup>-</sup> (µmol L <sup>-1</sup> )	1,140±485 260-1,785	340±200 10-950	25±40 0-120	75±70 0-275	310±260 40-860
NH <sub>4</sub> <sup>+</sup> (µmol L <sup>-1</sup> )	0.4±0.8 0-3.5	6.1±7.0 0-40	4.5±7.0 0.3-30	1.8±1.7 0-7.8	0.4±0.4 0-1.5
Fe <sup>2+</sup> (µmol L <sup>-1</sup> )	0.9±0.4 0.1-1.9	5.9±4.4 0.1-22	15±15 0.9±56	7.9±12.0 0.6±58	0.6±0.5 0.2-1.5
O <sub>2</sub> (µmol L <sup>-1</sup> )	220±65 100-315	290±45 160-400	20±30 0-110	280±50 110-370	100±70 0-170
CH <sub>4</sub> (nmol L <sup>-1</sup> )	40±25 15-130	460±950 20-4,900	1,770±1,830 50-6,700	240±300 20-2,370	1,470±1,490 30-4,150
pCO <sub>2</sub> (ppmv)	30,650±11,590 19,000-60,550	4,480±2,680 1,040-14,080	50,630±26,070 7,680-116,380	4,900±4,500 1,000-27,200	42,950±28,560 17,300-103,300
TA (µmol L <sup>-1</sup> )	90±25 35-130	100±50 30-300	70±30 30-135	90±50 30-280	70±15 45-85
δ <sup>13</sup> C-DIC (‰)	-19.8±1.3 -22 to -17.6	-18.2±3.5 -27.6 to -11.3	-26.7±1.0 -28.8 to -24	-19.8±2.8 -27.6 to -14	-25.2±1.1 -27.9 to -23.4
DIC (µmol L <sup>-1</sup> )	1,450±480 820-2,590	315±135 90-650	2,460±1,130 570-5,370	320±210 120-1,280	1,960±1,150 940-4,480
DOC (µmol L <sup>-1</sup> )	510±150 275-880	605±320 220-2,290	930±930 310-3,670	470±250 190-1,725	400±100 280-620
TSM (mg L <sup>-1</sup> )		5.6±8.6 0.1-50.5		2.3±1.7 0.4-8.2	
POC (%)		28±10 0-50		28±10 10-80	
POC (µmol L <sup>-1</sup> )		120±180 0-1,100		50±35 0-170	

1098 Tab. 2. Values of carbon and ancillary parameters throughout sampling period (Jan. 2014-Jul. 2015) in crop and forest continuums and in riparian  
1099 groundwater. Numbers between brackets are corresponding to the sampling size. For each parameter, the table showed average±standard  
1100 deviations and the range.

	Groundwater						
	Cropland_HF (4)	Cropland_BF (18)	Forest_HF (6)	Forest_BF (16)	Riparian_HF (2)	Riparian_BF (9)	
pH	4.6±0.3	4.5±0.2	4.4±0.3	4.5±0.3	4.7±0.1	4.6±0.1	
	4.3-4.9	4.3-5.0	4.0-4.8	3.7-4.8	4.6-4.8	4.4-4.8	
Temperature (°C)	12.8±1.7	14.9±1.6	10.8±1.4	13.5±1.4	12.2±0.6	15.6±2.2	
	10.7-14.5	11.6-17.5	8.5-12.2	10.7-15.1	11.8-12.6	12.1-17.9	
EC (µS cm <sup>-1</sup> )	370±60	360±70	90±15	90±10	200±20	150±50	
	320-460	220-470	70-115	70-115	185-215	95-270	
NO <sub>3</sub> <sup>-</sup> (µmol L <sup>-1</sup> )	1,040±300	1,160±420	30±50	20±40	510±20	260±270	
	760-1,320	260-1785	0-120	0-120	500-520	40-860	
NH <sub>4</sub> <sup>+</sup> (µmol L <sup>-1</sup> )	0.5±0.4	0.4±0.9	3.3±2.2	5.0±8.0	0.3±0.1	0.4±0.5	
	0.1-1	0-3.5	1.1-7	0-3-30	0.2-0.3	0-1.5	
Fe <sup>2+</sup> (µmol L <sup>-1</sup> )	0.8±0.2	0.9±0.4	10.0±8.2	15±15	0.4±0.2	0.7±0.5	
	0.7-1.1	0.1-1.9	2.7-25.5	0.9-56.6	0.2-0.5	0.2-1.5	
O <sub>2</sub> (µmol L <sup>-1</sup> )	250±90	220±70	20±20	20±30	170±0	100±80	
	180-310	100-320	0-40	0-110	170-170	0-200	
CH <sub>4</sub> (nmol L <sup>-1</sup> )	30±3	50±25	480±630	2,260±1,900	1,460±2,010	1,470±1,500	
	25-30	16-130	50-1,700	50-6,700	40-2,880	30-4,150	
pCO <sub>2</sub> (ppmv)	22,050±2,000	32,560±12,000	28,100±11,580	59,080±25,060	21,530±5,950	47,700±29,590	
	19,800-24,270	19,000-60,550	7,680-39,000	29,685-116,400	17,320-25,740	20,600-103,300	
TA (µmol L <sup>-1</sup> )	85±2	92±30	95±40	65±30	83±2	60-10	
	82-86	35-130	60-135	30-100	82-85	45-75	
δ <sup>13</sup> C-DIC (‰)	-20.7±1.1	-19.6±1.3	-26.6±1.3	-26.8±1.0	-26.9±1.4	-24.9±0.7	
	-22 to -19.7	-21.9 to -17.6	-27.6 to -24.0	-28.8 to -25.3	-27.9 to -25.9	-25.7 to -23.4	
DIC (µmol L <sup>-1</sup> )	1,100±180	1,520±490	1,500±550	2,830±1,080	1,160±315	2,140±1,200	
	930-1,300	820-2,590	570-2,040	1,650-5,370	940-1,380	1,020-4,480	
DOC (µmol L <sup>-1</sup> )	420±120	550±140	2,230±1,440	740±380	310±50	420±100	
	320-590	340-880	575-3,670	310-1,720	275-350	310-620	

1101 Tab. 3. Values of carbon and ancillary parameters throughout sampling period (Jan. 2014-Jul. 2015) in different types of groundwater across  
1102 hydrological seasons. Numbers between brackets are corresponding to the sampling size. For each parameter, the table showed the  
1103 average±standard deviations and the range. We defined six groups that are Cropland\_HF/Cropland\_BF, Forest\_HF/Forest\_BF and  
1104 Riparian\_HF/Riparian\_BF corresponding to groundwaters during high flow (HF) or base flow (BF); in either cropland, forest or riparian forest.

1105














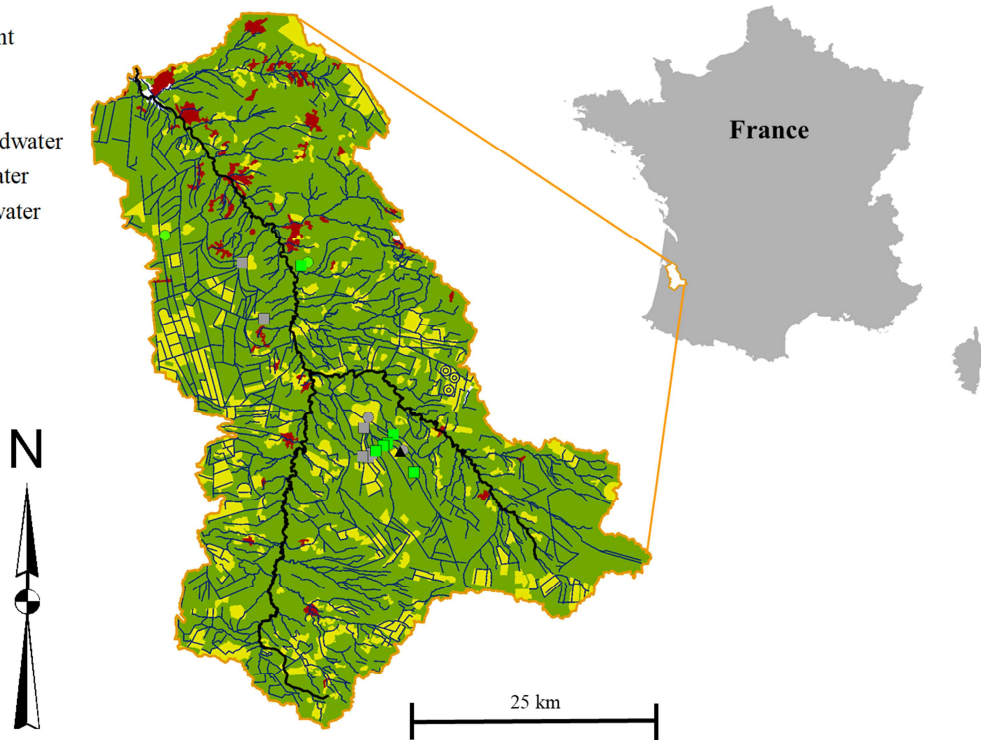
	First-order streams			
	Cropland_HF (22)	Cropland_BF (37)	Forest_HF (23)	Forest_BF (55)
pH	5.9±0.3 5.4-6.6	6.1±0.4 5.5-7.0	5.7±0.6 4.2-6.8	6.1±0.4 5.0-6.9
Temperature (°C)	10.2±1.6 6.4-12.1	15.7±3.9 9.1-25.8	9.0±1.9 4.8-12	14.6±3.3 8.1-22.1
EC (µS cm <sup>-1</sup> )	230±50 145-340	220±60 75-370	110±20 80-150	120±30 70-200
NO <sub>3</sub> <sup>-</sup> (µmol L <sup>-1</sup> )	420±220 180-950	290±170 8.5-705	95±70 0-275	65±70 0-275
NH <sub>4</sub> <sup>+</sup> (µmol L <sup>-1</sup> )	7.0±8.4 0.5-38.7	5.5±6.0 0-25.3	1.7±1.7 0.3-7.8	1.7±1.7 0-6.9
Fe <sup>2+</sup> (µmol L <sup>-1</sup> )	6.7±3.8 1.6-15.7	5.4±4.7 0.1-22	5.7±3.0 2.6-13.6	8.8±14.0 0.6-57.1
O <sub>2</sub> (µmol L <sup>-1</sup> )	290±50 190-400	290±40 160-370	300±40 210-370	270±60 110-360
CH <sub>4</sub> (nmol L <sup>-1</sup> )	580±1,080 30-4,380	390±880 20-4,900	185±190 40-980	270±340 20-2,370
pCO <sub>2</sub> (ppmv)	5,200±2,370 1,040-10,740	4,040±2,790 1,220-14,080	4,200±2,430 1,240±11,690	5,200±5,100 1,010-27,200
TA (µmol L <sup>-1</sup> )	105±50 40-300	100±50 30-255	70±40 35-195	95±55 30-280
δ <sup>13</sup> C-DIC (‰)	-20.6±3.9 -27.6 to -11.3	-16.8±2.4 -22.3 to -12.4	-22.1±2.5 -27.6 to -16.8	-18.9±2.3 -23.1 to -14.0
DIC (µmol L <sup>-1</sup> )	380±130 1,000-650	280±120 90-600	300±150 150-750	330±230 120-1,280
DOC (µmol L <sup>-1</sup> )	750±400 300-2,290	520±230 220-1,520	540±305 260-1725	450±220 190-1540
TSM (mg L <sup>-1</sup> )	9.3±11.5 0.9-51	3.1±4.9 0.1-27	2.8±1.7 0.5-6.6	2.1±1.7 0.4-8.2
POC (%)	26±10 15-48	30±10 16-48	29±8 20-50	29±10 12-80
POC (µmol L <sup>-1</sup> )	190±250 0-1100	65±100 0.3-540	65±40 0-170	40±30 0.5-140

1106 Tab. 4. Values of carbon and ancillary parameters throughout sampling period (Jan. 2014-Jul. 2015) in different types of streams across  
1107 hydrological seasons. Numbers between brackets are corresponding to the sampling size. For each parameter, the table showed the  
1108 average±standard deviations and the range. We defined four groups that are Cropland\_HF/Cropland\_BF, Forest\_HF/Forest\_BF corresponding  
1109 to streams during high flow (HF) or base flow (BF); in either cropland-affected or forest-dominated land use.

Figure 1: Land use map of the Leyre catchment showing river network and the sampling locations of groundwaters and streams.

**Legend**

-  Leyre catchment
-  Forest streams
-  Crop streams
-  Riparian groundwater
-  Crop groundwater
-  Forest groundwater
-  Main stems
-  River network
-  Urban
-  Cropland
-  Forest



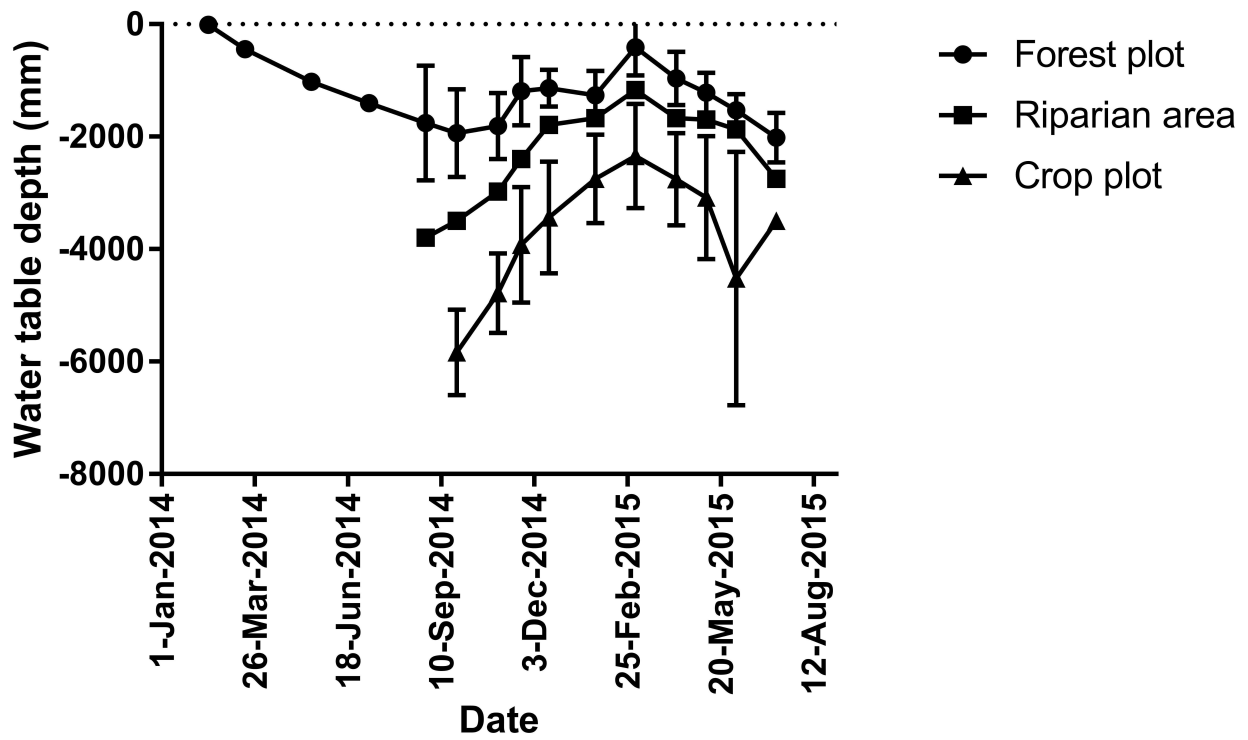


Figure 2: Water table depth during the sampling period (Jan. 2014-Jul. 2015) across land use in the Leyre catchment. The water table in riparian area is the water table at P1 (Tab. 1). The water table in crop plot is the average $\pm$ standard deviations of water tables at P2 and P3 (Tab. 1). The water table in forest plot is the average $\pm$ standard deviations of water tables at P4 and P5 (Tab. 1).

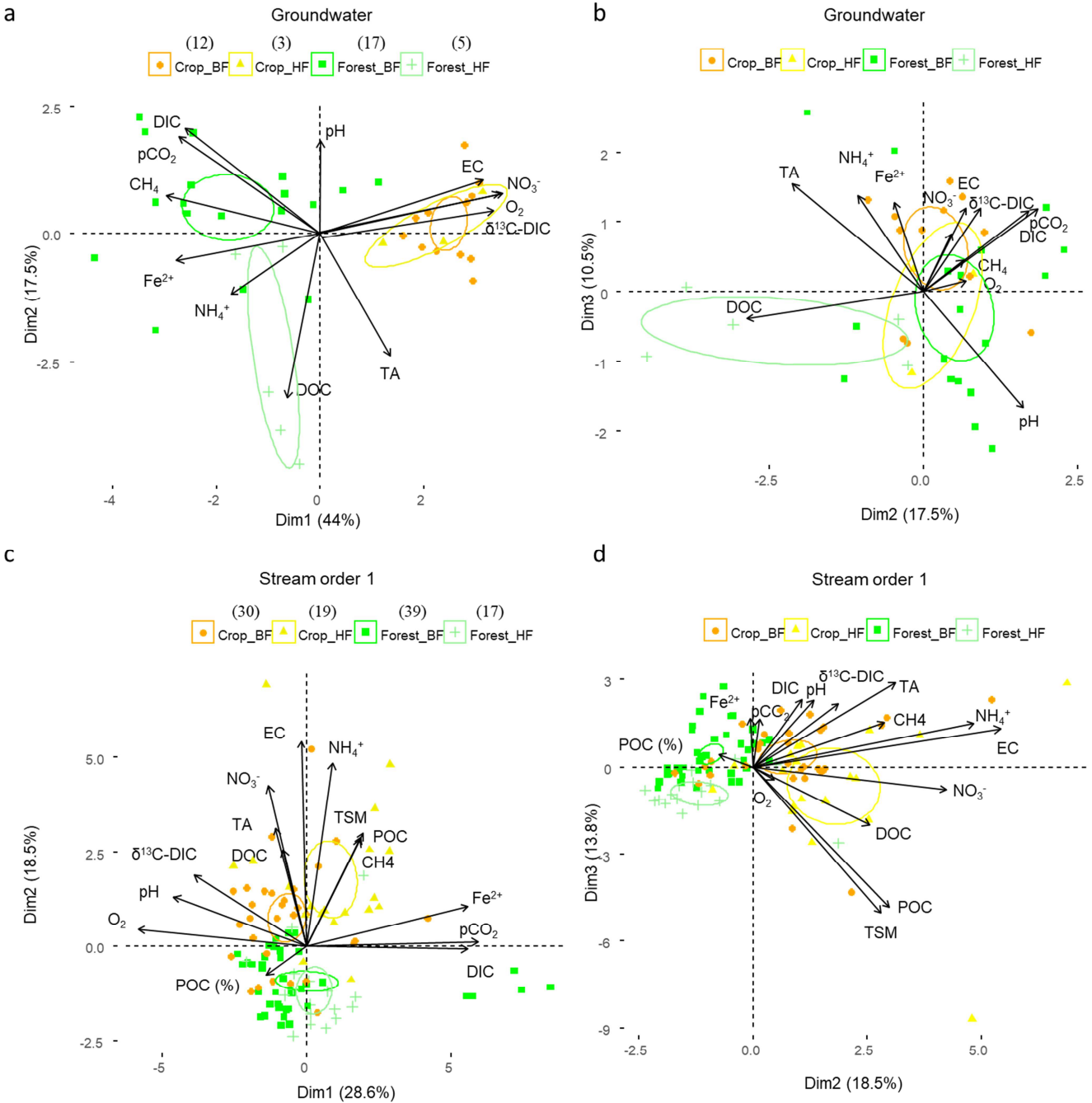


Figure 3: Principal component analysis (PCA) of shallow groundwater dataset (a-b) and first-order streams dataset (c-d). We represented only the first three dimensions. Numbers between brackets are corresponding to the sampling size. The sampling size in the PCAs did not correspond exactly to the sampling 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.

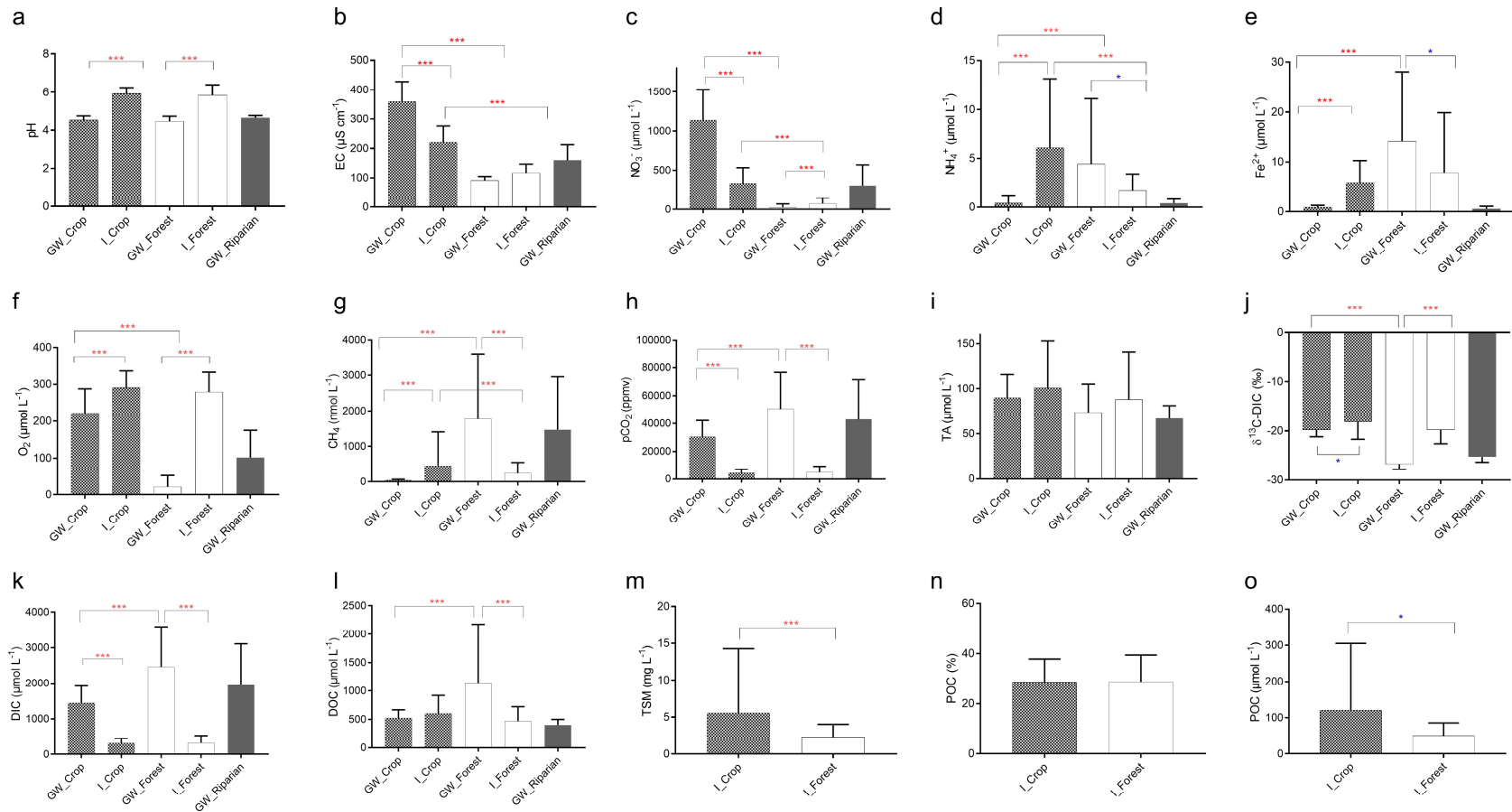


Figure 4: Values of carbon and ancillary parameters throughout the sampling period (Jan. 2014-Jul. 2015) in groundwater and streams across land use. Histograms represent the mean with standard deviations of a given parameter. We defined four groups that are GW\_Forest/GW\_Crop and I\_Forest/I\_crop corresponding 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 ( $p > 0.05$ ).

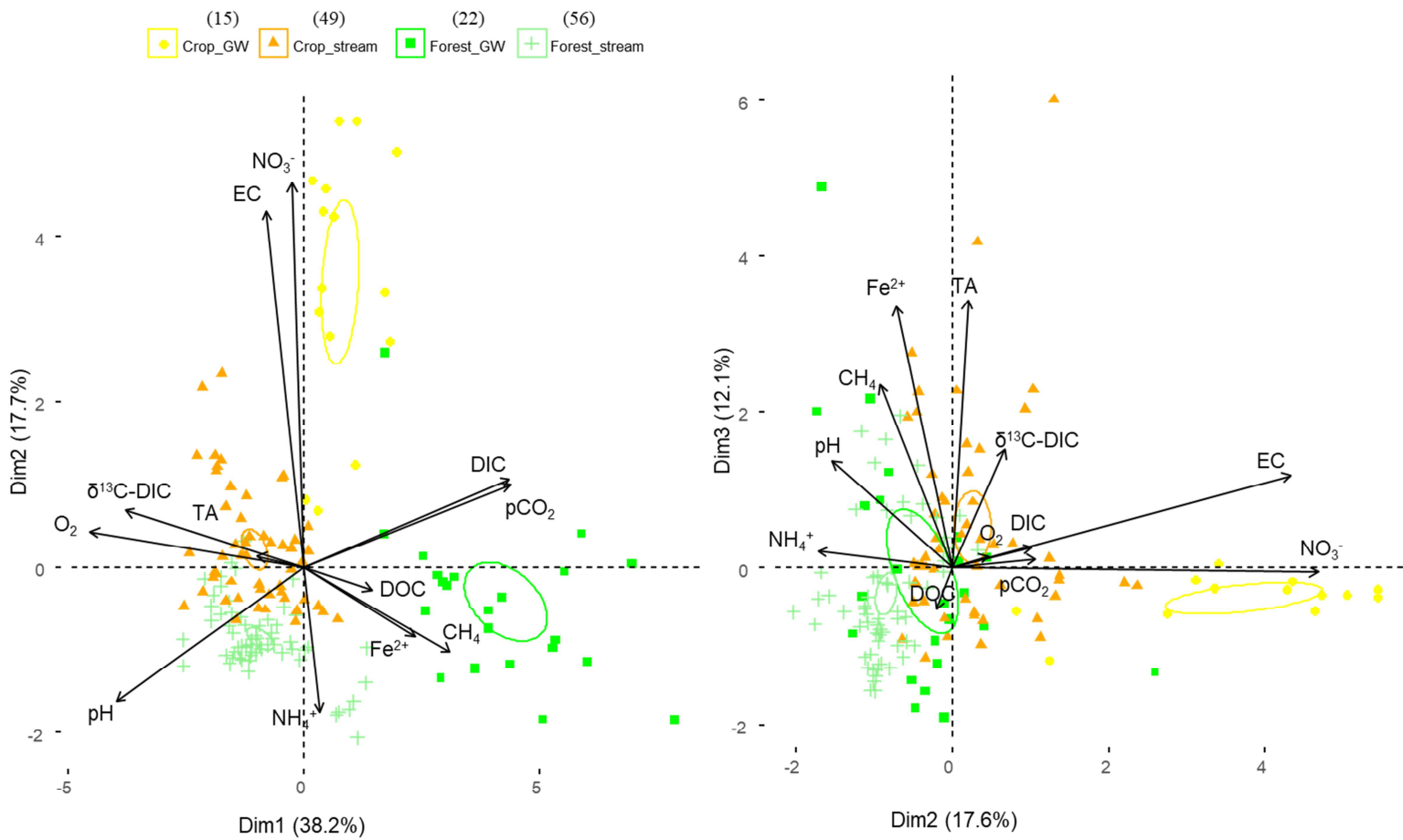


Figure 5: Principal component analysis (PCA) of shallow groundwater and stream datasets. We represented only the first three dimensions. Numbers between brackets are corresponding to the sampling size. The sampling size in the PCA did not correspond exactly to the sampling size in Table 2 because R software 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

Figure 6: Scatter plots of (a) CO<sub>2</sub> (ppmv) vs. O<sub>2</sub> (μmol L<sup>-1</sup>), (b) CO<sub>2</sub> (ppmv) vs. DOC (μmol L<sup>-1</sup>), (c) CH<sub>4</sub>(nmol L<sup>-1</sup>) vs. O<sub>2</sub> (μmol L<sup>-1</sup>), (d) CH<sub>4</sub> vs. DOC (μmol L<sup>-1</sup>), (e) CH<sub>4</sub>(nmol L<sup>-1</sup>) vs. CO<sub>2</sub> (ppmv), and (f) O<sub>2</sub> (μmol L<sup>-1</sup>) vs. DOC (μmol L<sup>-1</sup>), in all sampled groundwater and streams

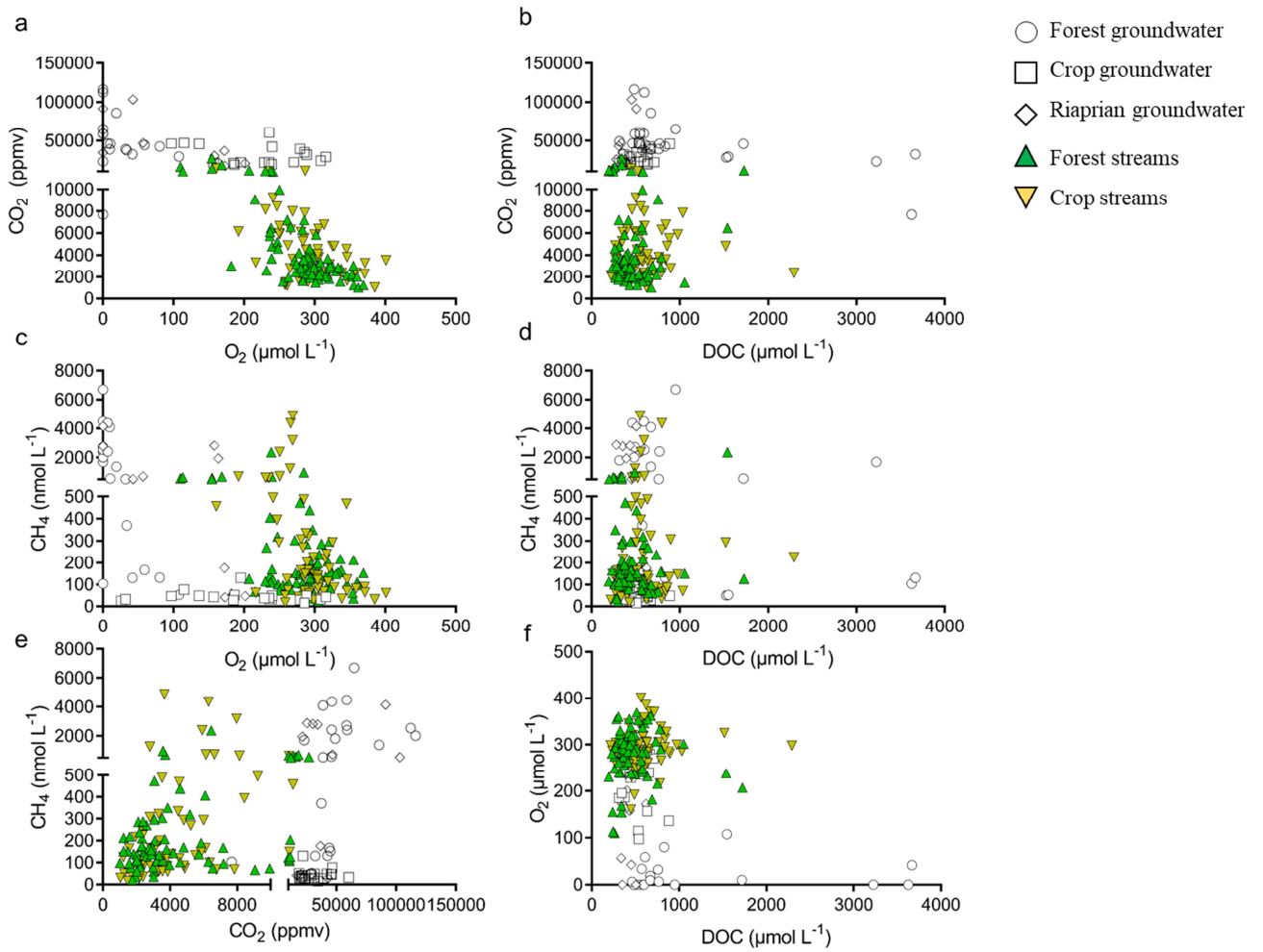
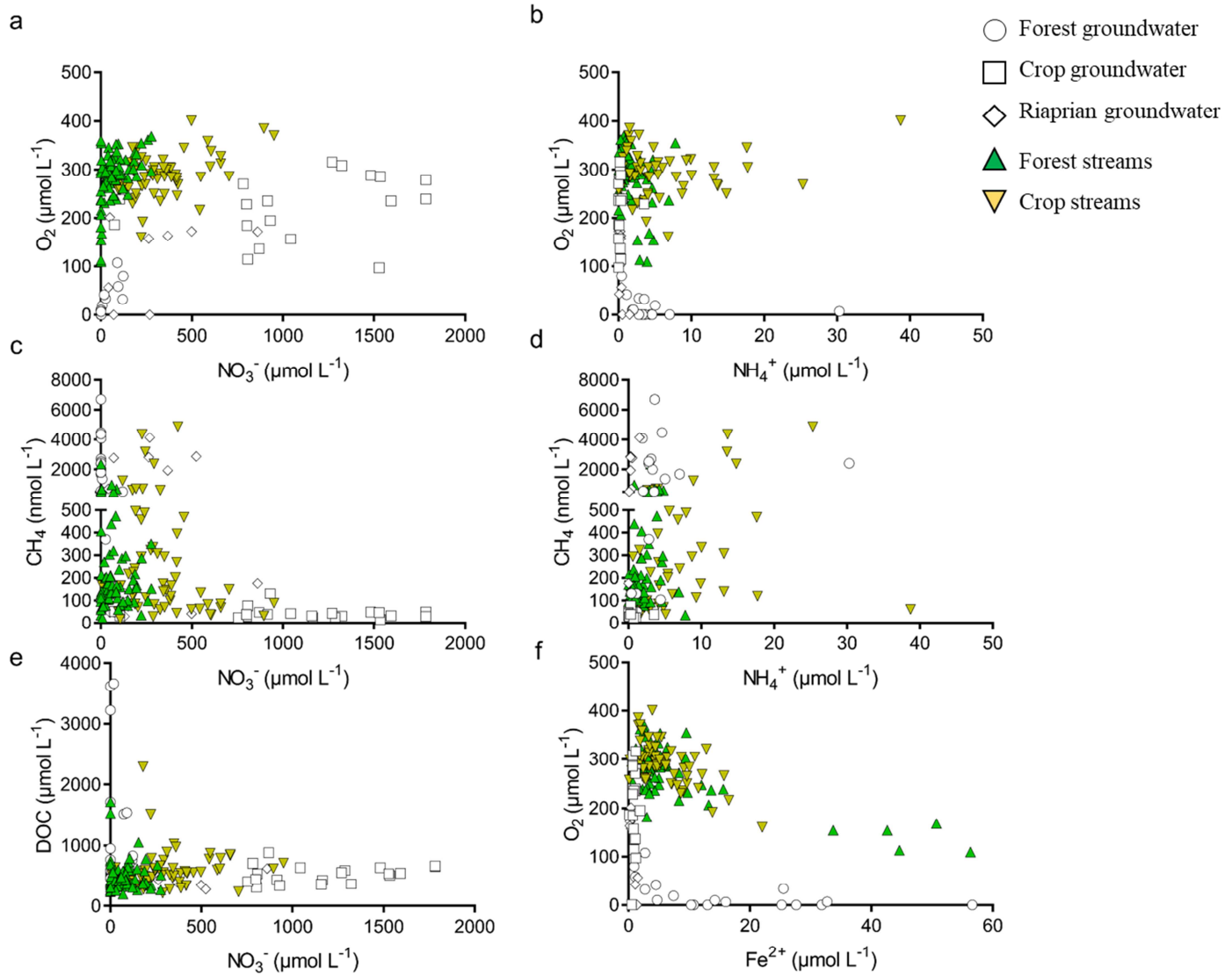




Figure 7: Scatter plots of (a)  $O_2$  ( $\mu\text{mol L}^{-1}$ ) vs.  $\text{NO}_3^-$  ( $\mu\text{mol L}^{-1}$ ), (b)  $O_2$  ( $\mu\text{mol L}^{-1}$ ) vs.  $\text{NH}_4^+$  ( $\mu\text{mol L}^{-1}$ ), (c)  $\text{CH}_4$  ( $\mu\text{mol L}^{-1}$ ) vs.  $\text{NO}_3^-$  ( $\mu\text{mol L}^{-1}$ ), (d)  $\text{CH}_4$  ( $\mu\text{mol L}^{-1}$ ) vs.  $\text{DOC}$  ( $\mu\text{mol L}^{-1}$ ), (e)  $\text{DOC}$  ( $\mu\text{mol L}^{-1}$ ) vs.  $\text{NO}_3^-$  ( $\mu\text{mol L}^{-1}$ ), and (f)  $O_2$  ( $\mu\text{mol L}^{-1}$ ) vs.  $\text{Fe}^{2+}$  ( $\mu\text{mol L}^{-1}$ ), in all sampled groundwater and streams.



Supplementary Material

Seasons	Date	Groundwaters			Streams
		P5	P1, P2, P3	P4	
HF	29/01/2014				X
HF	12/02/2014	X			
HF	07/03/2014				X
HF	17/03/2014	X			
BF	24/04/2014				X
BF	16/05/2014	X			
BF	21/05/2014				X
BF	25/06/2014				X
BF	17/07/2014	X			X
BF	27/08/2014	X	X		X
BF	24/09/2014	X	X		X
BF	31/10/2014	X	X		X
BF	21/11/2014	X	X		X
BF	16/12/2014	X	X		X
HF	27/01/2015	X	X	X	X
HF	04/03/2015	X	X	X	X
BF	10/04/2015	X	X	X	X
BF	07/05/2015	X	X	X	X
BF	03/06/2015	X	X	X	X
BF	09/07/2015	X	X	X	X

Table S1: Sampling dates of groundwaters and streams. X corresponds to a sampling. HF and BF are corresponding to high flow and base flow periods, respectively.

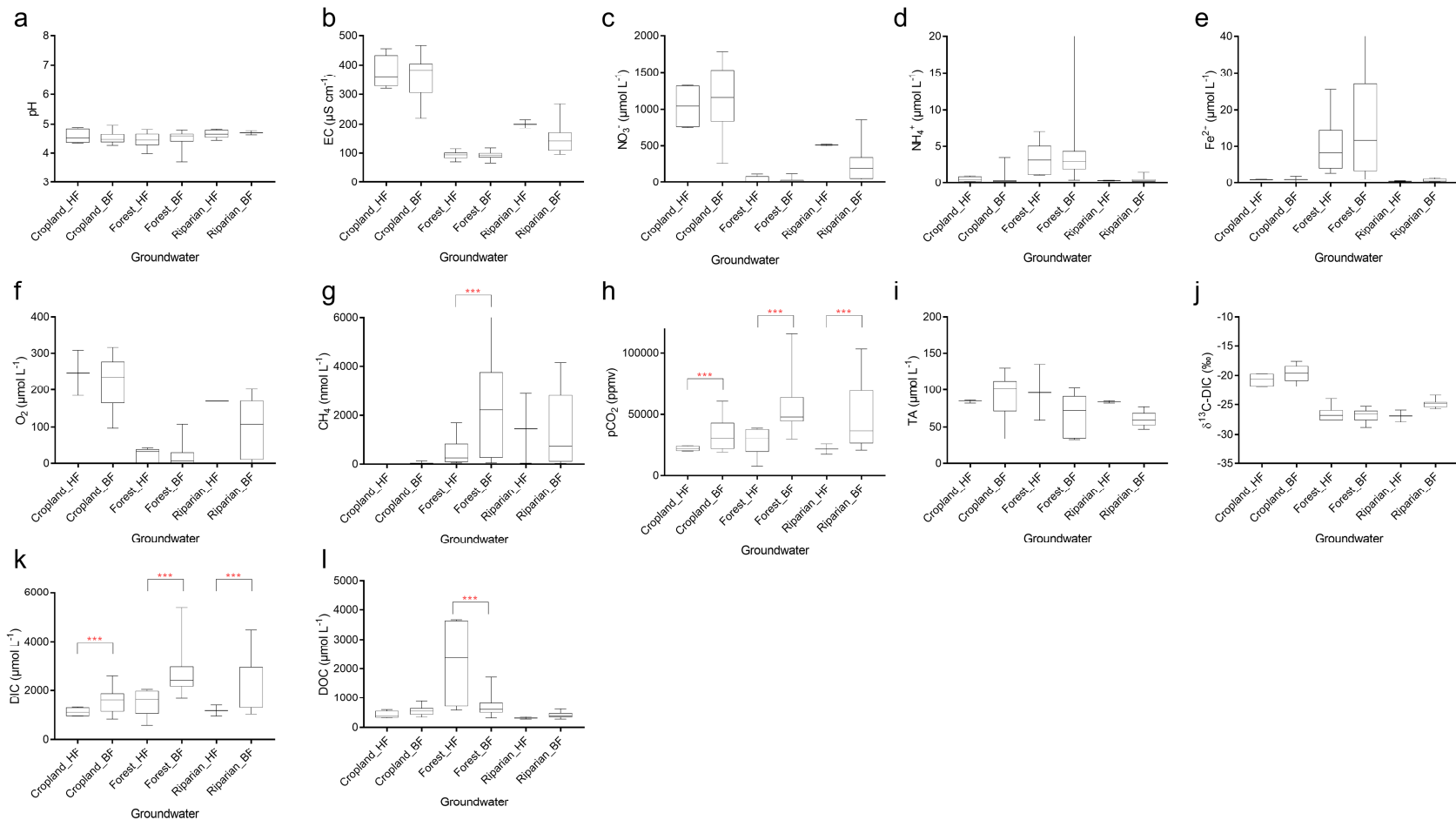


Fig. S2. Values of carbon and ancillary parameters throughout the sampling period (Jan. 2014-Jul. 2015) in groundwaters across hydrological seasons and land use. Box-plots represent the median (black bar) and the extreme (min-max) values. We defined six groups that are Cropland\_HF/Cropland\_BF, Forest\_HF/Forest\_BF and Riparian\_HF/Riparian\_BF corresponding to groundwater during high or base flow; in either cropland, forest or riparian forest. Then, based on Mann-Whitney statistical analysis, we compared Cropland\_HF vs. Cropland\_BF,

Forest\_HF vs. Forest\_BF and Riparian\_HF vs. Riparian\_BF. 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 ( $p > 0.05$ )

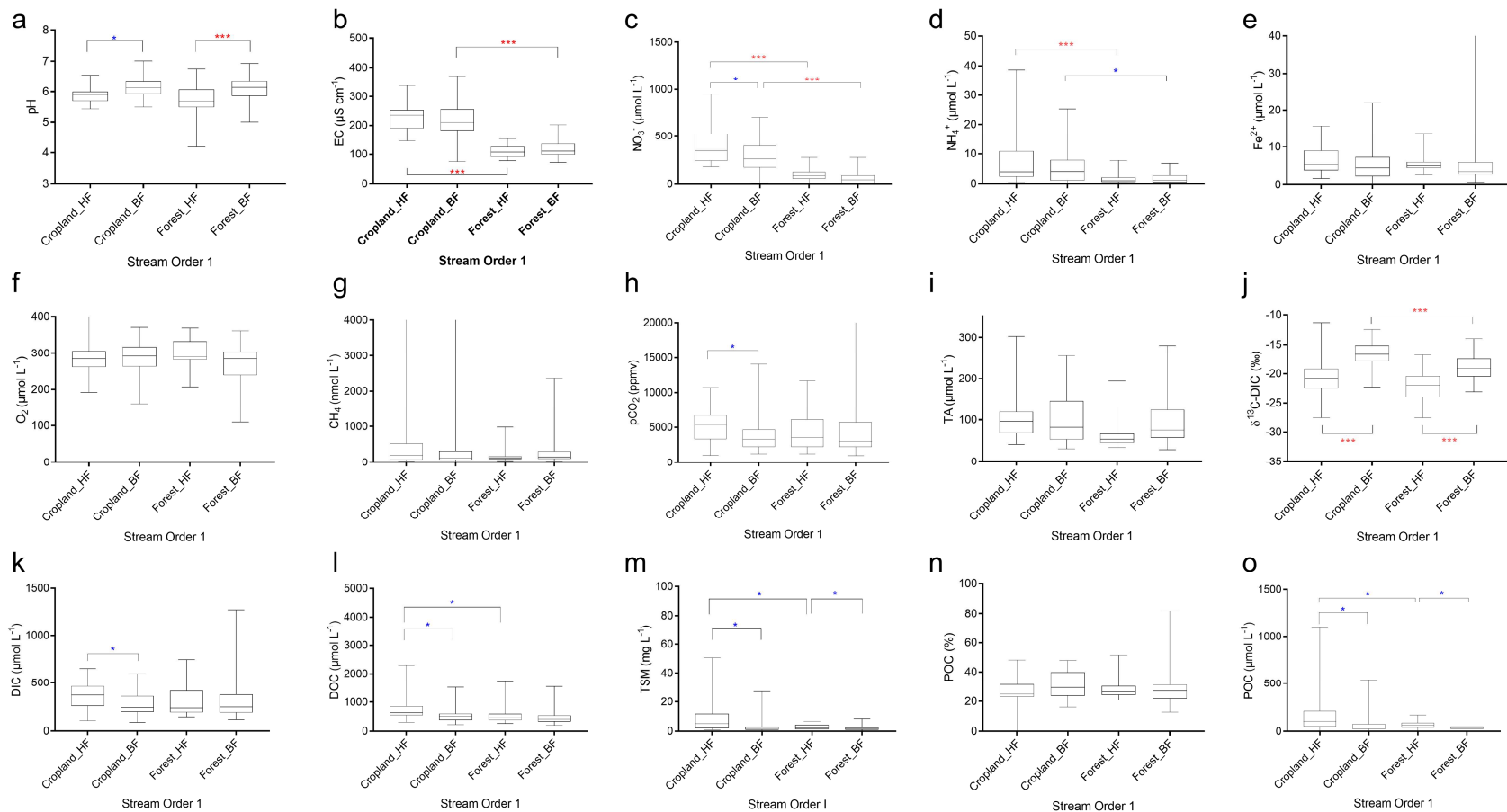


Figure S3. Values of carbon and ancillary parameters throughout the sampling period (Jan. 2014-Jul. 2015) in streams across hydrological seasons and land use. Box-plots represent the median (black bar) and the extreme (min-max) values. We defined four groups that are Cropland\_HF/Cropland\_BF, Forest\_HF/Forest\_BF corresponding to streams during high or base flow periods; in either cropland-affected or forest-dominated land use. Then, based on Mann-Whitney statistical analysis, we compared Cropland\_HF vs. Cropland\_BF, Forest\_HF vs. Forest\_BF, Cropland\_BF vs. Forest\_HF and Cropland\_BF vs. Forest\_BF. 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 ( $p > 0.05$ ).

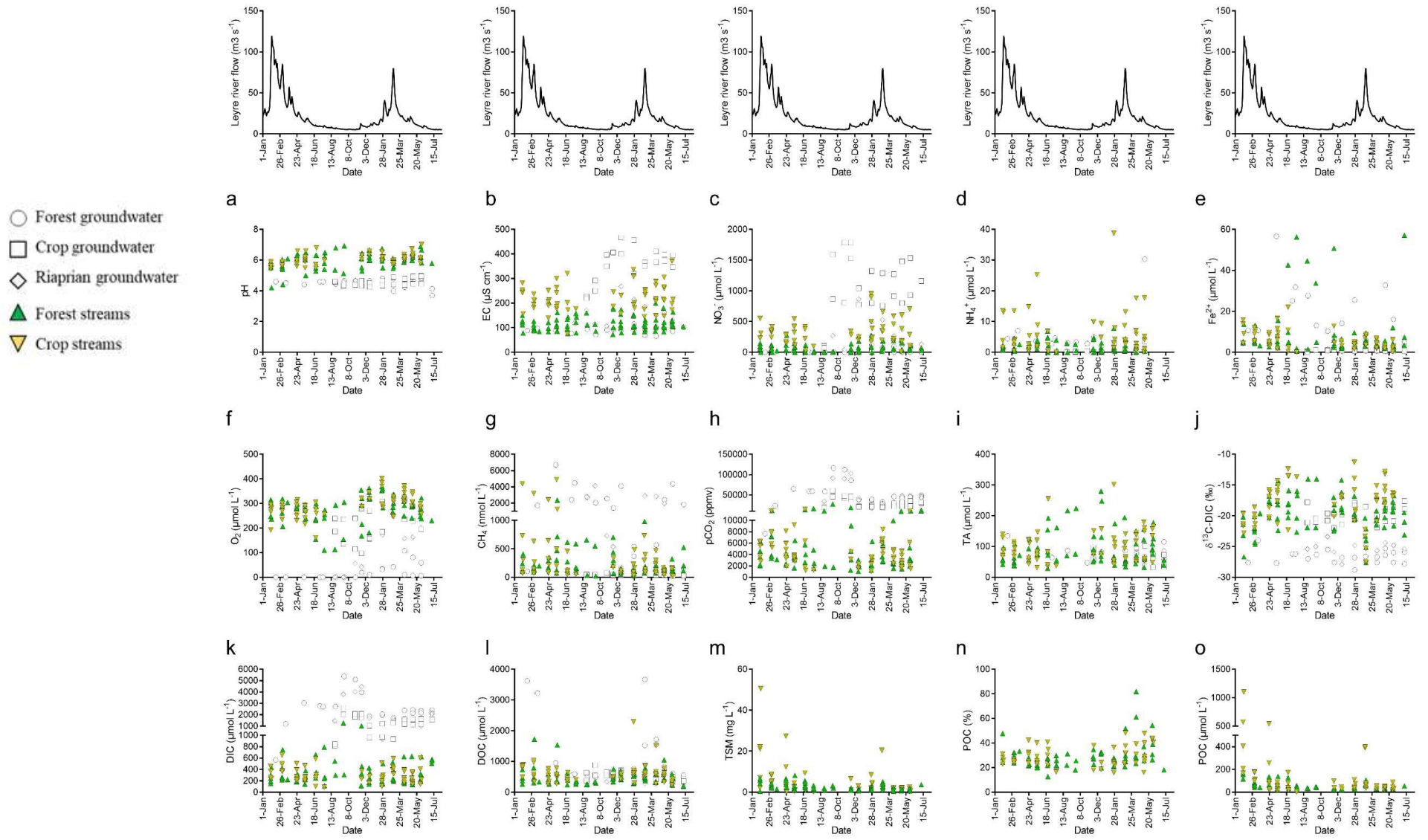
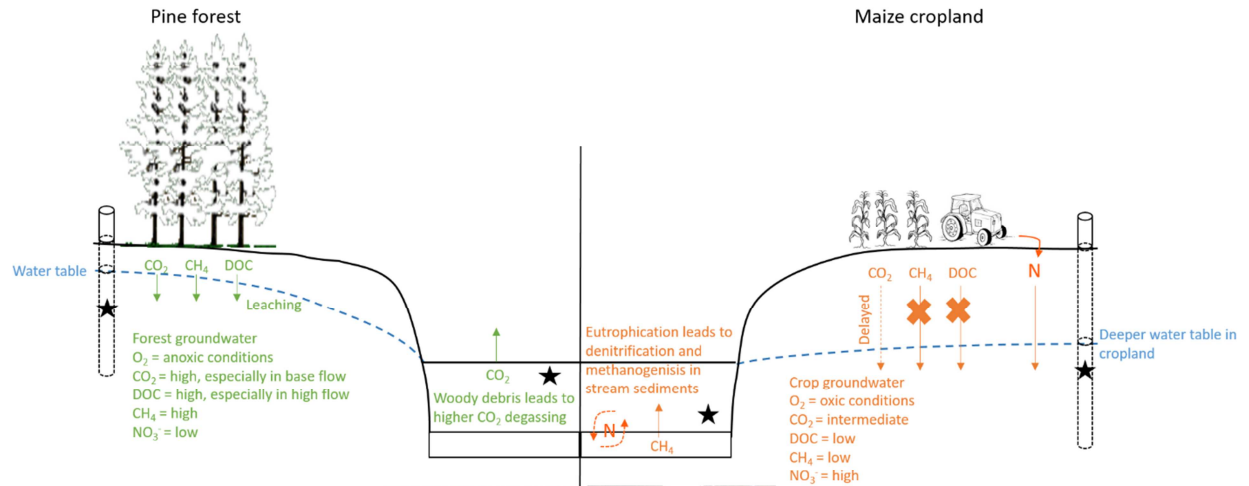


Figure S4: Temporal variations of carbon and ancillary parameters throughout the sampling period (Jan. 2014-Jul. 2015) in all sampled

groundwater and streams. Top panels represent the Leyre River flow (main stem).



★ Sampling stations

