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Solute transport dynamics in small, shallow groundwater-dominated agricultural catchments: insights from a high-frequency, multisolute 10 yr-long monitoring study

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Abstract. High-frequency, long-term and multisolute measurements are required to assess the impact of human pressures on water quality due to (i) the high temporal and spatial variability of climate and human activity and (ii) the fact that chemical solutes combine short- and long-term dynamics. Such data series are scarce. This study, based on an original and unpublished time series from the Kervidy-Naizin headwater catchment (Brittany, France), aims to determine solute transfer processes and dynamics that characterise this strongly human-impacted catchment.

The Kervidy-Naizin catchment is a temperate, intensive agricultural catchment, hydrologically controlled by shallow groundwater. Over 10 yr, five solutes (nitrate, sulphate, chloride, and dissolved organic and inorganic carbon) were monitored daily at the catchment outlet and roughly every four months in the shallow groundwater.

The concentrations of all five solutes showed seasonal variations but the patterns of the variations differed from one solute to another. Nitrate and chloride exhibit rather smooth variations. In contrast, sulphate as well as organic and inorganic carbon is dominated by flood flushes. The observed nitrate and chloride patterns are typical of an intensive agricultural catchment hydrologically controlled by shallow groundwater. Nitrate and chloride originating mainly from organic fertilisers accumulated over several years in the shallow groundwater. They are seasonally exported when upland groundwater connects with the stream during the wet season. Conversely, sulphate as well as organic and inorganic carbon patterns are not specific to agricultural catchments. These solutes do not come from fertilisers and do not accumulate in soil or shallow groundwater; instead, they are biogeochemically produced in the catchment. The results allowed development of a generic classification system based on the specific temporal patterns and source locations of each solute. It also considers the stocking period and the dominant process that limits transport to the stream, i.e. the connectivity of the stocking compartment. This mechanistic classification can be applied to any chemical solute to help assess its origin, storage or production location and transfer mechanism in similar catchments.

1 Introduction

In the context of global change, evaluating the impact of human pressures on water quality is a major concern. However, this evaluation is challenging, first, because climatic and human pressures are highly variable both in time and space, and second, because chemical components are affected by short- and long-term dynamics. Such impact of human pressures on water quality can be identified thanks to the establishment of long-term data observatories.

For years, hydrologists have highlighted the need for long-term hydrological data (Betton et al., 1991; Neal, 1997; Reynolds and Edwards, 1995). Many countries implemented long-term observatories for water quality. For instance, in the USA, the Long-Term Ecological Research (LTER) network began as early as 1977 with six sites. Currently, it comprises 26 sites covering the diversity of North American ecosystems (http://www.lternet.edu/). The Critical Zone Exploration Network (CZEN) provides another example of an American network (http://www.czen.org/). Presently, CZEN focuses on studying the interface between the atmosphere, hydrosphere, soil and ecosystem. It consists of six Critical Zone Observatories (CZO) and additional affiliated sites. In Europe, similar networks have been developed, such as TERENO in Germany (TERestrial ENvironmental Observatories, http://www.ufz.de/index.php?en=16350) and the FRECZ in France (French Resources for Exploration of the Critical Zone, http://rnbv.ipgp.fr/). All those observatories are complementary as they are located in diverse areas, encompassing different climatic and anthropogenic gradients.

The existing observatories cover a broad range of ecosystems. Some are located in relatively pristine areas (Boulder Creek CZO, Colorado, USA; Draix-Bléone ORE (Environmental Research Observatory), France; etc.), where studies focus mainly on understanding biogeochemical processes in the critical zone with minimum local human disturbance. Most sites (Hubbard Brook, New Hampshire, USA; Maimai, New Zealand; Plynlimon, UK; Strengbach, France; etc.) are forested. There, human impact depends on local forest policy and atmospheric deposition. Very few observatories are located in areas impacted by other human activities, such as urban development (Baltimore Ecosystem Study, Maryland, USA) or intensive agriculture (Kervidy-Naizin, France). Water quality issues differ according to the ecosystem and its land use. Long-term water quality monitoring is generally performed to capture temporal trends and potential differences. However, with the exception of the Plynlimon observatory (Neal et al., 2011), very little effort has been devoted to the analysis and publication of the obtained long-term databases.

Long-term water quality data exhibit high variability patterns depending on the timescales at which they are analysed (Reynolds et al., 1997). The conclusions that can be drawn about the impact of human activities on water quality and solute transfer mechanisms are influenced by time series length and sampling frequency as they create a temporal filter that emphasizes some timescales and processes and hides others (Feng et al., 2004; Halliday et al., 2012; Moatar et al., 2009). What is the appropriate timescale to identify the water quality response to a specific human pressure? In the literature focusing on catchment scale responses, three timescales are generally investigated: (i) short-term studies, mostly at minute or hour sampling frequency, analyse the variations of water chemical composition during storm or flood events (Morel et al., 2009; Williams, 1989), (ii) long-term studies,

defined as data series of at least 20 yr of water quality monitoring (Burt and Worrall, 2009), mostly sampled at a weekly frequency, focus on decadal trends (Gascuel-Odoux et al., 2010; Howden et al., 2010; Hrachowitz et al., 2013; Monteith et al., 2000), and (iii) intermediate scale studies focus on seasonal variations (Dawson et al., 2008, 2011; Martin et al., 2004; Mulholland and Hill, 1997). This intermediate timescale highlights annual variations that repeat themselves from year to year, enabling interannual variability analysis. The annual variations occur at any given period of the year, such as flow resuming after the dry season, groundwater recharge, snowmelt, etc. In the present paper, these annual variations constitute what is referred to as the hydro-chemical signature of a catchment.

This paper aims at defining the hydro-chemical signature of a typical livestock farming catchment, hydrologically controlled by shallow groundwater. It is based on an unpublished daily multisolute 10 yr-long time series of stream water chemistry in an agricultural catchment, Kervidy-Naizin, located in western France. The hydro-chemical signature is defined by the concentrations of five water solutes, analysed in terms of (i) mean concentrations in four water compartments within the catchment (stream and upland, wetland and deep downslope groundwater); (ii) mean annual patterns of stream concentrations; and (iii) year to year variability of stream concentrations. The three aspects are presented in the paper and lead to a generic conceptual model of stream water quality signatures.

2 Study site and data treatment

2.1 An outstanding study site

The Kervidy-Naizin catchment is located in western France (Central Brittany: 48° N, 3° W) (Fig. 1). It is a 4.82 km^2 headwater catchment, drained by a 2nd order stream, that can occasionally fall dry in summer. The catchment's observatory (ORE-AgrHys, for AgroHydrosystem) belongs to the French network of observatories SOERE-RBV (Long-term Monitoring and Experimental System for Research in the Environment-Network of Basin Catchments). Data, metadata and scientific papers about the catchment are available on the ORE-AgrHys website (http://www.inra.fr/ore_agrhys). Many soil, hydrological and biogeochemical studies have been performed. As of January 2012, 21 journal articles based on the catchment observations are referenced in the Web of Knowledge.

The catchment lies on upper Proterozoic schist covered by a layer of weathered material up to 30 m thick. A shallow-groundwater table develops in this unconsolidated layer. The soils are silty loams. Soils on the hill slopes are well drained and consist of Dystric Cambisols and Luvisols. Downslope soils, in the wetland domain, consist of Epistagnic Luvisols and Epistagnic Abvuvisols, in which Mn and

Fe-oxyhydroxides are depleted due to seasonal waterlogging by the rising groundwater and reduction of these oxides by heterotrophic bacteria. The topography of the catchment is rather subdued, with a few slopes reaching a gradient of 5 %. Elevation ranges from 98–140 m above sea level. The climate is temperate with oceanic influence, with a mean maximum daily temperature of 11 °C (1994–2000). Mean annual rainfall is 814 mm, with the maximum and minimum monthly mean reached in November (100 mm) and in June (38.5 mm), respectively. The annual stream specific discharge is approximately 350 mm yr^{-1}.

Kervidy-Naizin is an agricultural catchment with intensive animal farming. Twenty three farms have fields in this catchment. Animal production includes pigs (about 35 000 head per year), poultry (40 500 head) and dairy and beef cows (3000 head). As early as 1996, a survey pointed out that the catchment contained 24 pigs per ha, compared to 5.5 and 0.6, on average, for Brittany and France, respectively. In 2010, 20 % of the total surface was covered by cereals, 30 % by maize and 20 % by temporary or permanent pastures. Five farm types were identified: dairy-cow, beef-cow, pig, dairy-cow plus pig or poultry, and crop-only (9, 3, 5, 4 and 2 farms, respectively). N efficiency, defined as N output (sold animal and vegetal products, exported manure, etc.) divided by N input (mineral fertilizers, bought animal feed, bought animals, N fixation, imported manure), varied greatly (19–79 %) depending on the farm types and on the farms within each farm type. In 2010, a detailed survey estimated the total N surplus to be approximately 200 kg N ha^{-1} of usable agricultural area (Akkal, 2010).

2.2 Data collection

This study analyses data collected from September 2000 to August 2010 (10 hydrological years). Measurements of stream discharge at the Kervidy-Naizin outlet are available since autumn 2000 at a frequency of one measurement per 15 min. Discharge is measured at a gauging station including a float-operated sensor and a data logger (Thalimèdes OTT). The weather station at Kervidy (Cimel Enerco 516i) is located approximately 1 km from the outlet. It records hourly rainfall, air and soil temperatures, air humidity, global radiation and wind direction and speed, which allows the calculation of Penman evapotranspiration.

Solute concentrations, i.e. NO$_3$, SO$_4$, Cl, dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC), are measured at the outlet at a frequency of one measurement per day, except during the hydrological year 2002–2003 when the sampling frequency was reduced to once every 2–4 days for solute concentrations. Stream water samples used to determine solutes concentrations are collected manually at approximately the same time (17:00 LT (local time)), without specific sampling during floods. These instantaneous grab samples are immediately filtered (pore size: 0.2 μm) on site and stored in the dark at 4 °C in propylene bottles. The

bottles are filled to the top. Analyses are performed within a maximum of a fortnight. Major anion concentrations (nitrate, chloride and sulphate) are measured by ionic chromatography (DIONEX DX 100), with an accuracy of ±2.5 %. DOC and DIC concentrations are measured using a total organic carbon analyser (Shimadzu TOC 5050A) with a precision of 5 %, based on 10 repeated measurements of freshly prepared standard solutions (K-phthalate). DOC concentration was determined by the difference between total dissolved carbon and DIC.

Deep shallow-groundwater (GW) data were collected from a 4 m-deep downslope piezometer and from an 8 m-deep upland piezometer, set along a topographic transect (Gueriniec transect; see Fig. 1) (respectively referred to as deep downslope GW and upland GW throughout the rest of this paper). Shallow GW data were also collected from eight shallow (20–40 cm), zero-tension lysimeters set in the wetland domain (Mercy wetland; see Fig. 1) (referred to as wetland GW). Water-table depth in this catchment is measured every 15 min by pressure probes (Orpheus OTT) since 2000. Water-table chemistry is measured at different frequencies depending on water-table depth. In the deep piezometers, measurements are performed roughly every three months, providing 24 analyses for each piezometer since 2000. This is justified by the relative chemical inertness of the GW at that depth. In the 20–40 cm-deep lysimeters, a much higher sampling frequency was used due to water-table movements and changes in redox conditions. Several high-frequency sampling campaigns were performed during hydrological years 2000–2001, 2001–2002, 2007–2008 and 2010–2011, providing approximately 100 analyses for each lysimeter since 2000.

2.3 Data treatment

Based on the concentrations measured in the four studied water compartments (upland, deep downslope and wetland GW, and stream water) and on the mean annual pattern and year to year variability of solute concentrations in the stream, we identify what the hydro-chemical signature of a typical livestock farming catchment is. While the mean concentrations of the four hydrological compartments depict what is called a "static signature", the annual and interannual variations and variability of the 10 yr-long daily dataset allow us to identify what is called a "temporal signature". The annual patterns are observed at two scales: the hydrological year and the floods. As no specific sampling strategy was implemented to account for floods, we used the following decision rule (adapted from Morel, 2009, and Molenat et al., 2008) to distinguish between base-flow and flood-flow periods: if daily rainfall on the sampling day exceeded 1.5 mm or daily rainfall from the previous day exceeded 5 mm or daily discharge on the sampling day exceeded 200 L s^{-1}, then the sample was considered as taken during a flood; otherwise it was considered as taken during base flow. The interannual patterns of
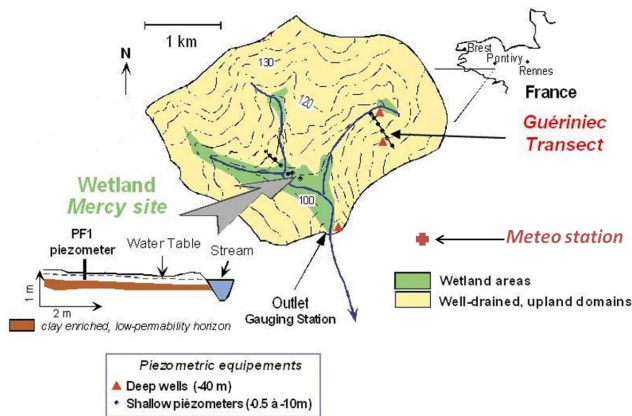
Fig. 1. Map of the Kervidy-Naizin experimental catchment and its location within Brittany, France.

each solute are established by analysing year to year concentration variability and concentration variograms.

Considering the whole dataset, descriptive statistics and boxplots were computed using R software. Temporal variograms were plotted using "gstat" and "variogram" functions in R (Zhang and Schilling, 2005). Temporal distance was given as a number of days. The chosen lag was 30 days, and the span 2000 days.

3 Results and discussion

3.1 The static signature: mean concentrations in the water compartments

Both nitrate and chloride were highly concentrated in the stream. Over the 10 yr, the mean in-stream nitrate concentration was 16.9 mg NO_3^--N L^{-1} (CV = 15.6 %) (Table 1). The concentration in upland GW was of the same order of magnitude (20.7 mg NO_3^--N L^{-1}) (Table 2, Fig. 2), whereas it was almost zero in the deep downslope GW (0.2 mg NO_3^--N L^{-1}) and much lower in the wetland GW (1.5 mg NO_3^--N L^{-1}). Mean stream nitrate concentration was high compared to that in other observatories. In the forested catchment of Plynlimon (Reynolds et al., 1997), concentrations range from below the detection limit to 0.9 mg NO_3^--N L^{-1}. In agricultural catchments such as Rothamsted or Wytham, annual maxima of 10.9 and 4.0 mg NO_3^--N L^{-1}, respectively, have been observed (CEH, 2012). In Kervidy-Naizin observatory, stream nitrate concentration was high even though denitrification was efficient in the deep downslope GW because of the presence of a pyrite layer reducing nitrate and in the wetland GW because of heterotrophic denitrification when soils are saturated. The very high nitrate concentration recorded in the Kervidy-Naizin stream is due to the very high N surplus generated by the intensive agriculture taking place in the catchment.

The mean in-stream chloride concentration was 34.0 mg L^{-1} (CV = 10.5 %). In upland GW, the concentration was similar (32.7 mg L^{-1}) as well as in the wetland GW (31.6 mg L^{-1}), but it was lower in the deep downslope GW (16.2 mg L^{-1}). Mean stream chloride concentration was also high in Kervidy-Naizin compared to that in other catchments described in the literature. Much lower concentrations have been reported in forested catchments, such as 0.9 mg L^{-1} (range = 0.4–8.4) in Oak Ridge (Koirala et al., 2010), 3.9 mg L^{-1} in Hubbard Brook (Lovett et al., 2005), 4–9 mg L^{-1} in Plynlimon (Kirchner et al., 2000) and about 13 mg L^{-1} in Tillingbourne (Hill et al., 2002). High chloride concentrations may come from the combined effect of dry deposition of sea salt aerosol and increase of concentrations due to evapotranspiration. However, even if Kervidy-Naizin is relatively close to the coastline (50 km to the south, 60 km to the north), stream chloride concentrations seem too high to originate only from the rain. In a catchment with the same soil, climate and land-use context as Kervidy-Naizin, similarly high chloride concentrations were obtained. They were ascribed to an agricultural origin, chloride being a component of KCl fertilisers, pig slurry and dairy manure applied to fields (Martin et al., 2004; Pierson-Wickmann et al., 2009). Since chloride concentration in rainfall is low in Kervidy-Naizin (precipitation weighted mean value 4.75 mg L^{-1}), we can conclude that mineral and, above all, organic fertilisation increases water chloride concentration in this catchment, as it does for nitrate. The high nitrate and chloride concentrations observed in Kervidy-Naizin can be regarded as the "agricultural signature" of the water compartments. Data from the Environmental Change Network (CEH, 2012) support this interpretation, with the UK and Brittany being comparable in terms of rainfall amount and geological substrate. Indeed, the two agricultural catchments of the CEH network (Rothamsted and Wytham) show a shift towards high nitrate and chloride concentration as compared to their forested or more pristine counterparts.

The other three solutes (i.e. SO4, DOC and DIC) were conversely not as concentrated as nitrate and chloride. Mean in-stream sulphate concentration was 2.6 mg SO_4^{2-}-S L^{-1}, associated with high variability (CV = 41.7 %). In-stream, upland GW concentrations (1.9 mg SO_4^{2-}-S L^{-1}) and wetland GW concentrations (2.6 mg SO_4^{2-}S L^{-1}) were lower than that in deep downslope GW (5.2 mg SO_4^{2-}-S L^{-1}). Stream sulphate concentrations in Kervidy-Naizin were similar to those found in the forested catchment of Plynlimon (range = 0.05–3.3 mg SO_4^{2-}-S L^{-1}) (Reynolds et al., 1997) and in Finland (maximum = 3.3 mg SO_4^{2-}-S L^{-1}) (Lahermo et al., 1995). Sulphate concentrations were lower than those observed in Rothamsted and Wytham agricultural catchments (approximately 9 and 20 mg SO_4^{2-}-S L^{-1}, respectively).

Mean in-stream DOC concentration was 4.4 mg L^{-1}, associated with comparably high variability (CV = 70.5 %).
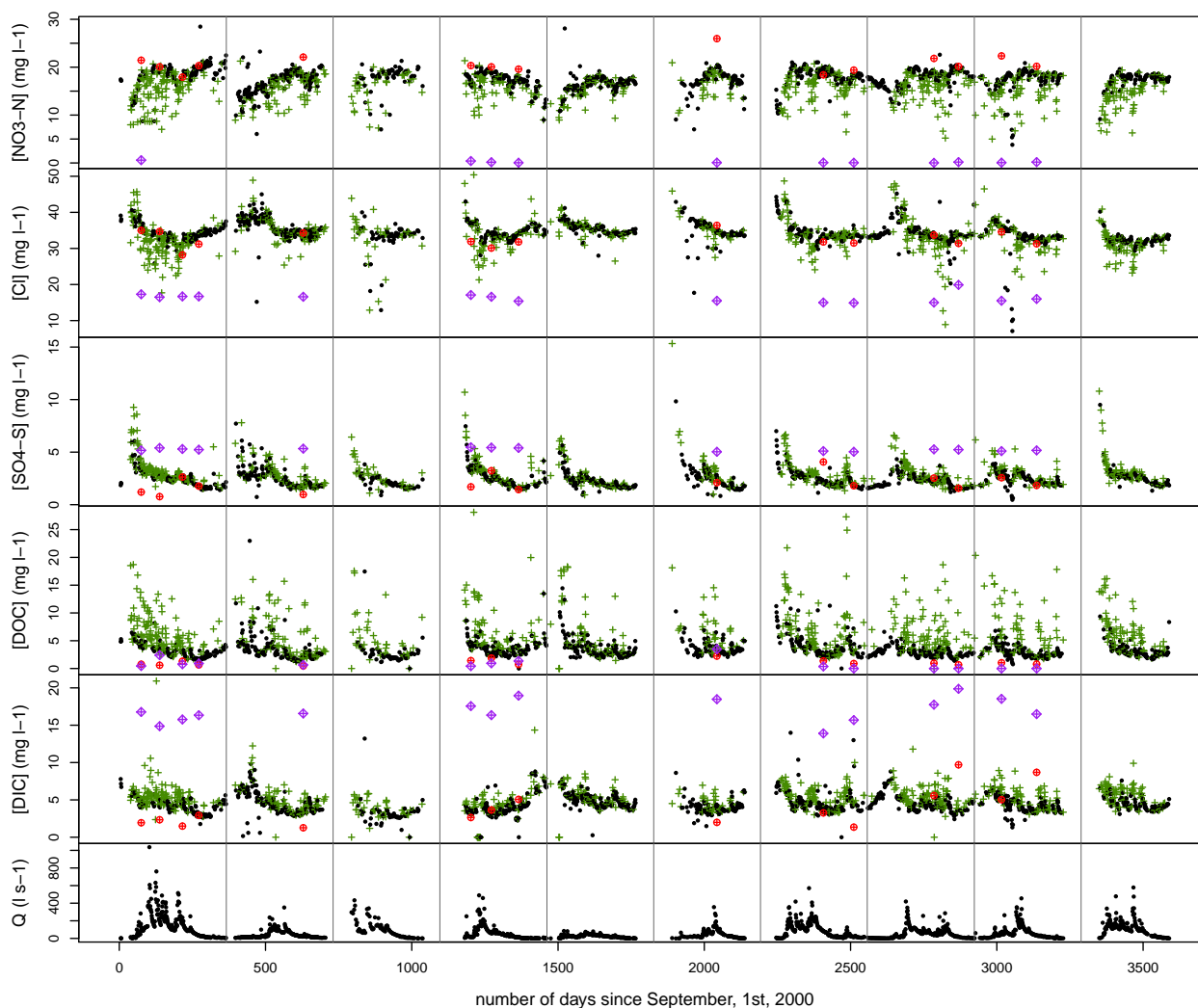
Fig. 2. Time series of daily stream concentrations and quarterly groundwater (GW) concentrations of nitrate, chloride, sulphate, dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC) from September 2000 to August 2010. Vertical lines represent the start of each hydrological year. Interflood concentration is plotted in black dots, while flood concentration is plotted in green crosses. Daily discharge ($L\,s^{-1}$) is shown in the last line. Purple diamonds represent deep downslope GW and red circles represent upland GW. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

DOC concentration in upland GW ($1.2\,mg\,L^{-1}$) and in deep downslope GW ($0.8\,mg\,L^{-1}$) were low, where as it was high in wetland GW ($19.8\,mg\,L^{-1}$). DOC stream concentration was low compared to that observed in other streams in Brittany (Morel, 2009) and has the same order of magnitude as that in Wytham (England) and Scottish catchments (Dawson et al., 2008). Mean in-stream DIC concentration ($4.7\,mg\,L^{-1}$; CV = 30.5 %) was in the same range in upland GW ($3.7\,mg\,L^{-1}$) and nearly three times higher ($17.0\,mg\,L^{-1}$) in deep downslope GW. Contrarily to nitrate and chloride, concentrations in sulphate, DOC and DIC are not so different from those found in natural catchments.

The concentrations of the four water compartments (stream, upland GW, deep downslope GW and wetland GW)

define the static signature. This static signature enabled to develop two points: one on solute origins and one on spatial source patterns. First, we distinguished two origins of solutes, anthropogenic and natural (Ouyang et al., 2006; Vega et al., 1998). In the first group, we see nitrate and chloride whose high concentrations clearly originate from excessive crop fertilisation. These two solutes, reacting little with the soil mineral phase, were leached and more or less stored in the GW. Sulphate, DOC and DIC constitute the second group of solutes. They have low concentrations in the upland GW and the most concentrated compartment is located downslope. Solutes from this group depend for a significant part on biogeochemical production processes taking place downslope (in the wetland for DOC, Morel et al., 2009, and in the

Table 1. Summary statistics for 10 yr of daily stream concentrations of nitrate, chloride, sulphate, dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) from the Kervidy-Naizin catchment ($n = 2229$). (Std – standard deviation; CV – variation coefficient).

	Stream concentrations (mg L^{-1})				
	Nitrate-N	Chloride	Sulphate-S	DOC	DIC
Min.	3.8	7.1	0.5	0.8	0.2
1st Qu.	15.8	32.7	1.9	2.5	3.7
Median	17.4	33.9	2.4	3.3	4.4
Mean	16.9	34.0	2.6	4.4	4.7
3rd Qu.	18.6	35.5	2.9	5.0	5.4
Max	28.5	50.4	15.3	28.1	20.9
Flow-weighted mean	16.4	32.2	2.9	5.4	5.0
Interstorm mean	17.6	34.4	2.3	3.3	4.3
Storm mean	15.6	33.4	3.0	6.3	5.3
Std	2.6	3.6	1.1	3.1	1.4
CV (%)	15.6	10.5	41.7	70.5	30.5

wetland and deep downslope GW for sulphate, Pauwels et al., 2010). Second, from this static signature (Tables 1 and 2, Fig. 2), we identified three spatial sources. Mean stream nitrate concentrations were 20 % lower than those in upland GW but still much higher than in wetland and downslope GW. Mean stream chloride concentrations were about the same as those in upland and wetland GW and higher than in the deep downslope GW. The dominant spatial source of nitrate and chloride is the upland GW. Nitrate spatial distribution showed that the hill-slopes were not directly connected to the wetland but rather to the stream. The low wetland nitrate concentrations were also due to the absence of fertilisation and to denitrification (Molenat et al., 2008). Mean sulphate concentrations were similar in the stream and upland and wetland GW, but higher in deep downslope GW. In the wetland GW, sulphate reduction to sulphur did not occur as the reduction chain stops with iron reduction. In deep downslope GW, sulphate is produced by the pyrite layer. DIC stream concentration would be in the same case as sulphate. For sulphate and DIC, a deep downslope GW contribution is not necessary to explain the level and variability in stream water concentrations: wetland GW concentrations and variability are sufficient. Lastly, mean stream DOC concentration had high variability and was much higher than in both upland GW and deep downslope GW, but not as high as in wetland GW; this indicated that DOC originated from the wetland domain. The static signature led to solute differentiations based on origins and dominant spatial sources.

3.2 The temporal agricultural signature: annual and interannual patterns

3.2.1 Annual patterns

Our results confirmed previous results on annual nitrate patterns and allowed us to extend the conceptualisation based on longer time series. On average, nitrate concentrations were lowest at the beginning of the hydrological year (September), then highest from January to March and finally slightly decreased during spring and summer (Fig. 3a). All rainfall events led to a dilution of stream nitrate concentrations (Fig. 2). Mean stream concentration during floods was 15.6 NO$_3^-$-N L^{-1} as against 17.6 mg NO$_3^-$-N L^{-1} during interflood periods. Means differed little (Table 1) because interflood concentrations were low at the beginning of each hydrological year and in summer, which decreased the annual interflood mean. In other words, nitrate concentration remains high in the stream as long as the latter was hydrologically connected to the upland GW, which behaves as an infinite nitrate reservoir (Molenat et al., 2008). Then, from June to August, nitrate stream concentration decreases slightly as (i) the upland groundwater progressively contributes less because the catchment is drying and thus reduced nitrate transport capacity is available (Molenat et al., 2008) and as (ii) other processes, such as denitrification and plant uptake also contribute to a reduced nitrate concentration (Betton et al., 1991). The combination of these processes explains the low concentrations observed in October. Mulholland and Hill (1997) also observed a sharp decrease of stream nitrate concentration in autumn in their forested catchment: leaf input to the stream increased, as well as photosynthetically active radiation, leading to more active in-stream decomposition. The Kervidy-Naizin stream is bordered by riparian hedges, which could have the same effect as forest trees on stream nitrate concentration. In autumn, there is a transition period when the upland water table progressively rises (Molenat et al., 2008), thus increasing nitrate transport capacity.

We propose a new seasonal conceptualisation for chloride. The stream chloride pattern was characterised by a flush of high concentrations at the beginning of the hydrological year (Fig. 3b), as the catchment is rapidly wetting-up, thus providing increased transport capacity. Concentrations then decreased and remained relatively stable until the end of the hydrological year when again a slight increase occurred. A seasonal change concerning the influence of floods on concentrations (called hereafter the seasonal flood effect) was noticed (Fig. 2), in which only floods occurring at the beginning of the hydrological year led to an increase in concentration, whereas later floods mostly had a dilution effect. Therefore, floods did not influence annual chloride concentration means (Table 1): chloride concentrations were 33.4 and 34.4 mg L^{-1} during and between floods, respectively. This seasonality of flood effects may have two explanations. First, at the beginning of the hydrological year, the rise of the water table allows the transport of chloride that was concentrated by summer evapotranspiration, particularly in the wetland domain. The second explanation might be that the chloride signal in rain is seasonal (Hrachowitz et al., 2009; Neal et al., 1988; Shaw et al.; 2008). However, we think that this second explanation has a minor effect in Kervidy-Naizin where (i) the mean concentration in GW is much higher than that

Table 2. Summary statistics for 10 yr of deep groundwater concentrations of nitrate, chloride, sulphate, dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) sampled from the Kervidy-Naizin catchment. (Std – standard deviation; CV – coefficient of variation).

	Upland GW concentrations (mg L^{-1}) (10 yr monitoring)					Deep downslope GW concentrations (mg L^{-1}) (10 yr monitoring)					Wetland GW concentrations (mg L^{-1}) (year 2010–2011)			
	NO$_3^-$-N	Cl$^-$	SO$_4^{2-}$-S	DOC	DIC	NO$_3^-$-N	Cl$^-$	SO$_4^{2-}$-S	DOC	DIC	NO$_3^-$-N	Cl$^-$	SO$_4^{2-}$-S	DOC
sample size	24	24	24	24	23	19	24	24	24	23	129	129	128	131
Min.	17.9	28.2	0.5	0.3	1.3	0.02	14.9	5.0	0.0	13.9	0.0	12.5	0.0	0.8
1st Qu.	19.6	31.4	1.2	0.6	2.0	0.1	15.5	5.1	0.0	15.9	0.2	25.4	1.5	12.9
Median	20.3	32.6	1.7	0.9	2.9	0.1	16.2	5.2	0.4	16.7	1.0	28.9	2.1	16.2
Mean	20.7	32.7	1.9	1.2	3.7	0.2	16.2	5.2	0.8	17.0	1.5	31.6	2.6	19.8
3rd Qu.	21.6	34.2	2.5	1.5	4.9	0.2	16.6	5.3	1.0	18.3	2.3	34.1	3.3	25.8
Max	26.0	36.4	4.1	2.8	9.7	0.6	19.9	5.5	3.5	19.9	5.9	71.8	8.1	56.6
Std	1.8	1.9	0.9	0.7	2.3	0.2	1.1	0.1	0.9	1.5	1.4	10.2	1.8	12.0
CV (%)	8.6	5.8	49.5	60.1	61.5	94.7	6.5	2.6	121.3	8.8	94.3	32.4	67.6	60.8
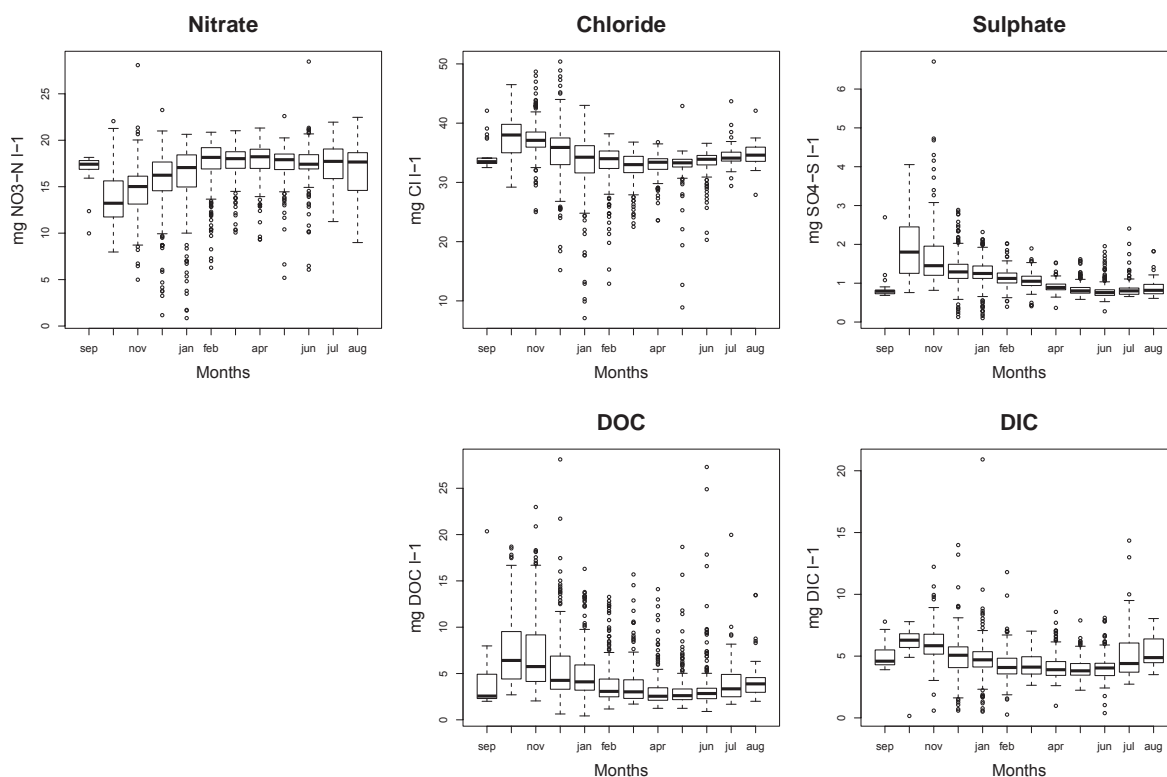
Fig. 3. Boxplots of monthly concentrations of nitrate, chloride, sulphate, dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC) based on daily data from the 10 yr dataset. The middle bar represent the median, the lower limit the 1st quartile ($q_{0.25}$) and the upper limit the 3rd quartile ($q_{0.75}$). The lower and upper dashed lines are, respectively, the 1st quartile minus 1.5 times interquartile range and the 3rd quartile plus 1.5 times the interquartile range.

of rainfall and (ii) rainfall water contributes less than 10 % of the flood flow, the major part coming from soil water. Gathering nitrate and chloride in the group of anthropogenic solutes, understanding the nitrate pattern and observing similar annual chloride variations, we propose a new concept describing the seasonal pattern. Few conceptualisations of seasonal chloride patterns in anthropogenically disturbed catchments have been described in the literature, partly due to the frequent assumption of chloride acting conservatively, meaning

that the outputs closely reflect the inputs (Koirala et al., 2010). However, some authors (Bastviken et al., 2007; Chen et al., 2002; Viers et al., 2001) have warned that chloride is not systematically a conservative element, i.e. the yearly balance is not null. They reported that adsorption-like processes in soil organic matter, hydrology and microbial soil activity influence stream chloride concentration. Other studies reported local storage of chloride in soils, for instance under hedges due to higher evapotranspiration (Grimaldi et

al., 2009), and in groundwater (Rouxel et al., 2011). Imbalances of the chloride budgets are also reported in catchments where land-use changes occurred (Guan et al., 2010; Oda et al., 2009).

We explained the stream chloride seasonal pattern as follows. By the end of spring–summer, evapotranspiration concentrates chloride. At the beginning of the hydrological year, first floods wash away chloride, explaining the October chloride concentration peak. The concentration increases quickly after resumption of flow. At this period, the chloride pool (wetland GW) is more superficial and closer to the stream than the nitrate pool (upland GW). After connection of the concentrated upland GW with the stream and according to the seasonality of the chloride signal in rainfall (albeit negligible here), chloride base-flow concentrations remain high but are diluted by floods.

The 10 yr-long dataset complemented earlier studies examining short timescale DOC concentration variations and enabled us to propose a new seasonal conceptualisation for sulphate. The pattern observed for DOC, sulphate and DIC was similar to that of chloride between floods (Fig. 3b–e). However, flushes occurred during the hydrological year with each rainfall event (Figs. 3c–e and 2) leading to concentration peaks. Mean stream DOC concentration during and between floods was 6.3 and 3.3 mg L^{-1}, respectively (Table 1). Stream sulphate concentrations were higher during floods (3.0 mg SO$_4^{2-}$-S L^{-1}) than between floods (2.3 mg SO$_4^{2-}$-S L^{-1}). The intensity of peaks decreased as the year progressed (Fig. 3). An increase in interflood concentration was observed during the summer. We were able to broaden Morel's (2009) study carried out in a particularly dry year. The seasonal DOC pattern in the Kervidy-Naizin catchment was explained as follows: there is a large stock of organic carbon in shallow soil horizons, particularly in the wetlands where soil organic matter concentration is about 0.1 g g^{-1}. During winter and spring floods, DOC is flushed and the magnitude of the release depends on the hydrological state of the catchment and temperature (Dawson et al., 2008, 2011). From our results, based on 10 yr, we concluded that in normally humid years, the high concentrations of DOC are depleted when raining. During summer, DOC concentrations increase due to biological soil activity and lack of transport. In-stream production contributes to the seasonal increase in the summer and beginning of autumn. Gathering DOC and sulphate in the group of natural solutes, understanding the DOC pattern and observing sulphate's similar annual variations, we proposed a new explanation for sulphate seasonal pattern. The sulphate cycle is of the same type as that of DOC, except that sulphate production appears seasonal (in summer). Therefore, we did not observe as many flushes during floods and their stream concentrations decreased rapidly.

Shallow groundwater connectivity plays an important role in controlling interflood stream concentration, as shown in the annual signature. The importance of upland GW connectivity is obvious on nitrate and chloride concentration. It confirmed previous conclusions drawn on Kervidy-Naizin or similar catchments stating that, for nitrate, (i) groundwater storage is the major control of nitrate concentration in stream water (Ruiz et al., 2002); (ii) groundwater concentration differs downslope, where denitrification induces lower nitrate concentrations (Martin et al., 2004); (iii) water-table level dynamics along hill-slope controls annual nitrate concentration variations in the stream, along with the spatial distribution of the solutes in groundwater (Molenat and Gascuel-Odoux, 2002); for DOC, (iv) hill-slope soils are rapidly DOC depleted when the water table rises upland, whereas wetland soils, from which > 80 % of the stream DOC come from, behave as an almost infinite DOC reservoir (Morel et al., 2009). Our study questions the connection of wetland GW with upland GW and stream. Upland GW must be contributing in minor proportions to the wetland during interflood periods, having direct flow pathways to the stream. The wetland GW contributed more to the stream during floods or high flow periods.

3.2.2 Interannual patterns

The temporal signature is also composed of interannual patterns: variations from year to year and variograms. All solutes present a higher variability in the autumn–winter period (Fig. 3). The period of lower variability occurred around April. This result emphasised the role of alternating dry and wet periods and their consequences on hydrological connectivity as well as production processes. The autumn–winter period is when different hydrological compartments connect to the stream. Early in the hydrological year following a dry summer, the wetland GW and the stream reconnect with the first rainfall events. Later, upland GW reconnects to the stream. These connections seem to determine the concentration of solutes, particularly the time when nitrate and chloride concentration increases. Therefore, variation of the recharge period (duration, quantity and intensity of rain) and temperature between years partly explains the high variability in the autumn–winter period.

Lastly, the dataset enables the study of variability over the whole time period. The observed interannual patterns reinforced the previously proposed groups. Plotting variograms over 2000 days with a 30 day time lag (Fig. 4), three groups were identified. DOC, sulphate and DIC signals were periodic, with a 360 day period, and similar to that of temperature. Chloride constituted a second group. Besides an annual periodicity, it showed a pluriannual variation marked by a break in the 36th month (1080 days). An equivalent break was observed in the discharge variogram. This pointed out the hydrological control on the export of chloride to the stream. The nitrate variogram seemed a mixture of the two previous groups. These observations confirm the grouping of solutes according to their origins. At the 10 yr scale, DOC, sulphate and DIC production relies mainly on surface
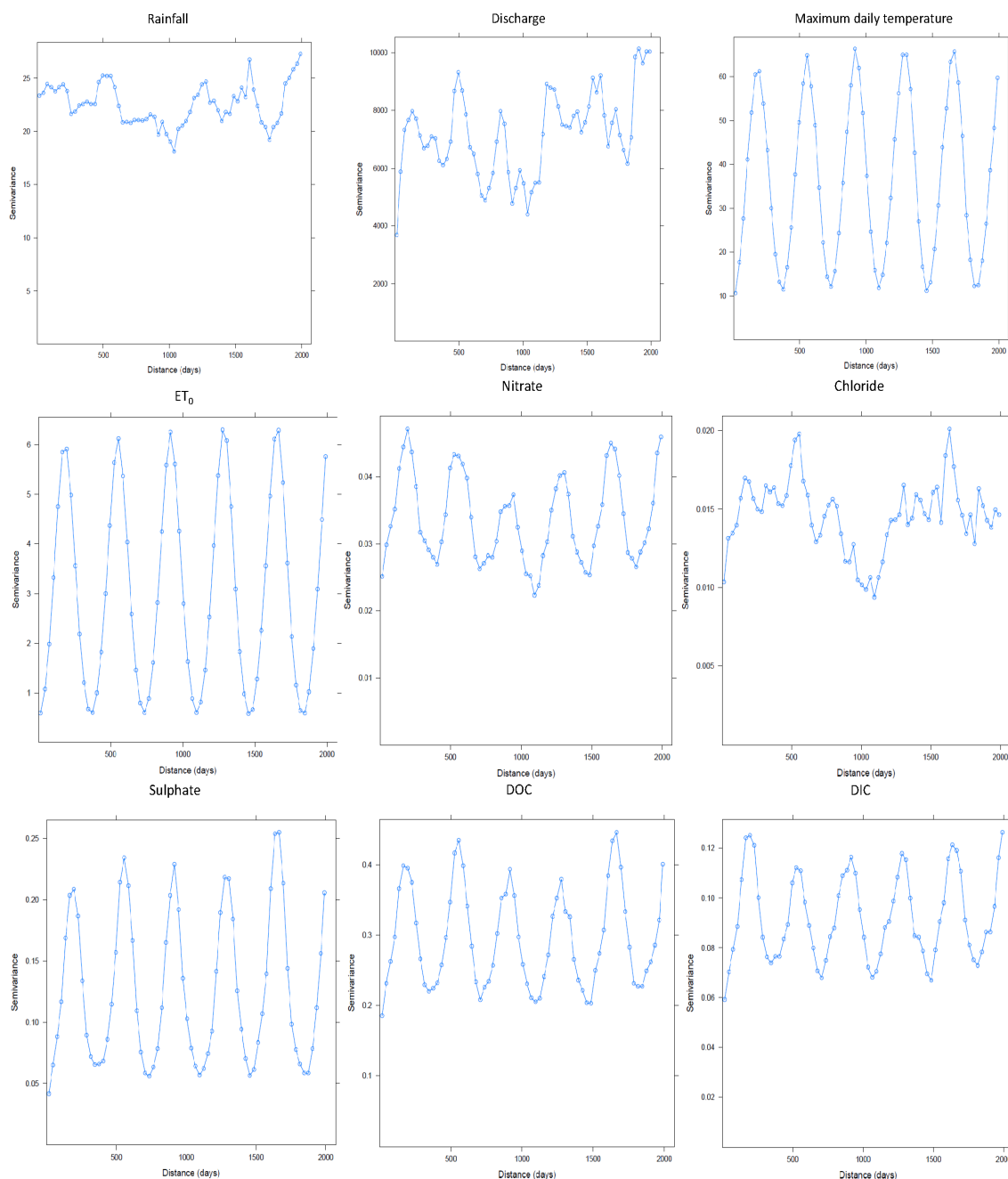
Fig. 4. Temporal variograms of hydro-climatic parameters and daily in-stream solute concentrations built for 2000 days with a 30 day lag.

biological processes influenced by temperature. Their temporal dynamic is linked with yearly processes occurring in the soil wetland domain. Nitrate and chloride are less influenced by the own catchment production, because they are in excess in the GW, and what is emphasized at the 10 yr scale are the transport conditions they depend on.

3.3 A generic classification of solutes applied to a livestock farming catchment

The 10 yr-long daily dataset allowed a representative description of the hydro-chemical signature of the catchment. Its conceptualisation leads to a generic classification of solutes. Many authors agree that element availability is a factor controlling export to streams (Creed et al., 1996; Hornberger et al., 1994; Reynolds and Edwards, 1995). Based on this major factor, Hornberger et al. (1994, for DOC) and Creed et
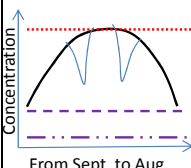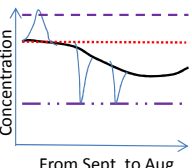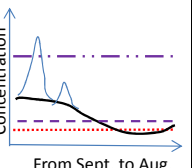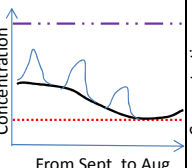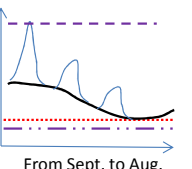
Solutes	nitrate	chloride	sulphate	DIC	DOC
Dominant source of solutes (1)	Anthropogenic inputs create internal catchment excess		Biogeochemical processes create internal patches of production within the catchment		
Dominant spatial source (2)	Upland GW		Deep down-slope GW		Wetland GW
Spatial distribution of GW concentrations (3)	Upland >> Wetland > Deep down-slope	Upland ~ Wetland > Deep down-slope	Deep down-slope >> Upland ~ Wetland	Deep down-slope >> Upland	Wetland >> Upland ~ Deep down-slope
Timing of concentration increase (4)	Seasonal	Seasonal + 1st flood		Seasonal + floods	
Summary graph					
Stocking period	Many years (past accumulation)		Summer (seasonal production)	Inter-flood periods (Continuous production)	
Transport-limited process	Limited by upland GW / stream connectivity i.e. hillslope GW gradient		Limited by wetland GW / stream connectivity i.e. GW variations in soils		
	a)	b)	c)	d)	e)

Fig. 5. Generic classification of the temporal patterns of elements and their determinants. Thick lines represent stream concentrations between floods throughout a year. Blue lines represent the reaction during a flood. Horizontal (red) dotted lines represent mean upland groundwater (GW) concentrations, while horizontal dot-dashed (purple) lines represent mean deep downslope GW concentrations and dashed (purple) lines represent mean wetland GW concentration. Criterion (1) is deduced from the bibliography. Criterion (2) is deduced from the comparison of stream concentrations to GW concentrations. Criterion (3) is deduced from the comparison of GW concentrations. Criterion (4) is deduced from the temporal patterns. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

al. (1996, for nitrate) proposed the "flushing hypothesis", which consists of the contribution of a productive area in the catchment at a given moment. This contribution leads to a concentration peak in the stream until the supply is depleted, thus leading to a decrease in concentration. The limiting stage is the production. Others consider transport processes as the controlling factor. The importance of flushing frequency (i.e., hydrological controls) was pointed out while studying base cations (Ca, Mg, Na, K) export in a catchment in which the solute supply was high (Burns et al., 1998). It was previously noted in an agricultural catchment that (nitrate and sulphate) production may take place in a catchment but is not the controlling factor (Schnabel et al., 1993). Different annual nitrate patterns from two adjacent catchments are explained by distinguishing "transport-limited" from "supply-limited" processes (Martin et al., 2004; Ruiz et al., 2002).

Applying these concepts developed from single solutes (either nitrate or DOC) in several catchments to five solutes in one catchment, and keeping in mind the solute distinctions presented in this paper, allows further classification (Fig. 5). First, nitrate and chloride depend on upland GW connection-limited processes: the seasonal pattern of shallow groundwater connectivity to the stream determines whether they

can be exported. The timing, rate and duration of the connectivity are controlling factors of the export. Nitrate differs from chloride as nitrate production exists, even if it is not the main source, whereas chloride is not produced in the catchment. In contrast, sulphate and DOC depend on wetland GW connection-limited processes: the exported solutes are produced in the catchment within the period preceding the export but exports occur only when the wetland is hydrologically connected to the stream, i.e. by floods and when the quickly reactive groundwater fluctuates in the upper soil organic layer. There is little time lag between production and export, even though production can be seasonal (sulphate) or continuous (DOC). Unlike nitrate for which export is continuous during the rainy period, DOC and sulphate exports are highly discontinuous: every flood leads to a peak in concentration. For DOC and sulphate, the wetland domain is the main productive compartment close to the stream and contributes mostly during floods. It would be interesting to analyse data from other agricultural catchments to corroborate our classification. A longer dataset would provide longer temporal variograms, which may verify the periodicity identified in this catchment.

4 Conclusions

From this original dataset, the hydro-chemical signature of a livestock farming catchment dominated by shallow groundwater flow has been defined. This signature was identified by analysing (i) mean concentrations in four water compartments in the catchment (stream water, upland, wetland and deep downslope groundwater), considered as a static signature, and (ii) annual patterns of stream water concentrations and their interannual variability, considered as a temporal signature. Our results broadened some previously proposed conceptual models, based on short-term studies, for nitrate and DOC. The data enabled us to explain annual patterns for chloride and sulphate. Both aspects of the signature, static and temporal, lead to a generic conceptual model of stream water quality.

The static signature is defined by average long-term concentrations in the stream and the contributing compartments. Nitrate and chloride concentrations were high in both the shallow groundwater and the stream due to fertilisation, while sulphate, DOC and DIC were present at similar concentrations as in other catchments. The temporal signature was characterised at annual and interannual scales. By analysing the annual patterns observed, we proposed a classification of solutes. In-stream nitrate and chloride concentrations depended on the connection of upland shallow groundwater with the stream, while in-stream DOC, DIC and sulphate concentrations were influenced by the connection of wetlands with the stream. Interannual patterns emphasised that nitrate and chloride in the stream were influenced mostly by discharge, thus transport, while sulphate, DOC and DIC showed sinusoidal signals, similar to those of temperature and ET_0. It also showed that solute concentration variability was much higher during the re-wetting stage than during other periods.

Stream nitrate and chloride concentrations depended on the connection of their storage compartment (upland groundwater), while sulphate, DOC and DIC concentrations depended on catchment production and the connection of the producing compartment (wetland soil) during rainfall events. These hydrological connections control solute transport. From these hydrological connections of the stocking compartment, the concept of "transport-limited" processes was further developed. This classification could be applied to any chemical solute and could help assess its origin, storage, or production location and transfer mechanism in similar catchments.

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