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The chemical signature of a livestock farming catchment: synthesis from a high-frequency multi-element long term monitoring

A. H. Aubert[1,2], C. Gascuel-Odoux[1,2], G. Gruau[3], J. Molénat[4], M. Faucheux[1,2], Y. Fauvel[1,2], C. Grimaldi[1,2], Y. Hamon[1,2], A. Jaffrézic[1,2,5], M. Lecoz-Boutnik[3], P. Petitjean[3], L. Ruiz[1,2], and Ph. Merot[1,2]

[1]Inra, UMR1069, Sol Agro et hydrosystème Spatialisation, 35000 Rennes, France
[2]Agrocampus Ouest, UMR1069, Sol Agro et hydrosystème Spatialisation, 35000 Rennes, France
[3]Université de Rennes I, UMR6118, CNRS, Géosciences Rennes, 35000 Rennes, France
[4]Inra, UR0388, Laboratoire de géologie science du sol, 34060 Montpellier, France
[5]Université Européenne de Bretagne, France

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Correspondence to: A. H. Aubert (alice.aubert@rennes.inra.fr)

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Abstract

Assessing the impact of human pressures on water quality is difficult. First, there is a high temporal and spatial variability of climate and human activity. Second, chemical elements have their own characteristics mixing short and long term dynamics. High frequency, long-term and multi-element measurements are required. But, such data series are scarce. This paper aims at determining what the hydro-chemical particularities of a livestock farming catchment are in a temperate climatic context.

It is based on an original and never published time series, from Kervidy-Naizin headwater catchment. Stream chemistry was monitored daily and shallow groundwater roughly every four month, for 10 yr and five elements (nitrate, sulphate, chloride, and dissolved organic and inorganic carbon).

The five elements present strong but different seasonal patterns. Nitrate and chloride present a seasonal flush, all along or at the beginning of the wet season, respectively. Sulphate, organic and inorganic carbon present storm flushes, with constant or decreasing peaks throughout the wet season. These depicted nitrate and chloride patterns are typical of a livestock farming catchment. There, nitrate and chloride coming from organic fertilisation have been accumulating over years in the shallow groundwater. They are seasonally flushed when the groundwater connects to the stream. Sulphate, organic and inorganic carbon patterns do not seem specific to agricultural catchments. These elements are produced each year and flushed by storms. Finally, a generic classification of temporal patterns and elements is established for agricultural catchments. It is based on the distance of the source component to the stream and the dominant controlling process (accumulation versus production). This classification could be applied to any chemical element and help assessing the level of water disturbances.

1 Introduction

In the context of global change, evaluating the impact of human pressures on the environment is a major concern. Assessing a signature of human activity on water quality is a difficult issue. First, because climatic and human pressures are highly variable, second because chemical elements characteristics mix short and long term dynamics. Such signature can be identified thanks to long term observatories.

For years, hydrologists have warned about the need for long-term hydrological data (Betton et al., 1991; Neal, 1997; Reynolds, 1995). Many countries implemented long-term observatories for water quality. For instance, in the USA, the Long-Term Ecological Research (LTER) network began with six sites as early as 1977. Currently, it comprises 26 sites covering the diversity of North American ecosystems (http://www.lternet.edu/). Another American network, the Critical Zone Exploration Network (CZEN), was established. Presently, CZEN comprises six Critical Zone Observatories and additional affiliated sites, which focus on studying the interface between the atmosphere, hydrosphere, soil and ecosystems (http://www.czen.org/). In Europe, similar networks have been developed, such as TERENO (TERestrial ENvironmental Observatories in Germany (http://teodoor.icg.kfa-juelich.de/overview-de), French Resources for Exploration of the Critical Zone (FRECZ or SOERE RBV, “Réseau de Bassins Versants”; http://rnbv.ipgp.fr/), etc. All those observatories are complementary as they are located in diverse areas.

The existing observatories cover a broad range of ecosystems. Some are located in quite pristine areas (Boulder Creek CZO, Colorado, USA; Draix-Bléone, France; etc.), where studies focus mainly on understanding mechanisms of a critical zone without 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. Clear-cutting has been a major studied topic. Very few observatories are located in areas strongly impacted by human activities, whether in urban (Baltimore Ecosystem Study, Maryland, USA) or intensive agricultural areas (Kervidy-Naizin, France). Water quality differs according to the ecosystem and its land use. However few have already published and analysed their long time series, as recently done on Plynlimon observatory (Neal et al., 2011).

Long-term water quality data varies considerably over different timescales (Reynolds, 1997). Time-series length and sampling frequency influence drawn conclusions (Feng et al., 2004; Halliday et al., 2012; Moatar et al., 2009). What is the right timescale to study water quality specificity according to land use? In the literature focusing on water quality at the catchment scale, three timescales are found: (i) short-term studies analyse the variation of water chemical composition during storm or flood events (Morel et al., 2009; William, 1989), (ii) long-term studies, defined by Burt and Worrall (Burt and Worrall, 2009) as data series of at least 20 yr, focus on trends over several decades (Gascuel-Odoux et al., 2010; Howden et al., 2010; Monteith et al., 2000) and (iii) intermediate scale studies focus on seasonal variations. This intermediary time scale highlights intra-annual variations repeated from year to year. These variations occur at any given period of the year, such as flow resuming after the dry season, groundwater recharge, snowmelt, etc. These variations constitute an intra-annual hydro-chemical signature of a catchment.

This paper aims at defining what the annual hydro-chemical signature of a livestock farming catchment is. It is based on an unpublished high-frequency multi-element 10-yr-long time series of stream water chemistry in an agricultural catchment, Kervidy-Naizin, located in western France. The hydrochemical signature is defined by the concentration levels of several water components and the mean intra-annual pattern and its year to year variability. Both aspects are presented in the paper and lead to a generic conceptual model of stream water quality signature.

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, out of which flows a stream of 2nd Strahler order, which can dry in summer. The catchment's observatory, named ORE-AgrHys for agro-hydrosystem, belongs to the French network of observatories SOERE-RBV. 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, the Web of Knowledge lists 20 journal articles from the catchment, from which the most cited are Carluer and De Marsily (2004), Cognard et al. (1995), Dia et al. (2000), Molenat and Gascuel-Odoux (2002), Payraudeau et al. (2007) and Pourret et al. (2007).

The catchment lies on Upper Proterozoic schist covered by a layer of weathered material a few to 30 m thick. A shallow-groundwater table develops in this unconsolidated layer. The soils are silty loams. Soils on the hillslopes are well-drained and consist of Alocrisols and Luvisols (brown soils).Soils in the lowest zones, often saturated by shallow water rising up to ground level, consist of unweathered and weathered Luvisol-Reduxisols, in which Mn and Fe-oxyhydroxides are depleted due to seasonal reduction by heterotrophic bacteria. They constitute wetlands. The topography is moderate. In the southern part, gentle slopes of 5 % are reached. Elevation ranges from 98–140 m above sea level. The climate is temperate, 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 heads per yr), poultry (40 500 heads) and dairy and beef cows (3000 heads). In 1996, 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). Among the farm types and farms, N efficiency varied greatly. In 2010, a detailed survey estimated the total N surplus to be approximately 200 kg N ha^{-1} of usable agricultural area (Akkal, unpublished data).

2.2 Data collection

This study analyses data from September 2000 to August 2010 (10 hydrological years). At least daily measures of stream discharge and water chemistry are available at the Kervidy-Naizin outlet since autumn 2000. Discharge has been continuously monitored at the outlet with a gauging station including a float-operating sensor and a data logger (Thalimèdes OTT). The weather station at Kervidy (Cimel Enerco 516i) is located approximately one 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.

Stream water was manually sampled daily at approximately the same hour, without specific sampling during storm events. Samples were immediately filtered (0.2 µm) and stored in the dark at 4 °C. During one hydrological year only (2002–2003) sampling frequency was reduced to once every 2–4 days. Major anion concentrations (nitrate, chloride and sulphate) were measured by ionic chromatography (DIONEX DX 100). DOC concentrations were measured on a total organic carbon analyser (Shimadzu TOC 5050A) with a precision of 5 %, based on repeated measurements ($n = 10$) of freshly prepared standard solutions (K-phtalate). DOC concentration was calculated by the difference between total carbon and DIC.

Shallow groundwater data from two four-meters-deep piezometers along the Gueriniec transect (Fig. 1) were also used in this study. Water-table depth was measured by ultrasonic probes from 2000 to mid-2001, then by float-operated sensors (Thalimèdes OTT) until December 2009, and every 15 min by pressure probes

(Orpheus OTT) since then. Water-table chemistry was measured roughly every three months, providing 24 analyses for each piezometer from 2000–2010. After purging, shallow groundwater was sampled at the screen level using a Teflon bailer. Water was filtered immediately at 0.45 µm (GNWP) and then stored in the dark at 4 °C. Anion concentrations were measured using an ionic chromatograph (DIONEX DX 100).

2.3 High frequency sampling strengthens data treatment

Considering the whole dataset, descriptive statistics and boxplots were constructed with R software. Monthly aggregation of data leads to about 300 repetitions, allowing a trustworthy description.

Temporal variograms were plotted using "gstat" and "variogram" functions in R to represent variability over the studied years (Zhang and Schilling, 2005). Temporal distance was given as a number of days. The chosen lag was 30 days, and the span 2000 days. For some stream concentration analyses, we distinguished samples taken during storm events from those taken during base flow. As no specific sampling was done, we implemented the following decision rule based on three conditions: 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 $\mathrm{l\,s^{-1}}$, then the sample was considered as taken during storm flow; otherwise it was considered as taken during base flow.

3 Results and discussion

Based on the results on concentration levels of the different water components and annual patterns of elements and their variability from year to year, we identify what the hydro-chemical signature of a livestock farming catchment is. It is achieved by analysing (i) concentration levels and the spatial source of the levels, considered as a static signature, (ii) annual patterns and their inter-annual variability, considered as a temporal signature. Our results enlarged some previously proposed patterns, based on short studies, for nitrate and DOC. The data enabled us to describe new annual patterns for the other elements. Both aspects of the signature leads to a generic conceptual model of stream water quality which is then proposed.

3.1 The static agricultural signature: various concentration levels of water components

Comparing our data to other long-term observatory catchments, we highlight two specificities. Both nitrate and chloride were highly concentrated in 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 mid-slope shallow groundwater was of the same order of magnitude (20.7 mg NO_3^--N l^{-1}) (Table 2, Fig. 2), whereas in the wetland it was almost zero (0.2 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, stream nitrate concentration was high even though denitrification was efficient in the wetland.

Second, the mean in-stream chloride concentration was 34.0 mg l^{-1} (CV = 10.5 %). In mid-slope groundwater, the concentration was similar (32.7 mg l^{-1}), but it was lower in the wetland shallow groundwater (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) and 4–9 mg l^{-1} in Plynlimon (Kirchner et al., 2000). High level of chloride concentration was pointed out earlier in a catchment in the same soil, climate and land-use context as Kervidy-Naizin, named Kerbernez (Martin et al., 2004; Pierson-Wickmann et al., 2009). These authors attributed such a high chloride concentration to agricultural origins, chloride being a component of KCl fertiliser, pig slurry and dairy manure applied to fields. Since chloride concentration in rainfall is low (annual mean of $4\,\mathrm{mg\,l^{-1}}$), we can conclude that mineral and, above all, organic fertilisation increases chloride concentration, as it does for nitrate. These particular concentrations represent the Kervidy-Naizin agricultural signature. Data from the Environmental Change Network (CEH, 2012) support this signature, with the UK comparable to Brittany in terms of rainfall and geological substrate. Both agricultural catchments in this database (Rothamsted and Wytham) have higher concentrations of nitrate and chloride than other catchments.

Conversely, other elements were not as concentrated in-stream. Mean sulphate concentration was $2.6\,\mathrm{mg\,SO_4^{2-}\text{-}S\,l^{-1}}$, associated with high variability ($\mathrm{CV} = 41.7\,\%$). In-stream and mid-slope groundwater concentrations ($1.9\,\mathrm{mg\,SO_4^{2-}\text{-}S\,l^{-1}}$) were lower than that in wetland groundwater ($5.2\,\mathrm{mg\,SO_4^{2-}\text{-}S\,l^{-1}}$). Sulphate concentrations in Kervidy-Naizin were similar to those found in the forested catchment of Plynlimon ($\mathrm{range} = 0.05\text{–}3.3\,\mathrm{mg\,SO_4^{2-}\text{-}S\,l^{-1}}$) (Reynolds et al., 1997) and in Finland ($\mathrm{maximum} = 3.3\,\mathrm{mg\,SO_4^{2-}\text{-}S\,l^{-1}}$) (Lahermo et al., 1995). Sulphate concentrations were lower than those observed in Rothamsted and Wytham agricultural catchments (approximately 9 and $20\,\mathrm{mg\,SO_4^{2-}\text{-}S\,l^{-1}}$, respectively).

Mean in-stream DOC concentration was $4.4\,\mathrm{mg\,l^{-1}}$, associated with significantly high variability ($\mathrm{CV} = 70.5\,\%$). DOC concentration in groundwater was low, both at mid-slope ($1.2\,\mathrm{mg\,l^{-1}}$) and in the wetland ($0.8\,\mathrm{mg\,l^{-1}}$). DOC 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 and other Scottish catchments (Dawson et al., 2008). Mean in-stream DIC concentration was $4.7\,\mathrm{mg\,l^{-1}}$ ($\mathrm{CV} = 30.5\,\%$). DIC concentration ($3.7\,\mathrm{mg\,l^{-1}}$) was in the same range mid-slope groundwater and nearly three times higher ($17.0\,\mathrm{mg\,l^{-1}}$) in the wetland. Sulphate, DOC and DIC did not show concentrations specific to intensive agricultural land use.

This static signature enabled to develop two points: one on element origin and one on spatial source patterns. First, we distinguished two origins of elements, anthropogenic and natural (Ouyang et al., 2006; Vega et al., 1998). In the first group, highly concentrated nitrate and chloride were suspected to have been added in excess of plant uptake during fertilisation of agricultural land. Being mobile, they were leached and stored in the shallow groundwater. Conversely, in the second group, sulphate, DOC and DIC, which had moderate to low concentrations, were suspected to have been governed mainly by natural processes in the soil catchment. They had low mid-slope groundwater concentrations and relatively higher wetland groundwater concentrations. Elements from this group seemed to depend on biogeochemical processes taking place in the wetland. Second, from this static signature in the stream and in mid-slope and wetland groundwater (Tables 1 and 2, Fig. 2), we identified three spatial source patterns. Stream nitrate concentrations are 20 % lower than those in mid-slope groundwater, likely due to wetland denitrification. Conversely, stream chloride concentrations are 4 % higher than those in mid-slope groundwater, indicating an additional chloride source. As chloride is a non-reactive element, shorter residence time in wetlands may explain why wetland chloride concentrations are lower (by 50 %) than those in the other two components. Sulphate concentrations were similar in the stream and mid-slope groundwater, but with high variability. Last, DOC concentration in the stream had high variability and is much higher than in both the mid-slope and wetland groundwater. It indicates that there is no permanent DOC storage in the catchment. The static signature leads to two element differentiations based on element origin and spatial sources.

3.2 The temporal agricultural signature: annual and inter-annual patterns

The intra-annual and inter-annual variations and variabilities of the 10-yr-long daily dataset allowed us to identify temporal patterns of elements. We distinguish two scales of intra-annual patterns: the hydrological year and the storm events. We study the inter-annual pattern analysing year to year variability and variograms.

3.2.1 Annual patterns

Our results reinforced the nitrate annual pattern and allow us to propose additional explanations. Nitrate concentrations were lower at the beginning of the hydrological year (September), reached a maximum from January to March and slightly decreased during spring and summer (Fig. 3a). All rainfall events had a dilution effect (Fig. 2). Mean stream concentration during storms and between storms was 15.6 and 17.6 mg NO_3^--N l^{-1}, respectively. Means differed little (Table 1) because inter-storm concentrations were low at the beginning of the hydrological year and in summer, which decreased the annual mean. In other words, nitrate concentration remains high as long as the high nitrate-concentrated upland water table contributes more to stream discharge than the low nitrate-concentrated water table in the wetland (Molenat et al., 2008). Then, from June to August, it decreases slightly as the upland groundwater progressively contributes less and as other processes, such as denitrification and plant uptake in wetlands and in-stream, also contribute (Betton et al., 1991). The combination of these processes could explain the low concentrations observed in October. The increased rate of decrease from September to October also might be due to in-stream processes, as suggested by Mulholland and Hill (1997). In their forested catchment during autumn, leaf input to the stream was highest, and photosynthetically active radiation increased, leading to more active stream decomposition. The Kervidy-Naizin stream is bordered by riparian hedges, which could have the same effect as forest trees. In autumn, there is a transition period when the upland water table progressively rises (Molenat et al., 2008).

We proposed new seasonal patterns for chloride. The chloride pattern was characterised by a flush of higher concentrations at the beginning of the hydrological year (Fig. 3b). Concentrations then decreased and slightly increased at the end of the hydrological year. A seasonal change in rainfall effect was noticed (Fig. 2), in which only storms occurring at the beginning of the hydrological year led to an increase in concentration, whereas later storms mostly had a dilution effect. Therefore, storms did not influence annual means (Table 1): chloride concentration was 33.4 and 34.4 mg l^{-1} during and between storms, respectively. Gathering nitrate and chloride in the group of anthropogenic elements, understanding nitrate pattern and observing chloride similar annual variations, we proposed a new seasonal pattern for chloride. Few annual chloride patterns have been described in the literature, due partly to the identification of chloride as a conservative element in the hydrologic system, meaning that the inputs usually equal the outputs (Koirala et al., 2010). However, some authors (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 and hydrology 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). We explained the chloride seasonal pattern as follows. By the end of spring-summer, evapotranspiration concentrates chloride in the storage compartment. At the beginning of the hydrological year, first rainfall events wash away chloride, explaining the October peak in concentrations. The increase in concentration occurs quickly after resumption of flow. Storage of chloride may be either more superficial and/or closer to the stream than that of nitrate. After connection of the storage site to the stream, chloride concentrations remain high and are diluted by rainfall events, as nitrate concentrations.

The 10-yr-long dataset proved complementary to studies based on shorter data for DOC and enabled us to propose new seasonal patterns for sulphate. The last pattern, observed for DOC, sulphate and DIC, was similar to that of chloride between storms (Fig. 3b–e). However, flushes occurred during the hydrological year with each rainfall event (Figs. 2 and 3c–e), leading to concentration peaks. Mean DOC concentration during and between storms was 6.3 and 3.3 mg l^{-1}, respectively (Table 1). Sulphate concentrations were higher during storms (3.0 mg SO_4^{2-}-S l^{-1}) than between storms (2.3 mg SO_4^{2-}-S l^{-1}). The intensity of peaks decreased as the year progressed. An increase in inter-storm concentration was observed during the summer. We were able to broaden Morel' study (2009) carried on a particularly dry year. Seasonal DOC pattern in the Kervidy-Naizin catchment was explained as follows. There is an unlimited stock of organic carbon in the superficial soil horizons of the wetland. During winter and spring, DOC is flushed from storage during storm events, and the magnitude of the release depends on the hydrological state of the catchment. From our results, based on 10 yr, we concluded that in normally humid years, the stock of organic carbon is depleted by each storm. Concentration peaks decrease throughout the year. During summer, the stock of DOC regenerates due to biological soil activity and lack of transport. In-stream production is another process that contributes to the seasonal increase in the summer and beginning of autumn. Gathering DOC and sulphate in the group of natural elements, understanding DOC pattern and observing sulphate similar annual variations, we proposed a new seasonal pattern for sulphate. The sulphate cycle is of the same type as that of DOC, except that sulphate production appears seasonal and requires a high summer temperature. Therefore, we did not observe as many flushes during storms and their concentrations decreased more rapidly.

This intra-annual signature confirmed the role of shallow groundwater in controlling inter-storm stream concentration, as shown by several authors (Martin et al., 2004; Molenat and Gascuel-Odoux, 2002; Molenat et al., 2008; Ruiz et al., 2002). The role of upland groundwater is particularly obvious for nitrate and chloride. It also emphasised the role of production processes in controlling DOC, sulphate and DIC concentration.

3.2.2 Inter-annual patterns

The temporal signature is also composed of inter-annual patterns: variability from year to year and variograms.

All elements present a higher variability in autumn-winter period (Fig. 3). The period of lower variability occurred around the month of April. This result emphasised the role of alternating dry-and-wet periods. The autumn-winter period is when different hydrological compartments connect to the stream. Early in the hydrological year following a dry summer, the wetland and the stream reconnect with the first rainfall events. Later, upland groundwater gradually reconnects to the stream. These connections seem to determine the concentration of chemical elements. Therefore, variation of the recharge period between years partly explains the high variability in the autumn-winter period. It is also due to the stronger effect of rainfall events during this time of the year. The rain dilutes nitrate and concentrates DOC and sulphate enhancing chemical transformations in a moist soil.

Last, the dataset enable the study of variability over the whole time period. The observed inter-annual patterns reinforced the suggested groups. Plotting variograms over 2000 days with a 30-day time lag (Fig. 4), three groups were identified. DOC, sulphate and DIC signals were "perfectly" 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 stream. The nitrate variogram seemed a mixture of the two previous groups. These observations confirm the grouping of elements according to their origins. DOC, sulphate and DIC production relies on surface biological processes influenced by air temperature. Nitrate and chloride are more influenced by discharge, i.e. transport conditions.

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

The 10-yr long daily dataset allowed a reliable, representative and accurate description of the hydro-chemical signature of the catchment. Its conceptualisation leads to a generic classification of elements. Many authors agree that element availability is a factor controlling export to streams (Creed et al., 1996; Hornberger et al., 1994; Reynolds, 1995). Based on this major factor, Hornberger et al. (for DOC) and Creed et al. (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-stream until the supply is depleted, thus leading to a decrease in concentrations. The limiting control is the production stage. Others consider transport as another controlling factor. The importance of flushing frequency (i.e., hydrological controls) was pointed out while studying base cations in a catchment in which the solute supply was high (Burns et al., 1998). It was previously noted in an agricultural catchment, that 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-controlled" from "supply-controlled or process-controlled" processes (Martin et al., 2004; Ruiz et al., 2002).

Applying these concepts developed from a single element in several catchments to five elements in one catchment, and keeping in mind the element distinctions presented in this paper allow further classification (Fig. 5). The seasonal pattern of the transport-controlled elements (nitrate and chloride) depends on the timing, rate and duration of shallow groundwater connection to the stream. The diluting effect of rainfall events remains constant in time. Within this group, a subdivision can be made. For some elements, production was possible but not the main origin of excess supply (nitrate), for others production did not exist (chloride, which depended on concentration/dilution processes due to evapotranspiration). In contrast, for process-controlled patterns (sulphate, DOC), the supply of elements, and thus their production, is limited in time. There is no time lag between production and export, even though production can be seasonal (sulphate) or continuous (DOC). In this case, element transport is linked more to storm period, groundwater fluctuation and its interaction with upper soil organic layer. Therefore, flush events are observed due to the temporal characteristic of storms (i.e., every rainfall leads to a peak in concentration). The wetland is the storage compartment close to the stream. There, the water table depth is highly reactive to storms. It would be interesting to obtain data from additional 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

Thanks to the original dataset, the hydro-chemical signature of a livestock farming catchment has been defined by static and temporal patterns. The static component is defined by the concentration levels and the spatial source of these levels. Nitrate and chloride concentrations were high in both the shallow groundwater and in-stream due to fertilisation, while sulphate, DOC and DIC were present at the same concentrations as in other catchments. The temporal component was characterised at annual and inter annual scale. By analysing the annual patterns observed, we proposed a classification of elements. The inter-annual patterns emphasised that nitrate and chloride were mostly influenced by discharge and sulphate, DOC and DIC showed perfect seasonality, as did temperature and ET_0. It also showed that element concentration variability was much higher during the re-wetting stage than other periods. Stream nitrate and chloride concentrations depended on the connection of the storage compartment, while sulphate, DOC and DIC concentration depended on catchment production. The concepts of “transport-controlled” or “process-controlled” elements were further developed, leading to a new classification composed of five possible groups. This classification could be applied to any chemical element and help assessing the level of water disturbances.

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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

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Table 2. Summary statistics for 10 yr of 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).

	Mid-slope groundwater concentrations (mg l^{-1})					Wetland groundwater concentrations (mg l^{-1})				
	Nitrate-N	Chloride	Sulphate-S	DOC	DIC	Nitrate-N	Chloride	Sulphate-S	DOC	DIC
Sample size	24	24	24	24	23	19	24	24	24	23
Min.	17.9	28.2	0.5	0.3	1.3	0.02	14.9	5.0	0.0	13.9
1st Qu.	19.6	31.4	1.2	0.6	2.0	0.1	15.5	5.1	0.0	15.9
Median	20.3	32.6	1.7	0.9	2.9	0.1	16.2	5.2	0.4	16.7
Mean	20.7	32.7	1.9	1.2	3.7	0.2	16.2	5.2	0.8	17.0
3rd Qu.	21.6	34.2	2.5	1.5	4.9	0.2	16.6	5.3	1.0	18.3
Max	26.0	36.4	4.1	2.8	9.7	0.6	19.9	5.5	3.5	19.9
Std	1.8	1.9	0.9	0.7	2.3	0.2	1.1	0.1	0.9	1.5
CV (%)	8.6	5.8	49.5	60.1	61.5	94.7	6.5	2.6	121.3	8.8

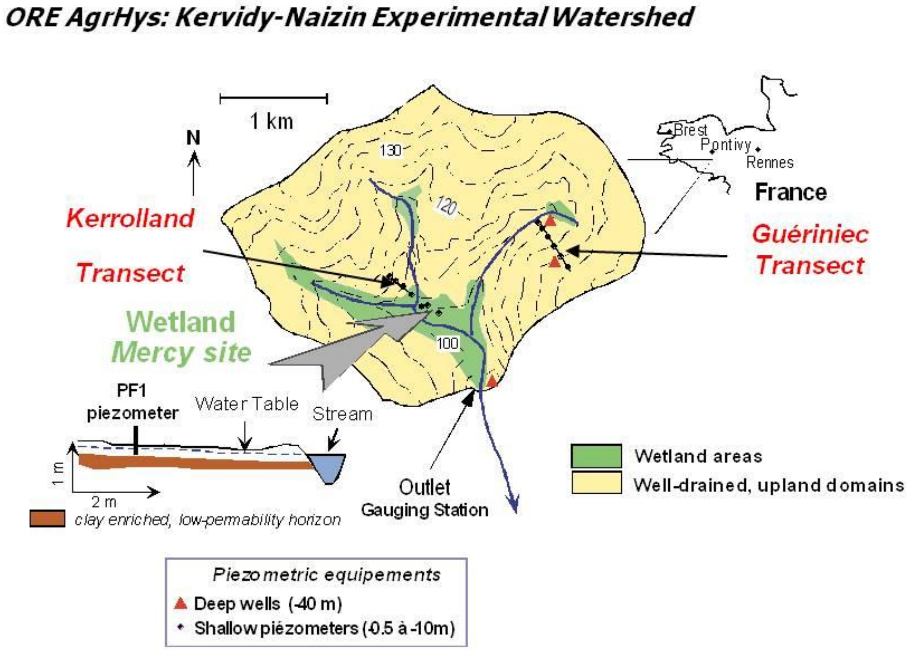

Fig. 1. Location and map of the Kervidy-Naizin experimental watershed, Brittany, France.

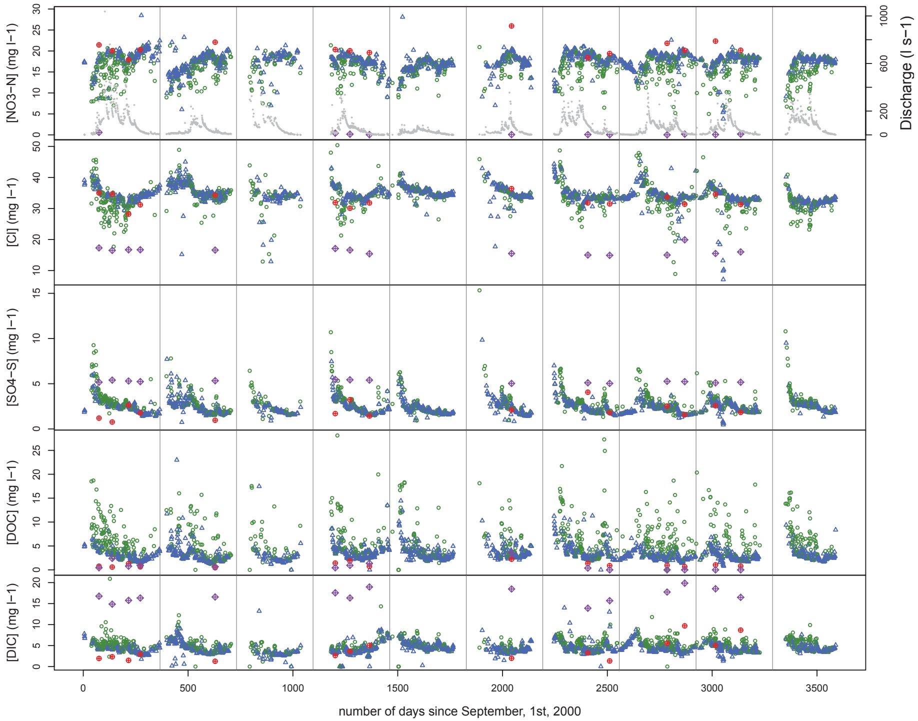

Fig. 2. Time series of daily stream concentrations and quarterly groundwater concentrations of nitrate, chloride, sulphate, dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC) from September 2000 to August 2010. The start of each hydrological year is marked with a vertical line. Inter-storm flow is plotted in blue triangles, while storm flow is plotted in green circles. Daily discharge ($\text{l}\,\text{s}^{-1}$) is presented in grey in the nitrate graph. Concentrations in the shallow groundwater are depicted in purple diamonds for the wetland and red circles for the mid-slope. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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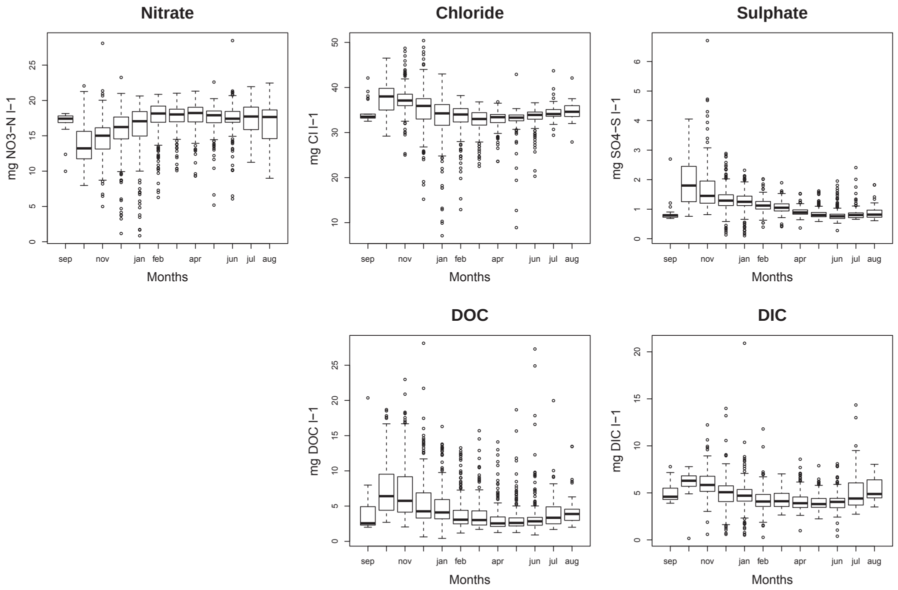

Fig. 3. Boxplots of monthly concentrations of nitrate, chloride, sulphate, dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC) based on daily data from the 10-yr dataset. The middle bar represented the median, the lower limit the 1st quartile ($q_{0.25}$), the upper limit the 3rd quartile ($q_{0.75}$). The lower and upper dashed lines were, respectively, the 1st quartile minus one and a half times the difference between the 3rd and the 1st quartile ($q_{0.25--1.5}\,(q_{0.75} - q_{0.25})$), and the 3rd quartile plus one and a half times the difference between the 3rd and the 1st quartile ($q_{0.75} + 1.5\,(q_{0.75} - q_{0.25})$).

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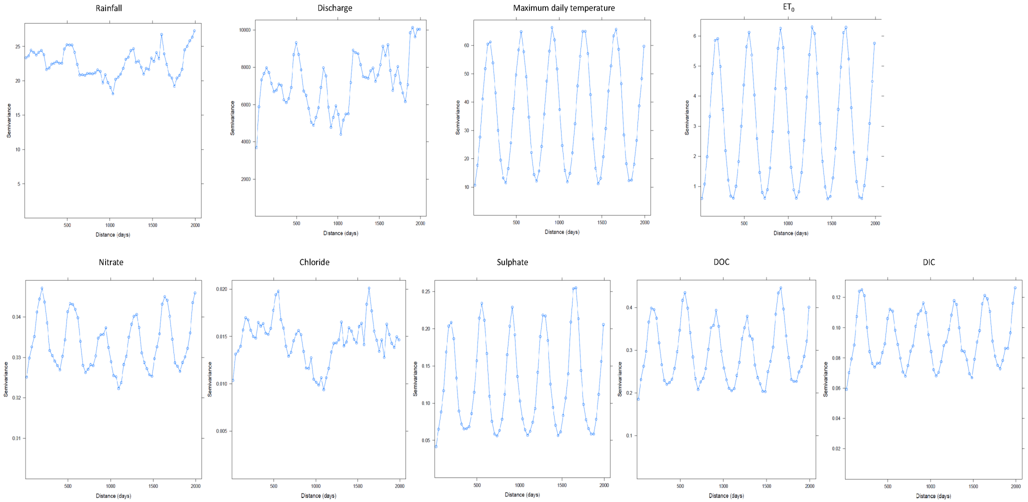
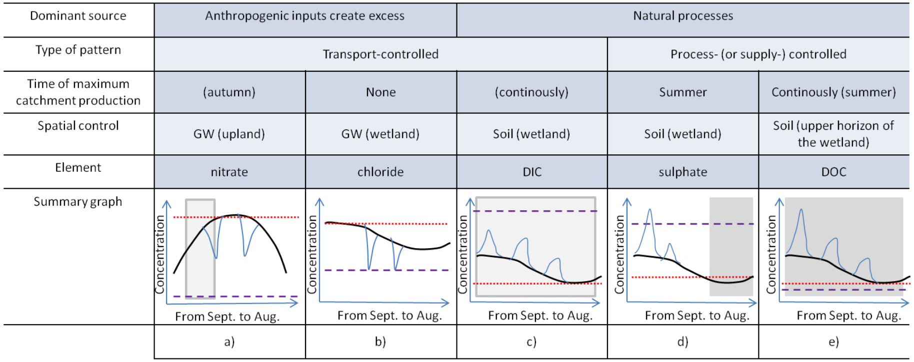


Fig. 4. Temporal variograms of hydro-climatic parameters and element daily stream concentrations built for 2000 days with a 30-day lag. DOC: dissolved organic carbon; DIC: dissolved inorganic carbon.



Dominant source	Anthropogenic inputs create excess		Natural processes		
Type of pattern	Transport-controlled			Process- (or supply-) controlled	
Time of maximum catchment production	(autumn)	None	(continously)	Summer	Continously (summer)
Spatial control	GW (upland)	GW (wetland)	Soil (wetland)	Soil (wetland)	Soil (upper horizon of the wetland)
Element	nitrate	chloride	DIC	sulphate	DOC
Summary graph					
	a)	b)	c)	d)	e)

Fig. 5. Generic classification of the temporal patterns of elements and their determinants. Thick lines represent stream concentrations throughout a year between storms. Grey zones represent element-production periods: dark grey when it is limiting (for process- or supply-controlled elements), light grey when it is not (for transport-controlled elements, the time of maximum catchment production is indicated in brackets). Horizontal dotted lines represent mean mid-slope groundwater concentrations, while horizontal dashed lines represent mean wetland groundwater concentrations. GW: groundwater; DOC: dissolved organic carbon; DIC: dissolved inorganic carbon.