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Annual hysteresis of water quality: A method to analyse the effect of intra- and inter-annual climatic conditions

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SUMMARY

Understanding annual patterns of stream water quality and the sensitivity of these patterns to climatic conditions is of great interest in the context of climate change. This paper proposes an alternative method to analyse the effect of climatic conditions on seasonal patterns of stream water chemistry. The method consists of plotting monthly means of stream concentrations against monthly means of the chosen hydro-climatic parameter. In our case, the monthly mean of the 30-day moving average of daily temperature behaved in the same way as discharge. This presentation enabled comparison of wet and dry years and cold and hot years, and a higher level of complexity was included by distinguishing storm from inter-storm concentrations. This method was applied to an original dataset from a long-term monitored agricultural catchment where samples have been taken daily from 2000 to 2010. Five elements were studied: nitrate, chloride, sulphate and dissolved organic and inorganic carbon. To construct the method, relations between two hydro-climatic parameters (discharge and air temperature) were studied. All elements displayed hysteretic loops, apparently due to the time needed to rewet catchment soils and connect the spatial source of elements to the stream. Temperature and discharge have equivalent relations with concentrations in this catchment because of its specific climatic conditions (temperate under oceanic influence), which makes evapotranspiration the main factor controlling seasonality. The proposed method could be used to study climate variability's effect and also to capture climate change effect over longer time-series.

1. Introduction

Climatic conditions influence water quality, which results from the interaction of many environmental factors. Among them, hydrological processes (flow pathways) and water quantity (discharge) are the most studied in hydrology. They dilute, concentrate and indirectly transform elements in the water and control their transport. Another widely studied controlling factor is land use and human activity (Chow et al., 2011; Howden et al., 2010; Poor and McDonnell, 2007). Climatic conditions modify solute loads in-stream mainly because they influence hydrological processes. River-flow regimes, like agriculture and forestry, are sensitive to climatic conditions (Bower et al., 2004; Zhang et al., 2001). Climatic conditions also impact biotransformation, which influences nutrient availability (Harms and Grimm, 2010), and transfer of solutes by other means (e.g., for nitrate, due to seasonality, drought, freeze–thaw and snowmelt; Reynolds and Edwards, 1995). The main climatic drivers are rainfall, temperature, and solar radiation (Delpla et al., 2009), the first of which (e.g., annual effective rainfall) plays a strong role in catchments (Gascuel-Odoux et al., 2010). Climatic conditions affect both element-emitting compartments (e.g., soil, air) and element-receiving ones (e.g., streams, lakes). For instance, in soils, drying and wetting cycles impact N and C cycles (Borken and Matzner, 2009). In rivers, summer droughts deteriorate temperature- and element-related water quality (van Vliet and Zwolsman, 2008).

Various methods are used to study the impact of annual climate on water quality. Research using methods to identify trends or cycles and to link chemical dynamics to climatic conditions benefits from long-term time-series. Statistical modelling techniques such as Spearman rank correlation (Monteith et al., 2000), Mann–Kendall rank correlation, the Sen slope estimator (Khaliq et al., 2009), spectral analysis and variograms (Zhang and Schilling, 2005) focus on trends and cycles in a single time-series. Methods to link chemical dynamics to climatic conditions include linear regressions (Khaliq et al., 2009; Monteith et al., 2000), distributed-lag regressions (Benitez-Gilabert et al., 2010), autoregressive modelling (Burt and Worrall, 2009; Jones and Smart, 2005), comparison of variograms and crossed spectral analysis (Kirchner

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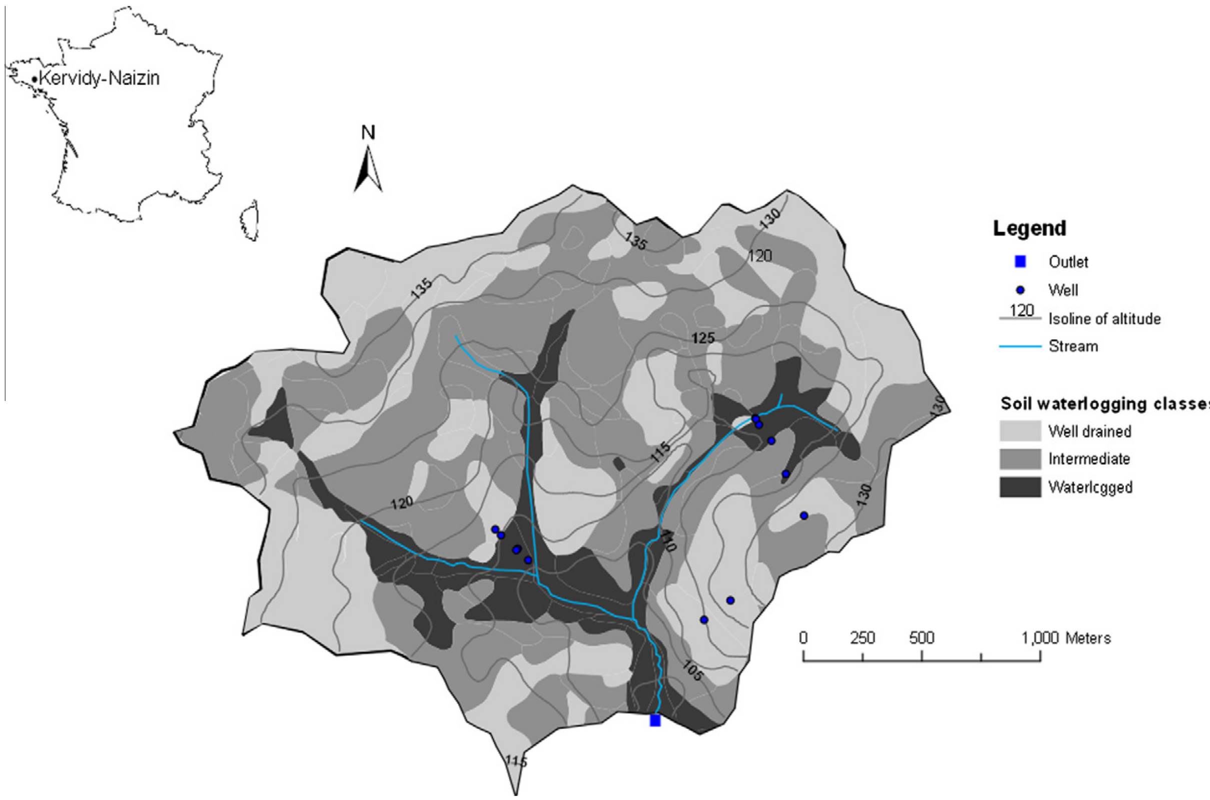

Fig. 1. Study-site map. (adapted from Molenat et al., 2008).

Table 1
Yearly cumulative rainfall, reference evapotranspiration, discharge and hydrological index for the 10 studied years (mm) and their means and standard deviations (SD).

Year	Rainfall	ET_0	Specific discharge	Hydrological index
2000–2001	1323.0	687.5	753.0	2.22
2001–2002	662.5	698.9	227.9	0.68
2002–2003	784.5	836.2	428.6	1.27
2003–2004	861.0	743.7	250.5	0.74
2004–2005	470.5	761.5	113.0	0.33
2005–2006	609.5	725.8	168.4	0.50
2006–2007	916.0	690.8	449.1	1.33
2007–2008	873.5	723.1	314.4	0.92
2008–2009	798.5	619.7	279.6	0.84
2009–2010	875.0	739.1	416.0	1.23
Mean	817.4	722.6	340.1	1.00
SD	226.7	56.3	183.2	0.50

et al., 2000; Zhang and Schilling, 2005) and comparisons of autocorrelation results with standardised climate medians (Jones and Smart, 2005). Mechanistic models are also used to study hypotheses (Ducharne, 2011; Gascuel-Odoux et al., 2010; Thodsen et al., 2008; Tu, 2009). Andermann et al. (2012) plotted monthly discharge against monthly rainfall and observed annual hysteresis. Annual hystereses have also been proposed from nutrient concentration measurements in stream water (Bhangu and Whitfield, 1997). Hysteresis loops are observed when a time lag exists between an event and its consequences, for instance, between a rainfall event and a peak in discharge (Andermann et al., 2012) or between a peak in discharge and one in concentration (Lefrançois et al., 2007; Seeger et al., 2004). Concentration-discharge hystereses have been intensively studied at the storm scale and for suspended sediment concentrations: Williams (1989) proposed a classification for five types of hysteresis: single-valued (linear or curved, also called "univocal"), clockwise, counter-clockwise, single-valued plus a loop, and figure-8-shaped. For single hydrological events, a clockwise loop is formed by the C–Q relation when discharge peaks before concentration. Conversely, a counter-clockwise loop occurs when concentration peaks before discharge. C–Q hysteresis loops have rarely been observed at the annual scale (Bhangu and Whitfield, 1997; MacLeod and Whitfield, 1996), leading to identification of "river" sites and "lake-fed" sites, evidence of loops increasing with downstream distance and discharge magnitude, and the relation of clockwise loops with erosion processes and counter-clockwise loops with conservative elements or groundwater-driven elements (Whitfield and Whitley, 1986); however, this latter relation is reversed in other catchments (Whitfield and Clark, 1992). Some elements are not related to discharge but still show seasonal patterns, most likely due to biological processes. These diagrams can be used to infer environmental controls (Whitfield and Clark, 1992). A unique annual concentration-temperature hysteresis, representing the monthly ammonia fluxes in Chesapeake Bay, USA, and bottom water temperature, was reviewed (Cowan and Boynton, 1996). Temperature is often studied for large water reservoirs such as lakes, bays and rivers of high Strahler order (Ducharne, 2008; van Vliet and Zwolsman, 2008) because it seems to be a controlling factor at these scales. Temperature variations are also considered when the focus is on climate change, as it is a global phenomenon and one factor modelled by the Intergovernmental Panel on Climate Change. Our results indicate that temperature also helps in understanding headwater catchment functioning and that chemical hysteresis can be used to analyse chemical production and dilution throughout the hydrological year.

As mentioned above, seasonal patterns of water quality have been clearly identified in the literature (Aubert et al., 2012; Cowan and Boynton, 1996; Mulholland and Hill, 1997; Ouyang et al., 2006; Reynolds et al., 1997; Webb and Walling, 1985). For instance, in an agricultural catchment, stream nitrate concentrations