

Original Articles

Long and short-term trends of stream hydrochemistry and high frequency surveys as indicators of the influence of climate change, agricultural practices and internal processes (Aurade agricultural catchment, SW France)

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## ABSTRACT

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The hydrochemical time series of stream water from a cultivated catchment were investigated at different time scales and survey frequencies. A 35-year time series of nitrate concentration and discharge, a 15-year time series of major elements and dissolved organic carbon (DOC) concentrations were analysed from a yearly to a daily/hourly basis during discharge recession after storm event periods, to determine the origin of elements, the time trends and the main controlling factors of the trends. A significant decrease over time of nitrate, base cations and other major anions was observed. These trends were controlled by agricultural practice changes (decrease of N-fertiliser input, grass-band set up) and discharge increase, especially in the last years of the period. On the other hand, K and DOC increased over the 15-year period. This increase might result from both 1) organic matter eroded from the soil surface by runoff during flood events and 2) an increase in mineralisation with increasing temperature. Seasonal variations and nycthemeral cycles indicated either calcite precipitation and nitrification processes and/or evapotranspiration, water and/or vegetation uptake during the day with increasing temperature. This paper highlights that the hydrochemical parameters measured at various time scales and frequencies can be used as powerful indicators of catchment internal processes, and of changes in agricultural management and climate change. Particularly, the multivariate high-resolution survey has shown its ability to evidence very tenuous processes not detectable by discrete sampling. The recent observed changes in hydrology argue for the need to continue the hydrochemical survey over decades.

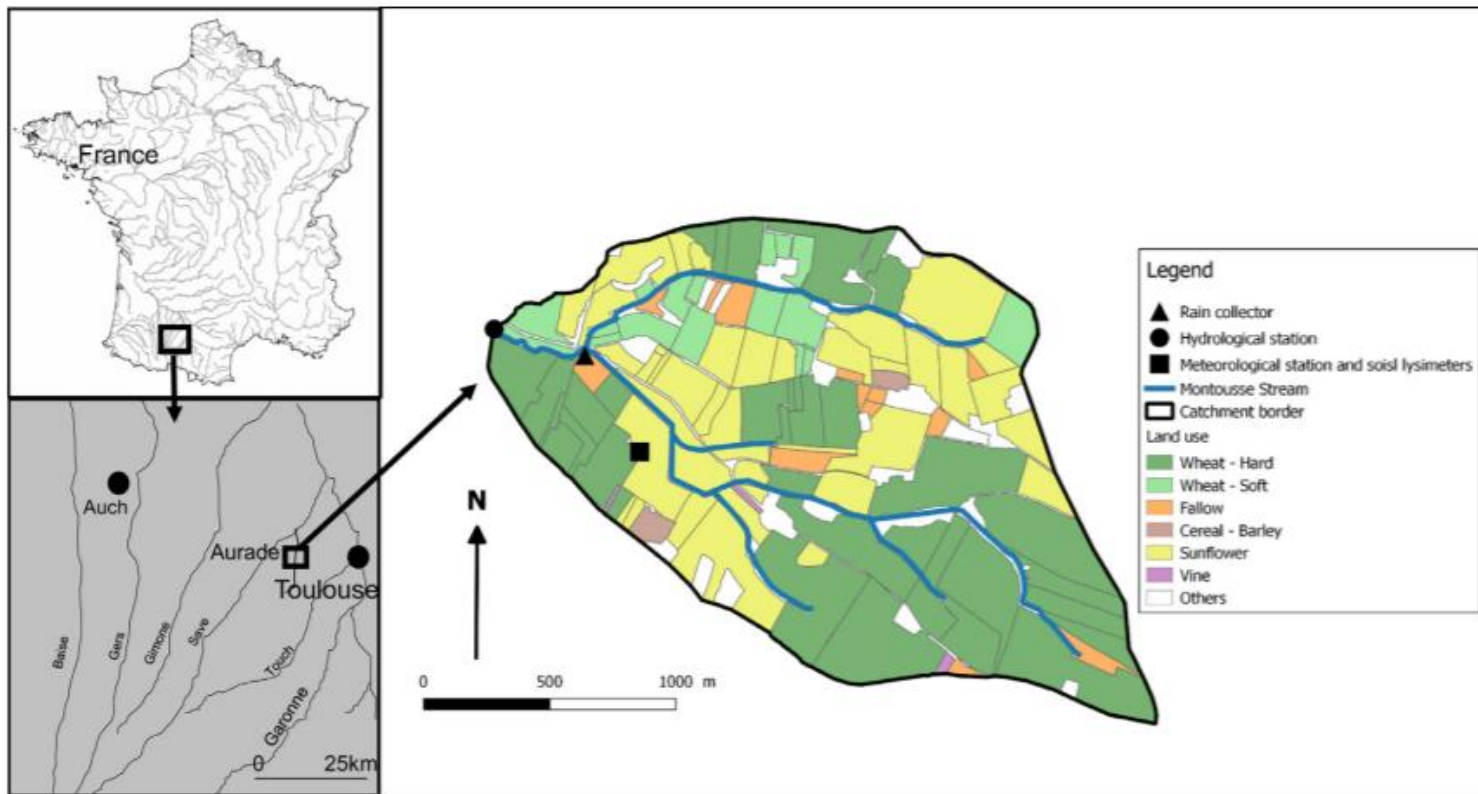


Fig. 1. Location of the Aurade catchment with the different sampling stations and the land use of the mean hydrological year (2008–2009) as an example.

In terms of land use, 90% of the Montoussé catchment is devoted to agriculture with an annual rotation of wheat (58%) and sunflower (38%) and marginally barley, garlic, grass and fallow. Forested (3%) and farmhouse (3%) areas represent the remaining surface (Perrin et al., 2008). In Fig. 1, as an example, the land use is shown for the hydrological year 2008–2009, which is considered as a mean year over the period (see results § 3.3.1). Applied fertilisers (around  $110 \text{ kgN ha}^{-1} \text{ a}^{-1}$ ) are mainly ammonium nitrate, sulphonitrate and potassium sulphate. Sulphonitrate is composed of  $(\text{NH}_4)_2\text{SO}_4$  (sulphate ammonium) and  $\text{NH}_4\text{NO}_3$  (ammonium nitrate). Potassium chloride and urea are also locally applied in the catchment. Fertiliser application generally occurs between mid-January and April for wheat (Paul et al., 2015), whereas it is very scarce on sunflower.

Nitrate measurements in stream waters were started in 1985 by AZF Company in Toulouse (today GPN-TOTAL) to survey nitrate concentrations and losses in relation to N-fertiliser input. This site has undergone experimental research and long-term environmental observations since 2004 by EcoLab (initially in collaboration with GPN-TOTAL). In 1992, 43 farmers created an association (AAA, Association des Agriculteurs du Bassin Versant d'Aurade) to promote water quality in relation to best agricultural practices and landscape management in the Aurade catchment. One of their main initiatives was to set up, in 1992, vegetated buffer strip bands (grass bands) along the stream, which was awarded, in 1995, the French Prize "Pierre Sarazin" (Foundation and French Academy of Agriculture). Nowadays, the association has grown up to a regional association (GAGT, Groupement des Agriculteurs de la Gascogne Toulousaine), which has gathered numerous farms and several sub-catchments. In 2017, they received another "Pierre Sarazin" prize for setting up an efficient experimental relay cropping relative to the site conditions.

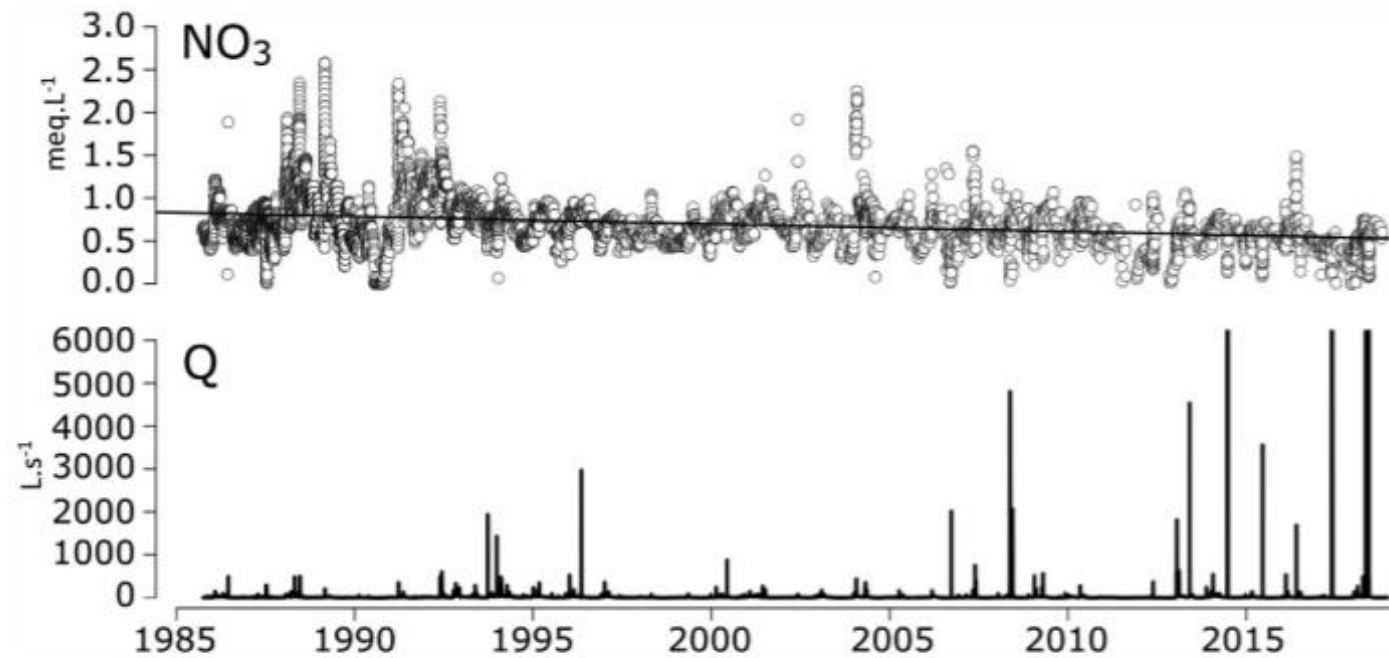


Fig. 4. Variations of instantaneous nitrate concentrations ( $\text{meq L}^{-1}$ ) and instantaneous stream discharge ( $Q$ ;  $\text{L s}^{-1}$ ) from 1985 to 2018 at the outlet of the Montousse catchment.

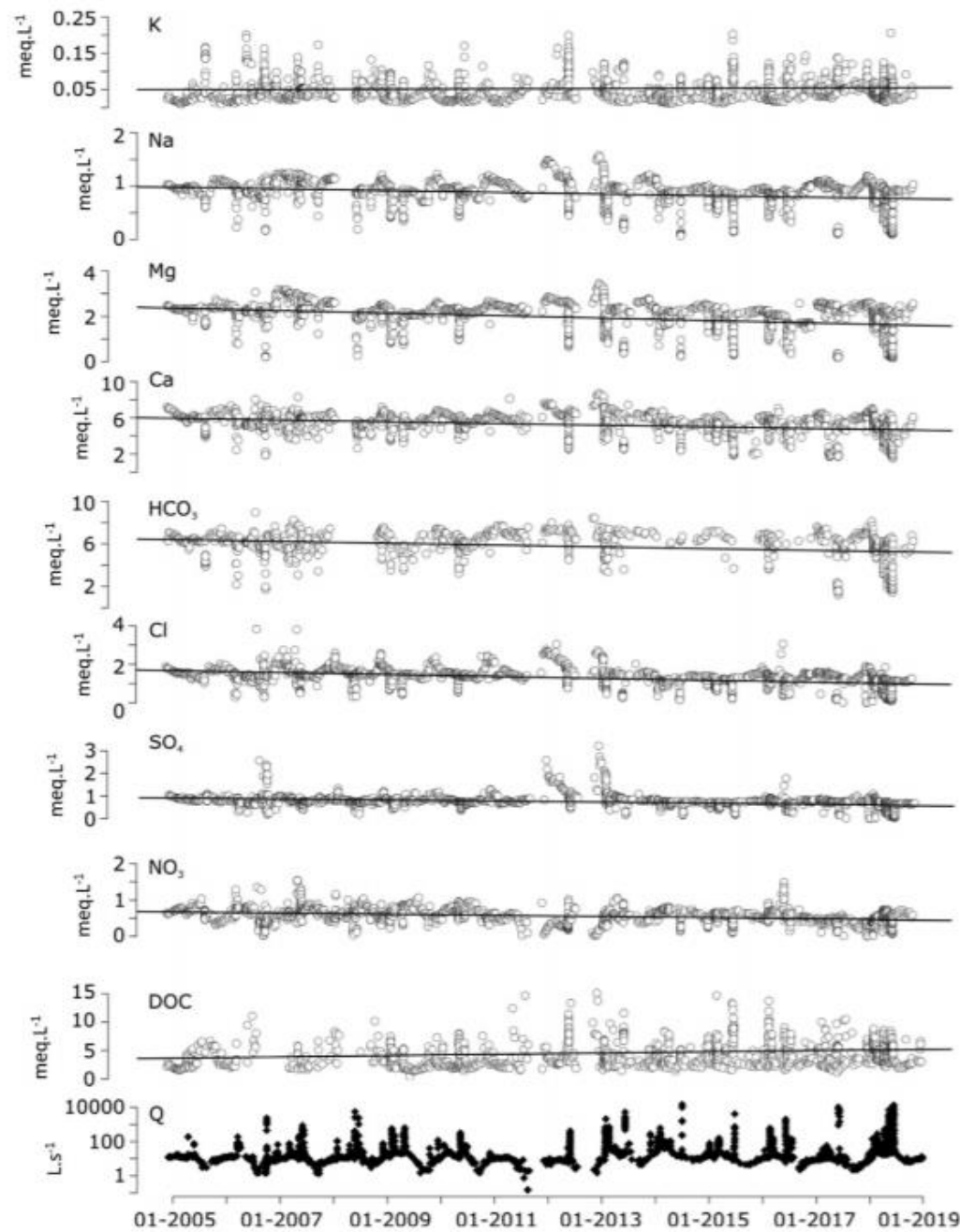


Fig. 5. Middle-term variations of instantaneous major ion concentrations (K, Na, Mg, Ca, HCO<sub>3</sub>, Cl, SO<sub>4</sub>, NO<sub>3</sub>), DOC and instantaneous corresponding discharge (Q in log10) for Montousse stream water over the period 2005–2019. Straight lines were linear regression trends over the period (for details of linear regression and Mann-Kendall refer to SM Table 1 and SM Table 4).

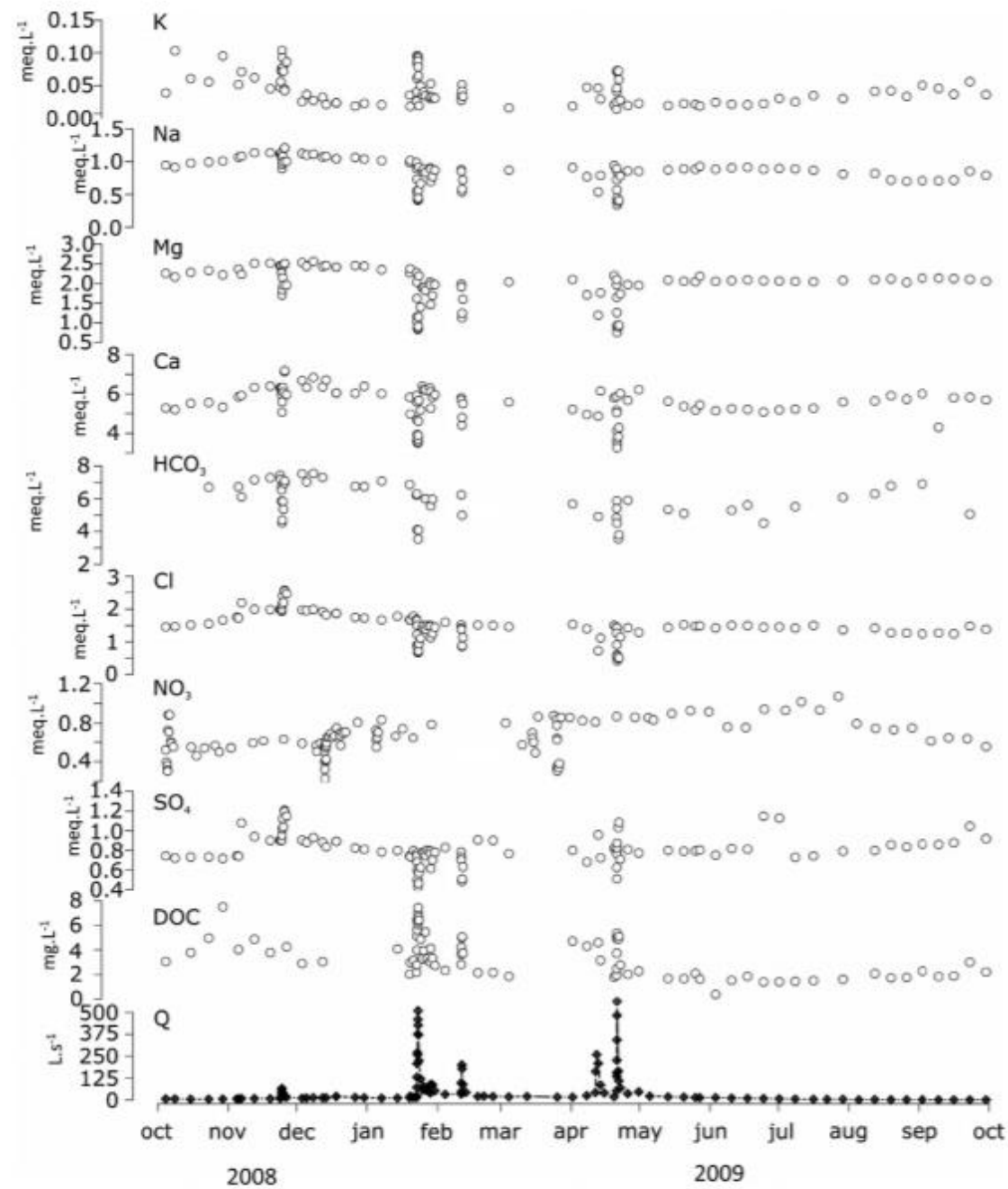


Fig. 6. Variations of instantaneous concentrations of major ions (K, Na, Mg, Ca, HCO<sub>3</sub>, Cl, SO<sub>4</sub>, NO<sub>3</sub>), DOC and discharge (Q) for stream water at the outlet of the Aurade catchment for the hydrological year 2008–2009. Due to technical problems, no data were registered during March 2009 for all elements, except discharge, and from mid-December 2008 to mid-January 2009 for DOC. Note also that for the November 2008 event, DOC was not registered extensively.

The target of this study was to use the power of the various time scales and frequency of observations of hydrochemical parameters in a cultivated catchment as indicators of the key factors influencing the concentration variations and the chemical transfer in the stream.

On a long-term survey (35 years), no change in mean annual discharge was detectable, but instantaneous discharge increased mainly due to more frequent and intense flood events in the last five years, in relation to an obvious temperature increase at the regional scale.

During this period, the nitrate concentration decreased, but more intensively during the last 15-year survey, like Ca, Mg, Na,  $\text{HCO}_3^-$ , Cl and  $\text{SO}_4$  concentrations. On the other hand, significant increasing trends of K and DOC concentrations were observed. The main explaining factors of these trends were: improved agricultural practices (reduced inputs of N fertilisers, more adapted spreading period, set up of strip bands, relay

cropping, no tillage, etc.), changes in hydrology (increasing runoff and surface soil erosion during storm events) and, increase in temperature (major organic matter mineralisation). Decadal (dry and humid period), yearly (dry and humid year) and seasonal (high concentration by flushing dry deposition after summer) variations were also evidenced with these time-scale surveys.

The changes observed within the last five years of the investigated period might be an initial step indicator of a new era of hydrochemical patterns in the CZ. In the context of climate change, the rise of temperature with the increase of dry periods and the higher frequency of heavy rainfall and major flood events detectable in long-term time series (35 years), will probably exhibit the trends of element exports by rivers, as well as soil erosion processes in similar agricultural catchments. Longer observations series are thus recommended. Moreover, high-frequency monitoring could help detect major biogeochemical changes difficult to capture in such highly-responsive catchments submitted to strong environmental changes.