Use of High Frequency measurements to better determine the concentration-flow relationship (C-Q) of the Avenelles watershed (ORACLE Obs.)

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The Water Framework Directive [1] has an ambition to reclaim the good ecological status of water bodies. The evaluation of this "good ecological status" is based on a set of biological, physicochemical and morphological criteria. Today, the assessment of the chemical quality of river water, mission of the Water Agency in France, currently focuses on two types of indicators: annual concentrations (arithmetic mean, median, higher quantiles, weighted averages flows) that are related to a quality grid (SEQ-Water) and annual flows generally brought to the surface of the producing watershed. This evaluation of concentrations is carried out with monthly measurements, or in the best of cases, twice a month. This type of data presents a long time series of measurements, and can be used for watershed input-output mass balances, or to detect and measure long-term trends in water quality [2],[3]. However, these one-off measurements do not make it possible to know thoroughly the concentration-flow relationships, or to apprehend both the dilution and leaching processes that occur on a sub-daily time scale [4], which can significantly bias the assessment of the water chemical quality [5].

As a result, over the last three decades, studies of continuous chemical concentration measurements have been conducted to address the lack of information to clarify the links between hydrological processes in watersheds and stream chemistry. Chemical measurements need to be adapted to the hydrological response of small watersheds, sub-hourly and not monthly[6]. The first high frequency measurements were first performed over short periods of a few days or during a rainy event[7], which largely underestimates the legacy of the previous hydrological conditions[8]. Today, the development of the in situ chemical measurement such as nitrate probes or the River-Lab for a set of parameters [9] allows us to have long series of high-frequency chemical measurements of river water, then we propose for our study to exploit these new high-frequency data. The ultimate goal of this work is to develop and / or adapt a comprehensive operational and affordable hydro-chemical conceptual model, requiring the minimum descriptive data, applicable to a regional and national level, directions for the charge of water monitoring.

High-frequency chemical measurements are an essential asset for testing hydrological models. Hydrological data alone are rarely sufficient to test the process assumptions embedded in the typical hydrologic models. The use of joint time series, hydrological and geochemical, are necessary to appropriately identify their parameters[10]. However, this parameterization was not possible with the usual (weekly) monitoring programs that could not capture the short-term chemical dynamics that best reflect the hydrological processes.

The study of water quality is generally done by analyzing the relationships between concentrations and flows[2], since these two components have a strong link, that has been studied and corroborated for a long time[3]. Our work benefits from the fact that today these two components are measured at the same high frequency.

For these study we use a mixing equation[11], based on the separation of the hydrographs to find the different flow inputs (runoff, subsurface and groundwater). This equation is the following:

\[
C_j(t) = C_{1j} + (C_{2j} - C_{1j}) \frac{Q_j(t)}{Q(t)}
\]

Contrary to previous studies, which have used medium and low frequency concentration measurements (daily, weekly, monthly), we will apply the sub-hourly high-frequency measurements (30 min) from the River Lab station [9], set up in the outlet of the Avenelles River (ORACLE observatory, 70 km Est of Paris). The series of data carried out from June 2015 to August 2016 (i.e. 22,000 measurements over 14 months), being more than one hydrological year in which we find the different rainy events from the low to the flood season. It should be noted that these series also contain recordings made during the exceptional flood of May-June 2016. For our study, we used of all major dissolved species (Mg\(^{2+}\), K\(^+\), Ca\(^{2+}\), Na\(^+\), Sr\(^{2+}\), F\(^-\), SO\(_4\)^{2-}\), NO\(_3^-\), Cl\(^-\), PO\(_4\)^{3-}\)) measured by the River Lab. In the Table 1 we show the summary of the measurements of the hydrogeochemical elements studied: the average values found for each concentration during the study time, as well as the minimum and maximum concentrations.
For the hydrograph separation we used the method called Recursive Digital Filter. This method is based on the approaches of digital filters used for signal processing [12]. The formula for this filter is as follows:

\[ f_k = \alpha f_{k-1} + \frac{(1 + \alpha)}{2} (y_k - y_{k-1}) \]  \hspace{1cm} (2)

\( f_k \) : fast response filtered at the kth instant of the sample.
\( y_k \) : total flow at the kth instant of the sample.
\( \alpha \) : filter parameter (between 0.5 to 0.99).

Finally the base flow \( Q_b (t) \) is defined as \( y_k - f_k \), and consequently \( Q_e (t) = Q(t) - Q_b(t) \)

Having the values of the concentrations and the \( Q_e (t) \) (calculated from the base flow), the only thing that we need is to find the values of \( C_1 \) and \( C_2 \). For this we will solve the equation using a simple linear regression. Thanks to the high frequency we can obtain daily values of \( C_1 \) and \( C_2 \).

From these results it is envisaged: 1) to find a single parameter of \( C_1 \) and \( C_2 \) that efficiently encompasses interactions between flows and concentrations, 2) to apply this method to medium and low-frequency measurements.

### References


