

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

José-Manuel Tunqui Neira, Gaëlle Tallec, Vazken Andréassian, Irstea HBAN Antony,  
Jean-Marie Mouchel, UPMC UMR Metis

**Key words:** High frequency, concentration-flow relationship, hydrograph separation

The Water Framework Directive [1] has an ambition to reclaim the good ecological status of water bodies. The evaluation of this "good ecological state" 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:

$$C(t) = C_{1j} + (C_{2j} - C_{1j}) \frac{Q_e(t)}{Q(t)} \quad (1)$$

$C(t)$  : Total concentration for the time step  $t$  (mg/L)

$Q_e(t)$  : Quick response runoff for the time step  $t$  (m<sup>3</sup>/s)

$Q(t)$  : Total flow for the time step  $t$  (m<sup>3</sup>/s)

$C_{1j}$  : Representative daily parameter of the concentration from the baseflow (mg/L)

$C_{2j}$  : Representative daily parameter of the concentration from the quick response runoff (mg/L)

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<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Sr<sup>2+</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>) 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.

item	Unit	Avenelles Catchment		
		Mean	Min	Max
magnesium	mg/L	8.58	2.98	11.46
potassium	mg/L	3.53	1.57	8.65
calcium	mg/L	118.55	56.51	168.04
sodium	mg/L	13.10	2.79	26.53
strontium	mg/L	0.35	0.17	0.57
fluoride	mg/L	0.15	0.03	2.88
sulfate	S mg/L	19.06	4.06	25.69
nitrates	N mg/L	11.85	3.08	18.36
chloride	mg/L	31.48	3.63	51.05
phosphate	P mg/L	0.13	0.00	0.22
rainfall	mm/30min	0.05	0.00	10.10
flow	m <sup>3</sup> /s	0.33	0.05	12.20

Table1: Summary of the average, min and max values of the chemical elements studied from the high frequency measurements at the Avenelles station

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:

$$f_k = \alpha f_{k-1} + \frac{(1 + \alpha)}{2} (y_k - y_{k-1}) \quad (2)$$

$f_k$  : 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

- [1] E.W.F. Directive, Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy" downloaded April 2010 from EC, Environment web site, (2000).
- [2] M. Meybeck, F. Moatar, Daily variability of river concentrations and fluxes: indicators based on the segmentation of the rating curve, *Hydrological Processes*, 26 (2012) 1188-1207.
- [3] F. Moatar, B. Abbott, C. Minaudo, F. Curie, G. Pinay, Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions, *Water Resources Research*, 53 (2017) 1270-1287.
- [4] C. Neal, B. Reynolds, P. Rowland, D. Norris, J.W. Kirchner, M. Neal, D. Sleep, A. Lawlor, C. Woods, S. Thacker, H. Guyatt, C. Vincent, K. Hockenhull, H. Wickham, S. Harman, L. Armstrong, High-frequency water quality time series in precipitation and streamflow: From fragmentary signals to scientific challenge, *Science of the Total Environment*, 434 (2012) 3-12.
- [5] D.C. Whyte, J.W. Kirchner, Assessing water quality impacts and cleanup effectiveness in streams dominated by episodic mercury discharges, *Science of the Total Environment*, 260 (2000) 1-9.
- [6] J.W. Kirchner, X. Feng, C. Neal, A.J. Robson, The fine structure of water-quality dynamics: the (high-frequency) wave of the future, *Hydrological Processes*, 18 (2004) 1353-1359.
- [7] C.M. Brick, J.N. Moore, Diel variation of trace metals in the upper Clark Fork River, Montana, *Environmental Science & Technology*, 30 (1996) 1953-1960.
- [8] J.W. Kirchner, Getting the right answers for the right reasons: Linking measurements, analyses, and models to advance the science of hydrology, *Water Resources Research*, 42 (2006).
- [9] P. Floury, J. Gaillardet, G. Tallec, P. Ansard, A. Blanchoin, E. Gayer, J. Bouchez, C. Gorge, New progresses in the high frequency acquisition of stream chemical data in hydrological observatories: the Orgeval River lab, in: EGU General Assembly Conference Abstracts, 2017, pp. 8883.
- [10] M. Mroczkowski, P.G. Raper, G. Kuczera, The quest for more powerful validation of conceptual catchment models, *Water Resources Research*, 33 (1997) 2325-2335.
- [11] J.L. Probst, NITROGEN AND PHOSPHORUS EXPORTATION IN THE GARONNE BASIN (FRANCE), *Journal of Hydrology*, 76 (1985) 281-305.
- [12] V. Lyne, M. Hollick, Stochastic time-variable rainfall-runoff modelling, in: Institute of Engineers Australia National Conference, 1979, pp. 89-93.