



## Optimisation of flux calculation in rivers from discrete water quality surveys, a step towards an expert system

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Good estimates of fluxes of suspended particulate matter (SPM), total dissolved solids (TDS) and nutrients and contaminants are required for both Earth System science and river basin management. However, in most cases discrete sampling (weekly to monthly) is the rule. Few flux calculation methods are commonly used, yet their performances, i.e. uncertainties for given frequencies, at given stations and for each water quality variables, remain unknown. Based on a rare set of 1085 station-year of daily flux record for SPM, TDS and nutrients (dissolved and total), the performance of 9 calculations methods is explored.

Discrete surveys at various frequencies (3 days to 30 days) are simulated by Monte-Carlo sorting (100 runs) on which the 9 fluxes are calculated (annual and interannual). At this stage, the sub-daily variations of fluxes for the medium and large basins are not considered. The dataset for SPM corresponds to 55 stations (600 to 600 000 km<sup>2</sup> basin area), 34 stations (700 to 1000000 km<sup>2</sup>) for TDS and for nutrients we consider 9 stations for NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup> and Ptot (600 to 30 000 km<sup>2</sup>). About 80% of the dataset originates from US records (USGS and Lake Erie tributaries survey) and 20% from French stations, this covering a wide range of hydrological and geochemical conditions in the temperate zone.

Each sorted flux is compared to known fluxes established on daily records: percentiles of their relative errors (e10, e50 and e90) are used to determine the biases (e50) and the imprecisions (e90-e10) (Walling and Webb, 1981) which are then compared for each of the 6 water quality variables, for each flux methods and for various simulated survey frequencies.

The calculation methods include 5 rating-curve approaches (linear "M1", "M2", Phillipps et al, 1999) with and without Ferguson correction (Ferguson, 1987), polynomial, truncated at discharges exceeding median annual or long-term water discharge), 2 methods based on hydrograph separation (Phillips et al, 1999) including a quadratic runoff module (Bustillo, 2005), 1 linear interpolation method and 2 discharge-weighted concentration methods ("M18", "M19", Philipps et al, 1999).

As expected, based on 55 stations and 430 years, SPM fluxes are the most uncertain ones with maximum biases determined on annual fluxes (monthly sampling simulations), ranging at stations from -75% to +55% by the classical rating-curves approach ("M1", "M2") dropping to -60% to +5% for the M18 method. At this frequency, biases are much less for Ptot and PO<sub>4</sub><sup>-3</sup> (-30% to +10%), nitrate (-5% to +10%) and are negligible for TDS. For higher frequencies, the biases are reduced: for instance for weekly surveys they drop to -25% for SPM and to -20% to 5% for Ptot for the M18 method.

The river basin size is influencing the performance of calculations methods: SPM flux errors are much higher for smaller basins (10<sup>3</sup> to 10<sup>4</sup> km<sup>2</sup>) than for larger ones (> 10<sup>4</sup> km<sup>2</sup>), probably in relation with the flow duration in 2% of time which is a key control factor of flux duration in 2% of time (Moatar et al, 2006). This indicator based on daily flow (Q) records is generally available at water quality stations. Other indicators based on discrete water quality surveys are being tested to explain the performance of flux methods for each variable: concentrations (C) variability, C vs Q relationship, concentration seasonality. For each variable and each station the optimal flux calculation method will be derived from the future expert system.

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