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Analysing in-stream observed and simulated nitrate concentrations using temporal variograms

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The scope of this study is to use variograms to reduce distributed physically-based model (DPBM) uncertainties when assessing nitrate concentrations for the year 2003 along a 250 km stretch of the Seine River from upstream of the Greater Paris to the estuary. Many combined sewer overflows and two main waste water treatment plants (1.5 M and 5 M connected inhabitants) are located along the stretch as well as ten nitrate sampling sites for validation data. Nitrate concentrations are measured weekly by the Sewage Public Company of the Greater Paris (SIAAP). Initial nitrate boundary conditions (BC) are daily mean concentrations based on hourly automatic sampling and provided by Veolia Water.

Systematic deviation between observed and simulated concentrations could be reduced thanks to more consistent nitrate BC obtained by temporal cokriging of weekly SIAAP measurements by daily Veolia Water measurements.

The main issue with DPBM is that, on the one hand, at the hydrological network scale, the number of measurements is not sufficient to estimate all the variables of the system of equations and to identify all the calibration parameters. On the other hand, the system of equations is physically-based, describing the behaviour of variables the best as it is understood. A new methodology for analysing in-stream water quality model's efficiency is proposed based on observations : simple and cross-variograms are used to compare the variability of observations to the one of the simulated values.

The analysis of temporal variograms (simple variograms of observed and simulated concentrations, and their cross-variogram) and their fitting reveal a clear mismatch between simulated values and observed ones that was not detected by classical objective functions (Average value, RMSE, ...). Variograms appear to be composed of three components that allow for analysing model response at three time scales (sub-weekly, monthly and annual). Moreover, the method allows for analysing mismatches between simulated and observed values as i) wrong quantification of inputs to the river (especially in terms of outflows and tributary contributions to the nitrate fluxes in the Seine River) and ii) wrong description of physical processes within the river. Finally, simple and cross variograms appear to be a sensitive analysing tool which provides useful information that can be used to reduce modelling uncertainties.