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Can we properly assess water quality status in streams with low-frequency data?

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The European Water Framework Directive uses the 90th percentile of concentration (C90) as a key metric to assess the water quality status in streams. The fact that most pollutant concentrations vary widely with changes in discharge on seasonal and event-scales throws doubt on the reliability of C90 estimates derived from low-frequency monitoring. To address this problem, we tested the effect of sampling frequency on C90 with a multi-decadal daily water quality dataset from 11 tributaries of Lake Erie in the United States. The dataset included common water-quality parameters including suspended solids, total and reactive phosphorus, inorganic nitrogen, silica, chloride, sulfate, and conductivity. We estimated C90 with subsets of these daily time series resampled at various frequencies from 1 sample every two days to a monthly sampling. Additionally, we generated a semi-synthetic time series based on concentration-discharge (C-Q) relationships and various statistical descriptors. These simulated time series allowed us to investigate the theoretical link between the C-Q slope and the error in C90 estimations for different sampling frequencies.
The largest errors in estimating C90 were in highly chemodynamic parameters such as suspended solids and phosphorus. For these parameters, even relatively high-frequency sampling (i.e. 1 sample every 2 days) substantially underestimated C90 by 20 to 40%. Surprisingly and for all parameters, errors in C90 estimates did not increase as sampling frequency decreased. However, the variability in C90 estimates increased with steeper C-Q slopes and lower sampling frequencies. This type of sensitivity analysis could be used to calculate confidence intervals for C90 estimates and readjust water quality standards accordingly.