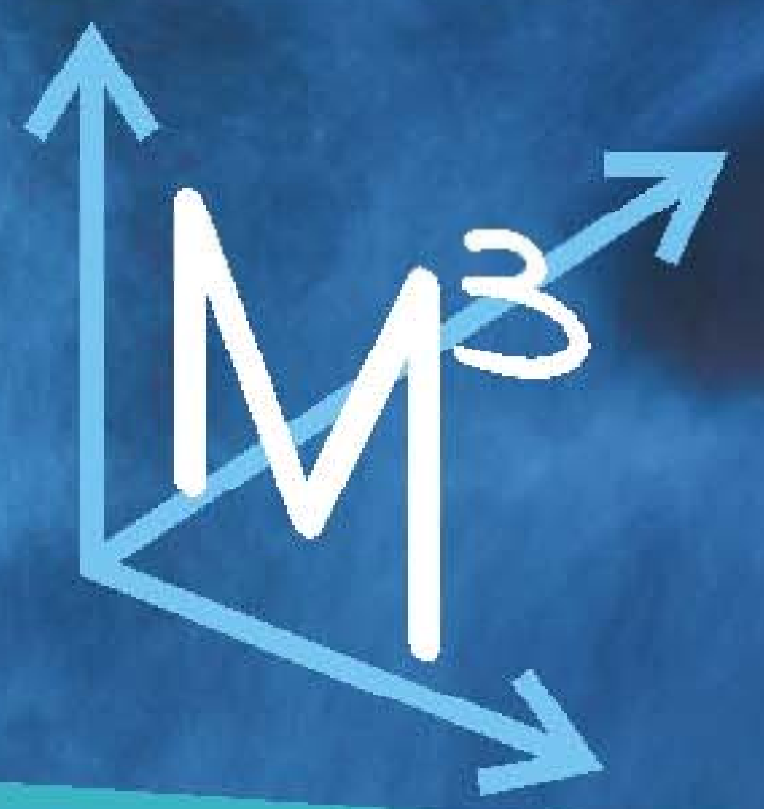


Data evaluation of grab sampling monitoring schemes

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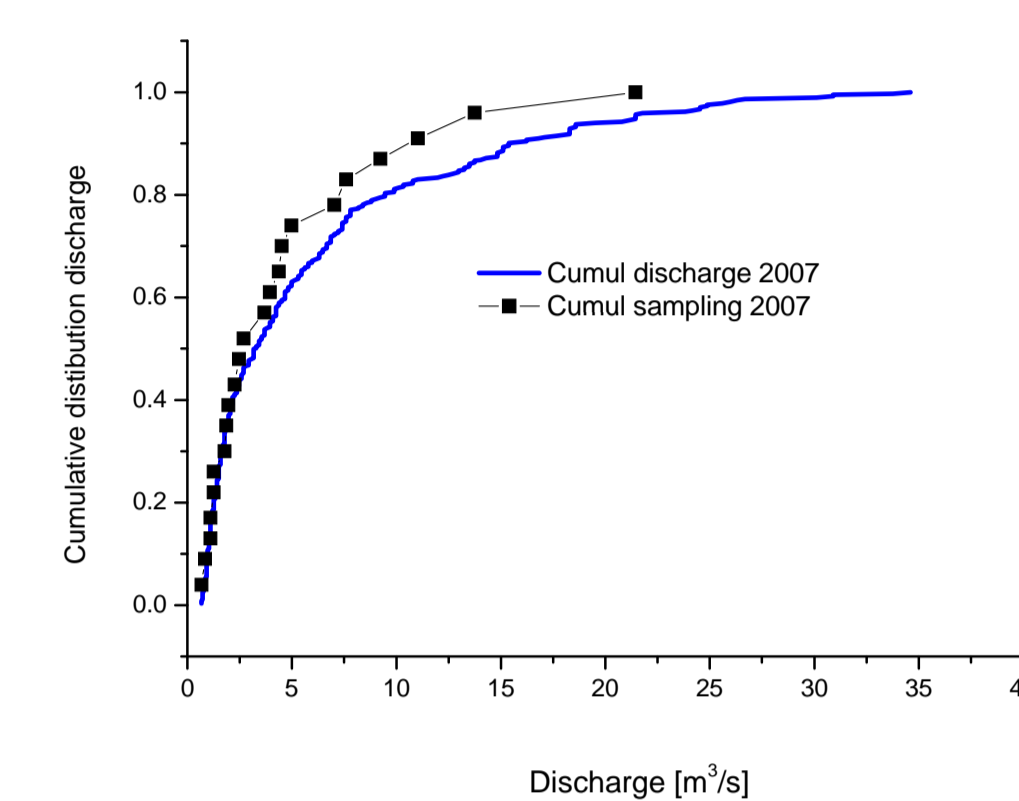


Abstract

Routine grab sampling schemes remain the backbone of monitoring efforts in the WFD implementation. Little effort has been put into the analysis of the representativeness of the data in terms of organism exposure and the appropriateness of the datasets to calculate accurate loads. The M³ project team used cumulative distributions (CD) of yearly discharge and discharge at sampling time to assess the hydrological representativeness of the sampling scheme. Bimonthly sampling schemes proved to match the discharge conditions best. Rating curves were used to analyze the pollutant behaviour at different discharges and confidence intervals were calculated for the regressions. The combination of CD and rating curves allowed for the calculation of discharge weighted annual mean concentrations and associated confidence intervals. This approach enables direct comparison of loads between years. Confidence intervals are strongly pollutant dependent. Dissolved pollutants like nitrate showed best precision with bimonthly sampling schemes. Particulate bound pollutants are much more variable and need to be addressed with stratified sampling schemes.

Hydrological representativeness of sampling

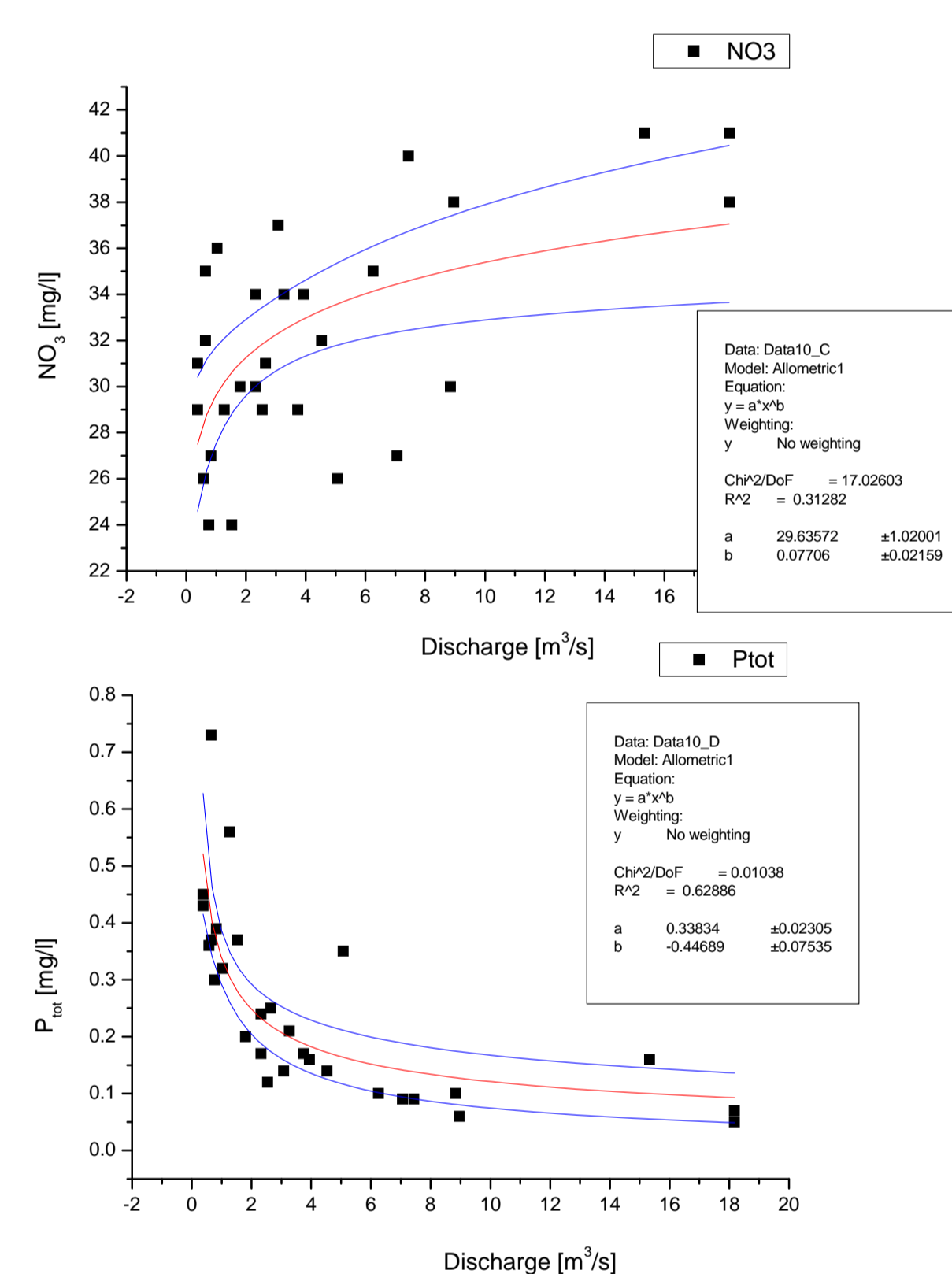
Regular grab sampling of graph below). In general weekly, bimonthly or monthly different discharge levels are frequency relies on randomly reasonably well represented capturing most of the with slight shortcomings for hydrologically relevant the upper 30% of the situations. If an average of distribution. The question exposure to pollutant should remaining is whether be calculated (to check for EQS scattering of pollutant compliance) the hydrological concentrations varies with conditions should be discharge.



Cumulative distributions for actual discharge and discharge at sampling date for a year

Rating curves as analytical tools

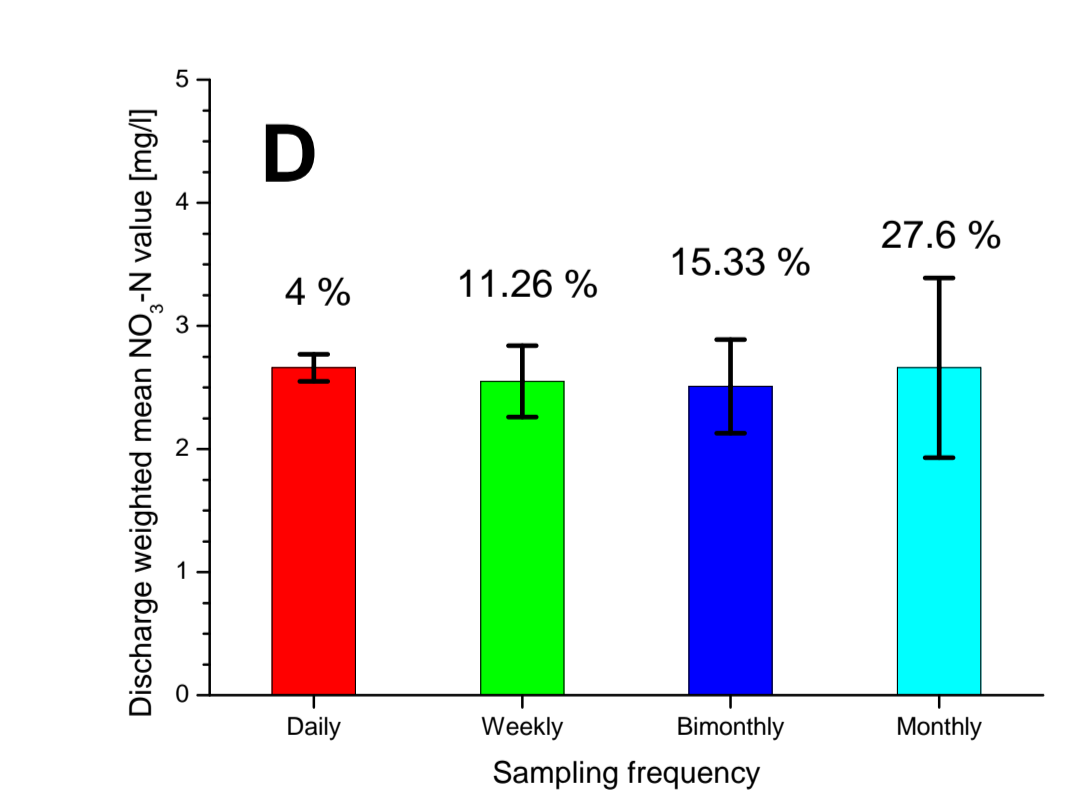
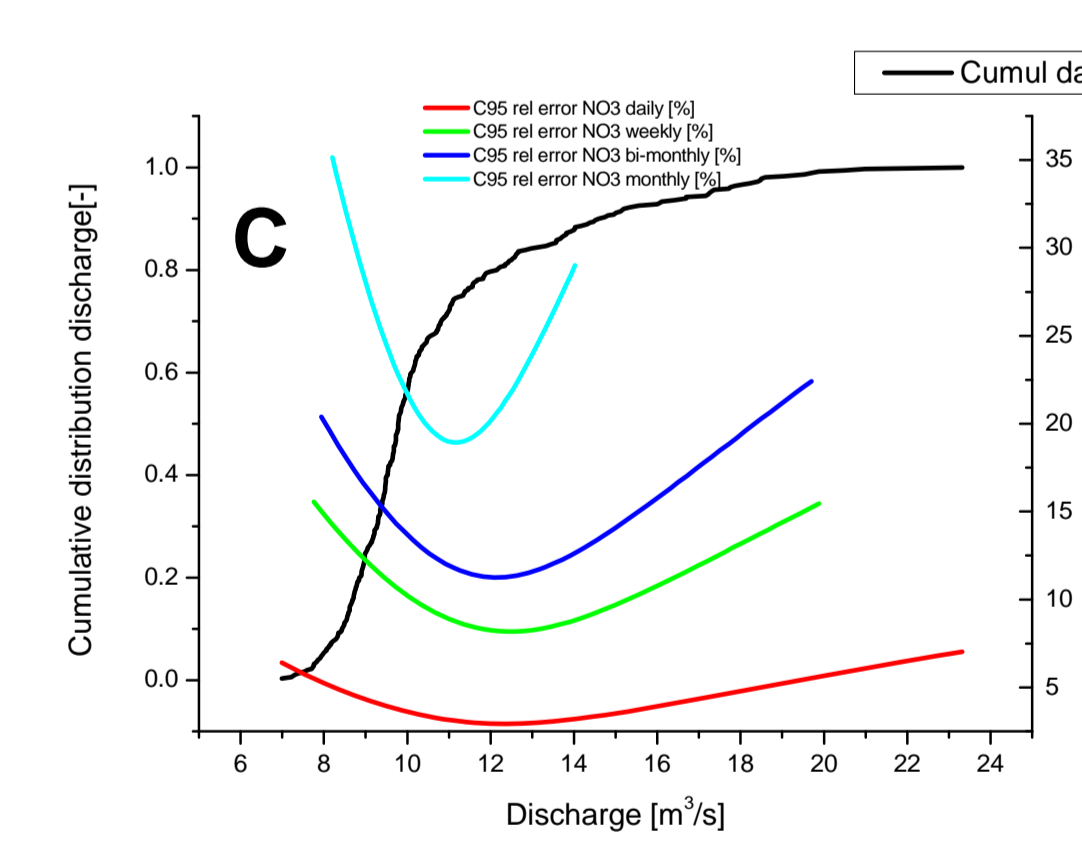
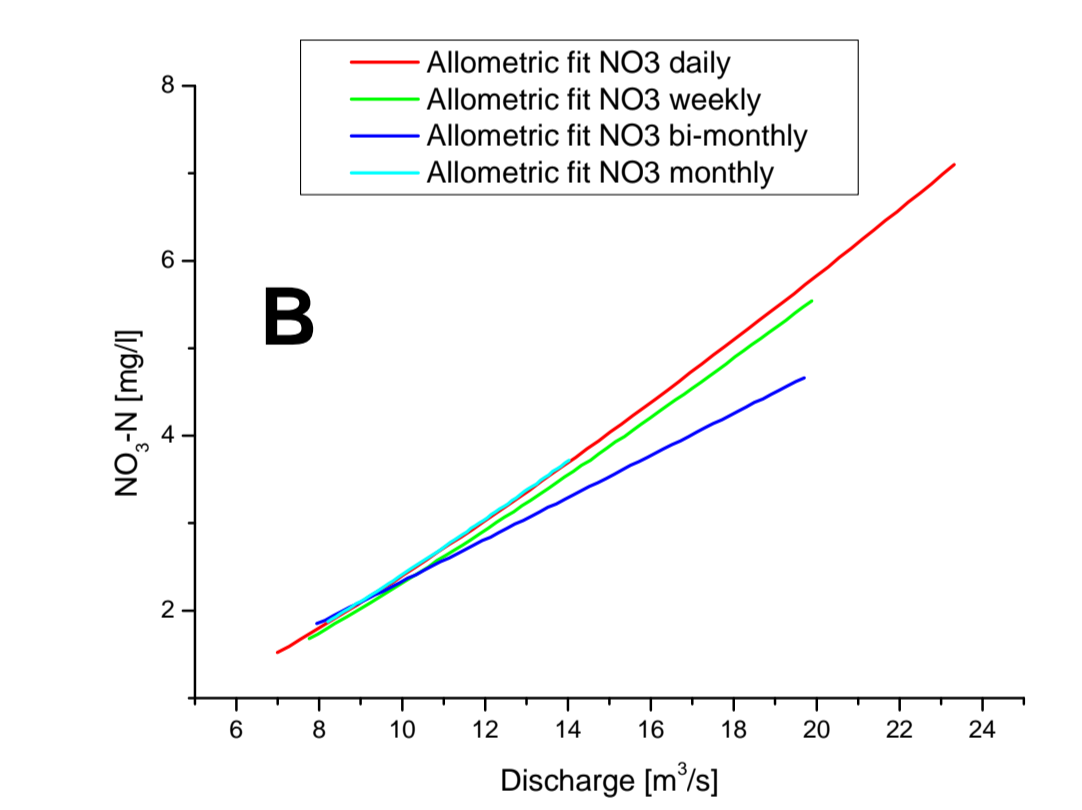
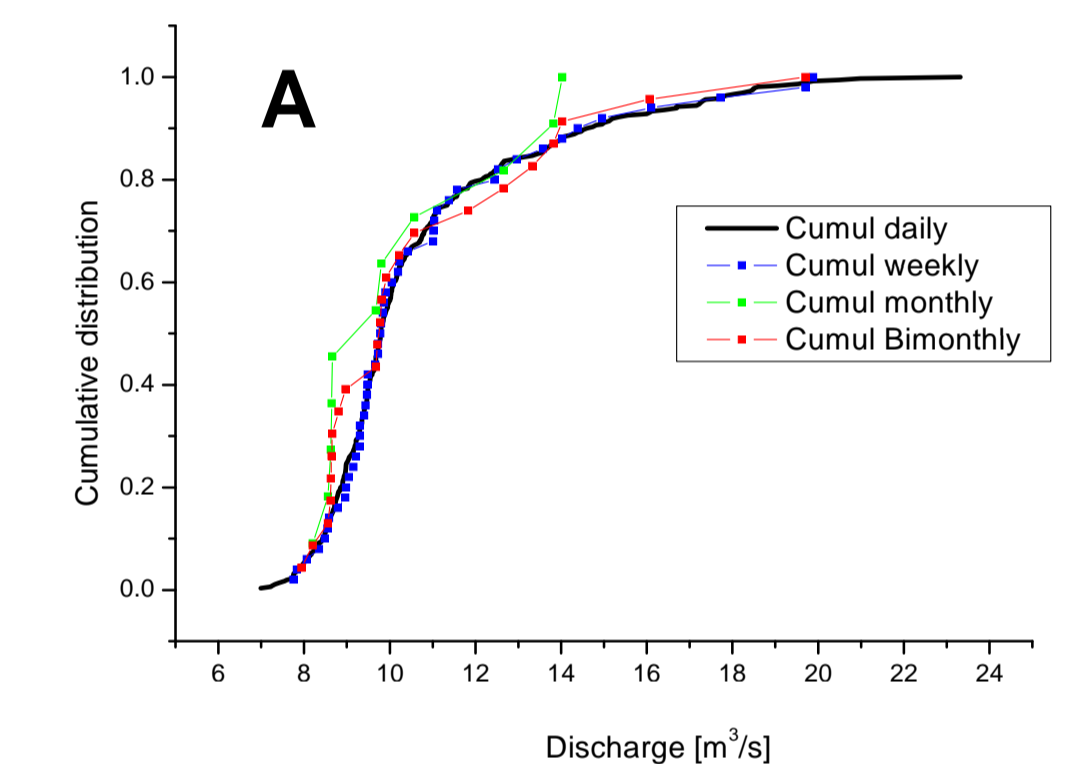
Rating curves are used as a method to extrapolate concentrations of a pollutant for a given discharge in a year following the set up of a regression of discharge vs concentration (Q-C-relationship). These regressions are also very powerful analysis tools to identify the source of a pollutant, the catchments properties and, last but not least, the variability of pollutant concentrations along the discharge axis. Confidence intervals can serve as a metric for parameter variability.



Rating curves for Nitrate (upper graph) and Ptot (lower graph) with C95 confidence intervals

Sampling frequency and confidence in discharge weighted annual mean

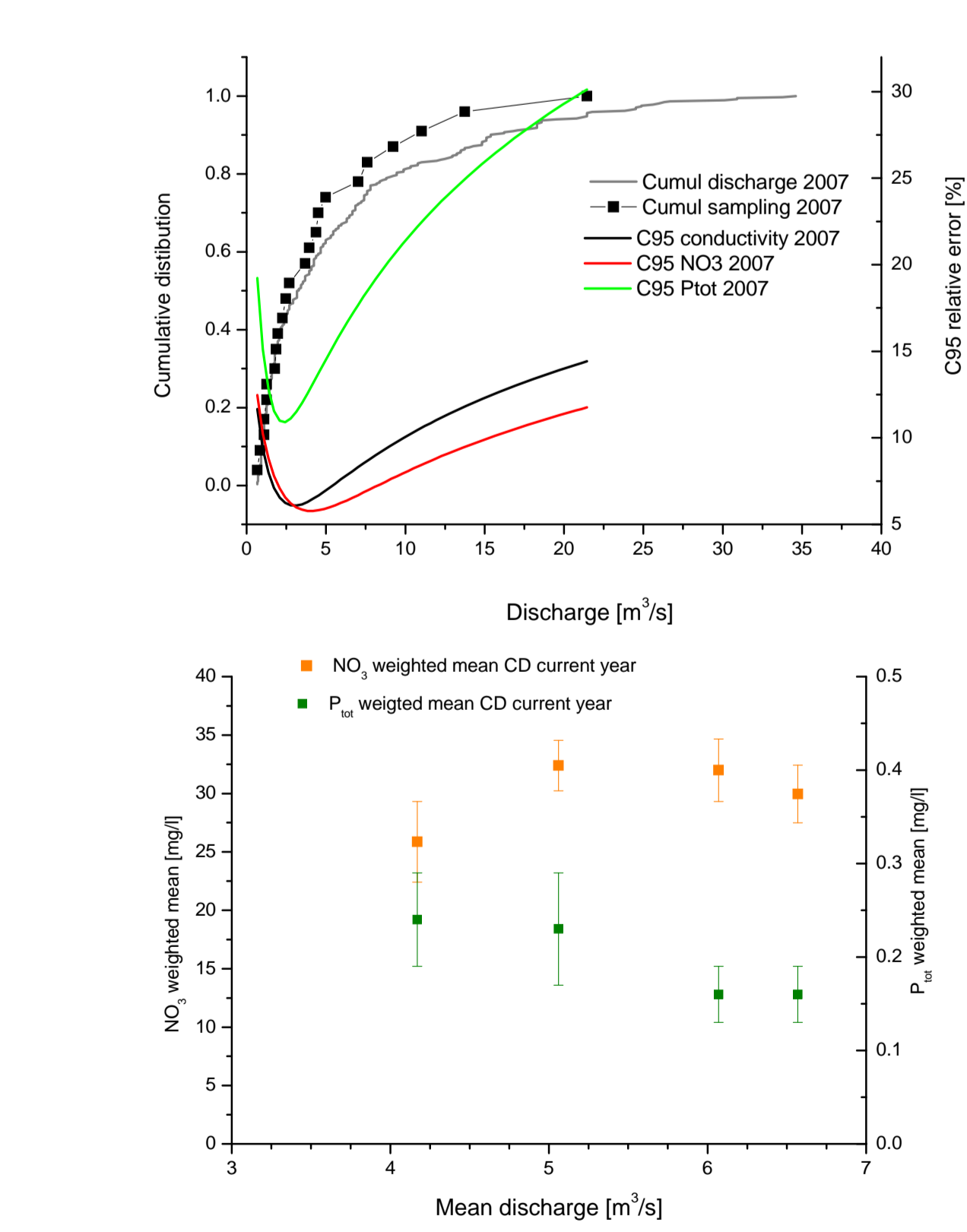
The optimal sampling frequency can be explored by artificially decimating highly resolved data sets with the most populated dataset serving as reference. The exercise was done for a nitrate dataset from a continuous measurement station of the Ertverband. The comparison featured daily, weekly, bimonthly and monthly data. The latter are the recommended minimum for EQS compliance assessment. Cumulative discharge distributions show that weekly sampling is representative of discharge conditions while less frequent paces are undersampling low discharge conditions. Regression curves are quite similar though and confidence intervals improve mainly because of higher n (prediction intervals do not improve with higher n). In the end, the discharge weighted annual means yield very similar results but with different confidence intervals. While nitrate's behavior can surely not be extrapolated to other pollutants, the results raise the question whether concepts like significant difference between years are applicable with these monitoring schemes.



Cumulative distributions for discharge (A), regression curves (B), associated C95 error curves (C) and discharge weighted means (D) for daily, weekly, bimonthly and monthly samplings.

Confidence intervals of extrapolations and discharge weighted means

Confidence intervals can be displayed relative to the mean with ascending discharge. If plotted for different pollutants these error curves allow for comparing the uncertainty of extrapolation from a sampling data set. Relative uncertainties for pollutants with particulate phase affinity are higher. A discharge weighted annual mean with its 95% confidence interval can be computed from the rating curve and its C95 interval. Uncertainties are larger than differences between averages.



Error curves for conductivity, (reference9, nitrate and Ptot (upper graph). Evolution of means and their confidence intervals over 4 years. (lower graph).

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