Hydrol. Earth Syst. Sci. Discuss.,
https://doi.org/10.5194/hess-2017-684-RC2, 2018

Hydrology and Earth System Sciences
Discussions

Interactive comment on "Comparison of high frequency, in-situ water quality analysers and sensors with conventional water sample collection and laboratory analyses: phosphorus and nitrogen species" *by* Steven J. Granger et al.

Anonymous Referee #2

Received and published: 28 February 2018

This manuscript compares the results of high-frequency water quality monitoring with in-situ sensors or analyzers versus laboratory analyses. Parameters of interest are TP, TRP, NH4 and NOx. Only one runoff event is studied, in three different sub catchments of the North Wyke Farm Plateform (UK).

Although the issue of measurement quality deserves an article in HESS, there are several flaws in the approach, that would need to be addressed before the manuscript can be accepted:

1. Lack of a "good" reference measurement. Lab analysis is assumed to be the true value although storage times of (unfiltered) samples was 48h. The NH4 graph seems to indicate problems of storage, as does the largest "noise" visible for other parameters in the lab analysis. In-situ equipment, however, can be subjected to poor resolution of the recorded value (10 μgP/l) which is interesting to highlight.

2. It would be interesting to present the method used to determine measurement accuracy and LOQ for both in situ and lab equipment, and make sure that they are the same. In the current version of the manuscript it seems that the authors quantified the LOQ of their lab equipment but used the LOQ provided by the manufacturer for their in situ equipment. And study the effect of sample storage on measurement accuracy and LOQ, in addition to the lab analysis alone. Some data analyses could be performed with the data > LOQ for both lab and field procedure.

3. One possibility for a fair comparison would be to bring samples of known concentrations (prepared in the lab and immediately analyzed in the lab) to the field equipment. By doing this, there would be no issue of sample storage and both methods could be compared. Another factor that make the comparison unfair is that the lab equipment is calibrated (probably?) and not the field equipment (maybe the PHOSPHAX is).

4. The comparison would be more solid with more storm events monitored, as only 30 data points are currently available (of which 5 are genuine paired samples), which seems to be little for some of statistical analyses done.

Detailed comments

Line 16 "The downside to this approach is that the data can be subject to more 'noise'" this seems to be in contraction with the data collected in this study, where lab analyses appear to be more subjected to analytical "noise". In-situ equipment, however, can be subjected to poor resolution of the recorded value (eg 10 μgP/l) which is interesting to highlight.

Line 18 and line 81 “This raises the question of whether high frequency, lower precision data are better than low frequency, higher precision data.” I think that the assumption that sample collection, storage and analysis has a higher precision than in situ equipment should be tested, including the effect of storage. It would be interesting to clarify “better” here, because depending on the objective of the monitoring (assess mean concentration or load during a given period, look at the temporal dynamics, et.c) either of the two methods can be better.

Line 25 “the NITRATAX can under report the concentration” or the lab measurement overestimates it.

Line 58 “In situ devices remove sample storage requirements and provide a means of avoiding water sample storage-associated chemical transformations” this is important and should be considered in the manuscript by analyzing the impact of storage on the quality of measurement.

Line 106 the sub catchments are not visible in Figure 1b

Line 166 “quality controls” please give more details, including the number of samples used.

Line 187 “on one of three occasion” that is to say 10 out of 30?

Line 204 “they should lie on the 45° line” call it the 1:1 line?

Line 218 “A final, but limited analysis was also conducted on the genuine paired samples found for TP and TRP only - i.e. only five pairs for each sub-catchment” I doubt this is a sufficient number for the statistical analysis conducted”.

Line 247 “In all three sub-catchments, TP data from both in situ analysers and the laboratory analysed grab samples exhibited a positive relationship with discharge (Figure 3a-c).” I did not see discharge in Figure 3.

Line 251 “In all cases, the chemographs generated by both analytical approaches ap-

pear similar and match the responses reported elsewhere” line 253 “Such relationships with discharge are less clear” to vague, use metrics and statistics

line 255 “and possibly even a two peaked chemograph” I did not see it.

Line 272 “Where high concentrations of NH4-N occur as spikes associated with discharge, it is often more related to incidental losses of recently applied NH4- N as a result of farmland management practices” interpretation should be moved to discussion section.

Line 257 “by very high R^2” used a fixed threshold throughout the manuscript to consider that R^2 is “high” and write $R^2 > \ldots$ instead

Line 395 “indicating that the in situ data were consistently lower than that measured in the laboratory.” Not really consistently lower in Figure 3.

Avoid subjective comments such as “albeit not one that is ideal” line 352, use metrics and statistics instead. Avoid double negative such as Line 269 “is not unusual”

Table 1: add other statistics such as the mean and standard deviation

Table 2: add units

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684, 2018.