

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 #1

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General comments

This paper presents high-frequency nutrient data through a single storm event, produced by in situ analysers and sondes, and compares the P and N data to lab analysis of grab samples obtained using water samplers, at the North Wyke research facility in the UK. It assesses the relative merits of these particular auto-analysers for the monitoring of TP, TRP, NO₃ and NH₄. The paper is well-written and structured, and the figures are informative. However, I have some major issues that would need addressing before I could recommend publication.

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Specific comments

1) The main focus of this study is to compare the autoanalyser data with the “gold standard” lab analysis. The degree of agreement between these two data sets is the key parameter that the authors use to evaluate the auto-analyser performance. However, there are a number of problems with this approach.

- The lab samples were only analysed after 48 hours (despite the text in the introduction discussing the issues of sample stability).
- The grab samples were not filtered for 48 hours, which is another major source of error.
- The nutrient concentrations at the study sites were often below the Limit of Quantification for the lab analysis
- The study sites were also below the LOQ for the autoanalysers and sondes.

Therefore, the lab data is somewhat unreliable, and the field instrument data is also unreliable. There is also an underlying assumption that the differences in the concentration data are due to inaccuracies in the autosamplers alone, which is unfair. It also ignores the previous studies (often using the Phosphax TP analyser) which have produced very good agreements with lab data (see referenced work by Palmer-Felgate, Rode, Skeffington, Mellander and Jordan) and others (Outram et al 2016, M Cohen). I would advise that the authors focus purely on the sites where both the lab and autoanalyser data is above the LOQ, to give a fair assessment of their effectiveness. Perhaps North Wyke was a poor choice for this particular study, but it does show that these instruments are maybe not suited to similar small agricultural catchments with low nutrient concentrations.

2) There is a major issue with the Phosphax data (Fig 3), which the authors state can only report data to the nearest 10 µg/l. I'm not sure this is correct, and other studies using the Phosphax (listed above) do not have the step changes that this study

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presents. This needs to be addressed and the data corrected.

3) In terms of the nitrate time-series, I would suggest that the sonde data is much better than the lab data at low concentrations (Fig 4a and 4b).

4) There is a lack of detail in the autosampler methods. The samplers sampled at “predetermined flow thresholds”. What were they and how were they chosen? What was the position of the sampling tube? Set depth? In main flow or marginal? How were the manual grab samples taken? Sample storage? How were they “kept cool”?

5) What lab quality controls were used? Were they external standards?

Technical corrections

Line 18: “this raises the question of whether high frequency lower precision data” This statement makes a presumption that the autoanalysers produce more inaccurate P and N data than standard grab sampling and analysis (which is subject to sample stability issues). This paper does not make the case that this is true

Line 26. The tone of this sentence is quite unfair to the instrument manufacturers and not supported by this study. It implies that the Phosphax and YSI data are poor, because they don’t match with the lab data (which is also poor, due to storage issues and been below the LOQ). Change to “At low P and N concentrations, the PHOSPHAX, YSI and lab analyses were below LOQ”. Better still, remove this data from the study.

Line 42. Change wet chemistry to colorimetry.

Line 67. “limited coverage of the stream cross section” should not be a problem in such small streams if sampling is taken from the main flow at mid depth.

Line 99. Remove green, red and blue farmlet. Not needed.

Line 105. Sentence doesn’t make sense.

Line 142. Sentence doesn’t make sense.

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Line 242. Change to Nutrient response to discharge.

Line 266. Should it be Figure 4d-f?

Figure 1. I couldn’t see the streams on the map.

Figure 3. Raw P data needs to be used, rather than being rounded to the nearest 10 ug/l. What happens to the TRP lab data at site 5 at 1pm Thursday? Is this real data, or a problem with the lab analysis? It really effects the plots in Figure 5. Remove the sites that are below LOQ.

Figure 4. YSI ammonium data seems to be much better than the lab data. Remove sites that are below LOQ.

Figure 5. The P data in Figure 3 goes up to 80 ug/l, but this data only goes up to ~65 ug/l. Is some data missing?

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