Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 26 January 2018

Hydrology and Earth System Sciences
Discussions

Comparison of high frequency, in-situ water quality analysers and sensors with conventional water sample collection and laboratory analyses: phosphorus and nitrogen species

Steven J. Granger[1], Juan A. Qunicke[12], Paul Harris[1], Adrian L. Collins[1], Martin S. Blackwell[1]

[1]Sustainable Agriculture Sciences, Rothamsted Research, North Wyke, Okehampton, Devon, EX20 2SB, U.K.

[2]Instituto National de Investigación Agropecuaria, La Estanzuela, Ruta 50, Km. 11, Colonia, Uruguay.

Correspondence to: S. J. Granger (steve.granger@rothamsted.ac.uk)

Abstract

The long-term collection of water samples for water quality analysis with high precision laboratory instrumentation is routine in monitoring programmes however, such sampling is labour intensive, expensive, and therefore undertaken at a low temporal frequency. Advances in environmental monitoring technology however, mean that it is now possible to collect high temporal frequency measurements for a wide range of water quality parameters without the need for the physical collection of a sample. The downside to this approach is that the data can be subject to more 'noise', due to environmental and instrument variables. This raises the question of whether high frequency, lower precision data are better than low frequency, higher precision data. This study reports the findings of an investigation of agricultural land drainage comparing measurements of total phosphorus (TP), total reactive phosphorus (TRP), ammonium (NH_4-N) and total oxidised inorganic nitrogen (NOx-N) collected using both equipment in situ and concurrent water samples analysed in the laboratory. Results show that both in situ PHOSPHAX TP and NITRATAX NOx-N instruments can provide comparable

data to that measured using samples analysed in the laboratory; however, at high discharge and low NOx-N concentrations, the NITRATAX can under report the concentration. In contrast, PHOSPHAX TRP and YSI sonde NH_4-N data were both found to be incomparable to the laboratory data. This was because concentrations of both parameters were well below the instruments accurately determinable level, and because the laboratory data at low concentrations were noisy.

Keywords: water quality; phosphorus, nitrogen, ammonium, sensors; in situ; runoff; field drainage

1. Introduction

Long-term routine, but infrequent, water quality sampling used widely in strategic scale monitoring provides insight into longer-term trends (Howden et al., 2010). However, such sampling fails to capture higher resolution data necessary for insight into hydrological and biogeochemical processes and responses (Granger et al., 2010) including evidence of non-stationarity, self-organisation, and fractals (Harris and Heathwaite, 2005; Milne et al., 2009; Kirchner and Neal, 2013). Advances in environmental monitoring technology mean that it is now possible to collect high resolution measurements of a wide range of water quality parameters, providing detailed insight into hydrochemical temporal dynamics. Technologies vary depending on the parameters being measured, but typically include, automated wet chemistry apparatus in situ (e.g. for phosphorus (P) analysis) or ultra-violet optical sensors (e.g. for total oxidised nitrogen) (Palmer-Felgate et al., 2008; Donn et al., 2012; Carey et al., 2014; Skeffington et al., 2015; Bieroza and Heathwaite, 2015; Mellander et al., 2016). Frequency of measurements vary, ranging from every minute (or less) to hourly, depending upon the parameter, but are more typically undertaken at 15-minute intervals. Wet chemistry in situ

analysers and optical sensors have been shown to deliver important insights into nutrient fraction dynamics in response to runoff (Mellander et al., 2015) and catchment management (Perks et al., 2015). High resolution sampling and analysis in situ captures a broader range of pollutant concentrations than routine infrequent sampling and thereby elucidates hysteresis, diurnal patterns and non-storm dependent transfers (Heffernan and Cohen, 2010; Bende-Michl et al., 2013). Monitoring in situ can be used to identify pollutant transfer typologies. For example, Jordan et al. (2005) used in situ wet chemistry analysis to detect three types of total P (TP) transfer events: chronic storm-independent transfers reflecting on-farm slurry and fertiliser applications; acute storm-dependent transfers associated with agricultural diffuse pollution, and; acute storm-independent transfers reflecting specific incidental pollution events. In situ devices remove sample storage requirements and provide a means of avoiding water sample storage-associated chemical transformations (Bende-Michl and Hairsine, 2010).

Previously, studies were limited to the collection of water samples either manually or using automated water samplers, and then transfer of samples to laboratories for analysis by wet chemistry and colourimetric methods. However, despite transforming the hydrologic sciences over the past 50 years (Rode et al., 2016), questions remain about the precision of measurements made using these technologies relative to standard sample collection and laboratory analysis. The traditional auto-sampler approach followed by laboratory analyses of nutrient content can carry risks and uncertainties associated with a number of problems, including small sampling volume, preferential sampling effects, limited coverage of the stream cross-section and transformation risks during storage in conjunction with time delays between sample collection and subsequent laboratory analyses (Kotlash and Chessman, 1998; Harmel et al., 2006; McMillan et al., 2012). Storage-associated transformations are caused by a range of physical and biochemical processes including hydrolysis, sorption, precipitation, microbial uptake or release and complexation (Jarvie et al., 2002a; Harmel et al., 2006). Previous work

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 26 January 2018

(McMillan et al., 2012) has suggested that biogeochemical effects during sample storage can contribute more to uncertainty than errors due to preferential sampling or lower extraction of sediment-bound nutrients. The greatest proportional losses of dissolved nutrients in stored water samples occur when concentrations are low, with losses up to 50 % for nitrate and 67 % for soluble reactive P after six days of storage with no refrigeration (Kotlash and Chessman, 1998). Such uncertainties are also reported by Lloyd et al. (2016) who describe an almost 10-fold increase in uncertainty of both nitrate and TP loads measured over 2 years in a river in the U.K. when comparing laboratory and automated sensor data.

This raises the question of whether high frequency, low precision data is better than low frequency, high precision data. Rode et al. (2016) recognise that there are major issues related to calibration of automated sensing equipment and the need for regular servicing, along with a pressing need for the development of automated tools and standards for data quality assurance (Campbell et al., 2013). There is still much work to be done in quantifying the precision of automated water quality sensors, and accordingly, herein we report the findings of a study comparing measurements of TP, total reactive P (TRP), ammonium nitrogen (NH_4-N) and total oxidised inorganic nitrogen (NOx-N) collected using both automated equipment and concurrent water samples analysed in the laboratory. We test the hypothesis that in situ measurements of these parameters can be as precise as those acquired by laboratory analysis of manually collected water samples analysed using standard laboratory techniques.

2. Material and Methods

2.1 Study Site

The study was undertaken on the North Wyke Farm Platform (NWFP), an instrumented research grassland farm of 63 ha, split into 15 hydrologically isolated sub-catchments, over

97 which three different 21 ha livestock and grassland management systems are imposed (Orr et
98 al., 2016). From April 2013 to July 2015, all 15 NWFP sub-catchments were assigned to one
99 of three treatments: (i) permanent pasture ('green' farmlet); (ii) increased use of legumes
100 (blue farmlet), and; (iii) innovation (red farmlet), via a gradual and planned re-seeding
101 campaign (Figure 1a). The soils of the NWFP are clay loams (Figure 1b). Within each sub-
102 catchment a range of instrumentation takes measurements on water, air and soil parameters in
103 situ, much of this data being at a high temporal resolution (15 mins).

104 2.2 Sampling Strategy

105 For this study, one sub-catchment from within each of the three management systems was
106 chosen for investigation (numbered 2, 5 and 8; Figure 1b) of drainage caused by a rainfall
107 event on the 3rd December 2015. A tipping bucket rain gauge (Adcon, Austria) located in the
108 centre of each catchment measured the rainfall at a resolution of 0.2 mm per tip. During this
109 event, measurements of discharge, TP, TRP, NH_4-N and NOx-N were taken using the
110 instrumentation in situ. Auto-samplers (Teledyne ISCO, New England, USA) were used to
111 sample the discharge automatically at pre-determined flow thresholds. Manual grab samples
112 were also collected throughout the discharge event and both these and the auto-sampler
113 samples were analysed in the laboratory. Grab samples were taken to both sample the
114 discharge before and after the main storm drainage, and a sub-set during the storm drainage
115 were taken at exactly the same time as the automated in situ analysis so as to generate paired
116 results for TP and TRP. Grab samples were kept cool, and a sub-sample filtered through a
117 0.45 µm cellulose nitrate filter, before all samples were analysed in the laboratory within 48
118 hours.

119 2.3 Measurement of Discharge

Each of the sub-catchments drain, via French drains, to a monitoring station where H flumes are located with a capacity designed for a 1 in 50-year storm event. The flumes intercept and channel drainage in such a way that discharge can be determined by a rating curve calculated based on the the height of the liquid in the flume. Drainage in this context is defined as all the water that moves from the sub-catchment through the flume irrespective of its hydrological pathway. Water heights within the flumes were measured by pressure level sensors (OTT hydromet, Loveland, CO., USA). These sensors measure the depth of water by means of an integrated controller and ceramic pressure-measuring cell. The level offset (to the flume bed) was checked fortnightly and updated, if required, in the logger software.

2.4 Automated in situ Measurements

2.4.1 Phosphorus

Total P and TRP are measured in a sample collected from a sump at the monitoring station by a separate device (SIGMATAX 2, Hach, Salford, UK) which homogenises an unfiltered sample using ultra-sound before passing it to a process photometer (PHOSPHAX sigma, Loveland, Colorado, USA). The analyser analyses ortho-phosphate colourimetrically using standard molybdenum blue chemistry. Total P samples are digested prior to colourimetric analysis by heating, under pressure, with sulphuric acid and sodium peroxydisulphate while TRP analysis occurs on an undigested sample. The PHOSPHAX was calibrated daily through the running of an internal standard; however, it was not possible to run further quality controls or references. The lowest concentration the instrument is reported to measure is 50 (± 1) µg PO_4-P l^{-1}.

2.4.2 Nitrogen

Drainage the sump in the conduit upstream of the flume is automatically pumped every 15 mins into a purpose built stainless steel by-pass flow cell that houses the sensors. Water is

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 26 January 2018

144 pumped into, and out of, the base of the flow cell and this, coupled with the V shape design,
145 ensures that there is no retention of sediment or particulate matter either between samples or
146 over time. Within the flow cell, NH_4-N (NH_4 + ammonia) is measured using an ion selective
147 electrode contained within a multi-parameter sonde (6600V2, YSI, Hampshire, UK). Total
148 oxidised inorganic nitrogen is measured by a self-cleaning, optical UV absorption sensor
149 (NITRATAX Plus SC, Loveland, Colorado, USA). There is no specified lowest working
150 concentration for this sonde; however, as it has an accuracy of ± 2 mg NH_4-N l^{-1} at its lower
151 range, anything below this is considered 'not accurate' (YSI, Ohio, USA. *pers. comm.*).
152 Oxidised inorganic nitrogen dissolved in water absorbs UV light at wavelengths below 250
153 nm, so by passing UV light through the medium and measuring the absorption using a 2-
154 beam turbidity compensated photometer, the NOx-N concentration is calculated. The lowest
155 accurately determinable concentration for the instrument is 0.503 ± 0.5 mg NOx-N l^{-1}.

156 Both probes were calibrated monthly and drift corrected, but no additional in situ quality
157 controls were applied.

158 2.5 Laboratory Measurements

159 Unfiltered samples presented to the laboratory were analysed for both TP and RP thus giving
160 equivalent data to that generated from the Phosphax instruments (i.e. TP and TRP).

161 Samples requiring TP analysis were initially subject to an oxidation reaction using acidified
162 potassium persulphate thus converting all P forms to RP. Both digested and undigested
163 samples were then analysed for RP colourimetrically on an Aquachem 250 analyser using a
164 molybdenum blue reaction (Murphy and Riley, 1962). The limits of quantification (LOQ: the
165 lowest accurately determinable concentration) for TP and RP were 10 (± 1.4) and 2 (± 0.04)
166 µg PO_4-P l^{-1}, respectively. The accuracy of TP digestions was checked using quality controls
167 which were always within 8 % of the target value and with 78 % being within 5 %. Similarly,

quality controls were run during the analysis of RP which were always within 5 % of the target value.

Unfiltered samples were also analysed colourimetrically for NH_4-N and NOx-N on the Aquachem 250 analyser. Total oxidised inorganic nitrogen was determined through the reduction of nitrate to nitrite by hydrazine sulphate and total nitrite is diazotized with sulphanilamide and coupled with N-1-naphthylethylenediamine dihydrochloride to form an azo dye with an absorbance maximum at 540 nm. The LOQ for this method was 0.1 (± 0.003) mg NOx-N l^{-1} and quality controls were always within 3 % of their target.
Ammonia/ammonium was determined by the chlorination of ammonia with sodium dichloroisocyanurate to monochloramine, which reacts with salicylate to form a second intermediate, 5-aminosalicylate. Oxidative coupling of 5-aminosalicylate with salicylate forms an indophenol dye with an absorbance maximum at 660 nm. Nitroprusside stabilises the monochloramine intermediate and also promotes the final oxidative coupling stage. The LOQ for this method was 0.4 (± 0.01) mg NH_4-N l^{-1} and quality controls were always within 5 % of their target.

2.6 Data Pre-processing

For TP and TRP, the manual grab sampling and in situ flume measurements only occurred simultaneously on five out of 30 occasions for all three sub-catchments, thus only five paired samples could be compared directly, with the same time stamp. For the nitrogen species, measurements only occurred simultaneously on one of three occasions. Thus, to make efficient use of all the grab sampling data, the in situ flume chemistry data were infilled (or predicted) to provide an exact match to the grab sampling times. This was achieved using a splines fit (via the na.spline() function in the 'zoo' R package of Zeileis and Grothendieck (2005)). Outputs of prediction uncertainty for the infilled data were not sought, although future work could

transfer this uncertainty into the subsequent relationship analyses (e.g. via weighted correlation or regression analysis). In this respect, all infilled in situ data points are effectively viewed as measured in situ data for subsequent statistical analyses (this assumption is still checked visually, however). Constraints were also set in place to ensure the infilling did not provide values below zero or provide values at a higher level of precision than that measured.

2.7 Statistical Procedures

Once the infilling had been conducted, paired in situ flume and laboratory grab sampling data were graphically related using time series and scatterplots for all four water quality parameters. Time series plots are useful in that they can indicate systematic effects, such as sustained periods of over- or under-estimation, but where the general temporal pattern of the data is retained. The time series plots also provide an important visual assessment of the spline infilling procedure described above. For scatterplots, if the two methods of measurement were an exact match, then they should lie on the 45^{o} line. Data points that lie below the 45^{o} line indicate where the in situ data under-estimates the laboratory data, and vice-versa.

These visual summaries were complemented by a basic set of statistical goodness-of-fit diagnostics. The intercept and slope parameters from linear regression fits (between the in situ and laboratory data) are found, together with *p*-values for significance from zero and from one, respectively. Associated R^2 values from the same regressions are also reported and should tend to 1. Mean error (ME), root mean squared error (RMSE) and Normalised RMSE (NRMSE) values are reported (via functions in the 'hydroGOF' R package), where all three diagnostics should tend to zero. In this case, the *errors* referred to *in situ minus laboratory* data, thus a negative ME value would indicate that the in situ data under-estimates the laboratory data, on average. RMSE reflects the variance of the errors, which ideally needs to be as small as possible. The NRMSE diagnostic is a relative measure of RMSE, and thus relays quite clearly

when the in situ data has a good or poor correspondence with the laboratory data, regardless of different scales of measurement from the different sub-catchments.

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. This data was analysed using paired *t*-tests and analysis of variance (ANOVA), and was presented using Tukey mean-difference plots. Further analyses could have considered random sampling for five pairs from the infilled data of 30 pairs, and repeating the tests considered here, on each random sample. This would assess the sensitivity of the results to sample variation and to an extent, the infilling. However, this was considered beyond the scope of this study; and in any case, the outcomes would always be severely limited due to the very small sampling size.

All statistical analyses were conducted in R (https://www.r-project.org/), where in all cases, the in situ data were compared to the *unfiltered* laboratory data.

3. Results

3.1 Data summaries

In the first instance, it is useful to summarise the measured data, where infilled data or paired data are not needed. In this respect, sample size and the ranges (minimums to maximums) for TP, TRP, NOx-N and NH_4-N measured in the drainage from sub-catchments 2, 5 and 8, obtained by both the automated in situ analysers and laboratory analysed manually collected samples are presented in Table 1. Values of TP ranged between 40 to 770 µg P l^{-1} and for TRP between 0 to 70 µg P l^{-1} as measured by the in situ Phosphax analysers. For NOx-N and NH_4-N, the values measured in situ ranged between 0.62 to 4.8 mg N l^{-1} and 0.04 to 1.5 mg N l^{-1}, respectively. The range of values measured in the manually collected samples analysed in the laboratory, in general, compare favourably to the in situ data. This is even though there are

much fewer data and that potential highs and lows in concentration could have been missed in the manually collected samples.

3.2 Chemistry Response to Discharge

Data on the discharge from the three sub-catchments and rainfall is presented in Figure 2. The results show three similar twin peaked hydrographs but with different magnitudes of peak discharge of 15, 22 and 28 l s^{-1} for sub-catchments 2, 5 and 8, respectively. The different scales of the hydrographs reflect differences in, amongst other things, sub-catchment size, rainfall, slope, soil moisture and soil type. 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). The highest values of TP were associated with the initial smaller peak in discharge, and a latter smaller peak in TP associated with the second, large, peak in discharge. In all cases, the chemographs generated by both analytical approaches appear similar and match the responses reported elsewhere (Heathwaite and Dils, 2000; Granger et al., 2010; Lloyd et al., 2016). Such relationships with discharge are less clear with the lower concentration TRP data (Figure 3d-f). In situ TRP concentration data again exhibit a positive relationship with discharge, and possibly even a two peaked chemograph, similar to that of the TP data. However, the low concentration range compared to that of the TP, means that when the data is rounded to the nearest 10 µg P l^{-1}, the resolution of the chemograph is severely affected and detail is lost. The TRP data generated via laboratory analysis are not subject to this rounding effect; however, these data exhibit considerably more 'noise', and while it is possible to visualise some relationships with discharge, in all but the data from sub-catchment 8, this is highly subjective.

The NOx-N chemographs generated by the in situ analysers and the laboratory analysed samples display the classic dilution effect reported elsewhere (Webb and Walling, 1985; Granger et al., 2010; Lloyd et al., 2016) with concentrations dropping rapidly with the onset of

increased discharge, and slowly recovering to pre-storm flow values over time on the falling limb of the hydrograph (Figure 4e-f). The data generated for NH_4-N from the in situ sensors clearly show a positive relationship with discharge from all sub-catchments and, interestingly, even a second NH_4-N peak on the chemograph of sub-catchment 8 associated with the main spike in discharge (Figure 4a-c). This positive relationship is not unusual (House and Warwick, 1998a; Inamdar, 2007; Fucik et al., 2012), although it tends to be much lower in concentration compared to NOx-N and often this is not very discernible as the NH_4-N is rapidly nitrified to NOx-N (House and Warwick, 1998b). Where high concentrations of NH_4-N occur as spikes associated with discharge, it is often more related to incidental losses of recently applied NH_4-N as a result of farmland management practices (Granger et al., 2010). Data generated from the laboratory analysed grab samples provide a slightly more mixed picture. Where concentrations were highest (sub-catchment 8), these data appear to confirm the positive relationship of NH_4-N with discharge, even reproducing the second NH_4-N peak. In sub-catchment 5, where NH_4-N concentrations were lowest, the laboratory data are noisier, but it is still possible to observe an increase in NH_4-N concentration with increased discharge. In sub-catchment 2, however, the laboratory NH_4-N data show no relationship with discharge (Figure 4a).

In all chemographs (Figures 3-4), the outcomes of the in situ spline infilling described above, is shown. Here in filling never required a difficult extrapolation, but instead was always a simple interpolation that was richly informed by actual measured data that were temporally similar. Clearly, no unusual predictions result and the infilling should be considered reliable, and can be safely viewed as strongly comparable to the in situ data for subsequent statistical analyses.

3.3 Comparison of In Situ and Laboratory Analysis

290 The data obtained for genuine paired laboratory analysed manual grab samples and
291 PHOSPHAX in situ TP and TRP are presented in Table 4 (it is of no value to do this for nitrogen
292 species, as only one to three genuine pairs were available). The differences between the two
293 sets of data are reported relative to the laboratory data which have been subject to full analytical
294 quality control. Using this comparison, it can be seen that differences between TP values are
295 lower than for TRP, with respective ranges between +56 to -30 µg P l^{-1} (+29 % to -38 %) and
296 +13 to -33 µg P l^{-1} (+186 % to -57 %).

297 The difference between the two methods of measurement were assessed using paired *t*-tests.
298 The average difference between laboratory and in situ values for TP was -3.933 (standard error
299 of difference 4.947, 95 % CI -14.54, 6.677) and the standard deviation of differences was 19.16.
300 The *t*-test for TP indicated that there was no evidence of a difference between laboratory and
301 in situ measurements (t_{14} = -0.8, p = 0.44). However, the average difference between lab and
302 in situ values for TRP was 8.933 (standard error of difference 3.534, 95 % CI 1.353, 16.51)
303 with the standard deviation of differences being 13.69. This indicated that for TRP, that there
304 was evidence of a statistically significant difference between laboratory and in situ
305 measurements (t_{14} = 2.53, p = 0.024).

306 Differences between the two measurement methods was also assessed using ANOVA in order
307 to take into account that the data came from three different sub-catchments. This did not suggest
308 any influence of the sub-catchment difference on the size of measurement difference. Tukey
309 mean-difference plots are presented in Figure 5 and plot the difference between the two values
310 against the average of the two measured values. Limits of agreement (dashed lines) are plotted
311 at ± 2 standard deviations from the mean difference and indicate the range that approximately
312 95 % of the data is expected to fall in. From these plots the data suggest that, while there is no
313 obvious trend in TRP data, differences in the TP values are greater at lower concentrations with

the laboratory generating higher values but that this difference reduces as the TP concentration increases.

3.4 Comparison of Modelled In Situ and Laboratory Analysis

Given the small sample number of actual in situ and laboratory analysed grab samples, assessing the differences between these two approaches is extremely limited. We therefore compare the modelled in situ and laboratory analysed samples. This is because we consider error in the data obtained from the laboratory to be relatively low (Madrid and Zayas, 2007), with these data subject to analytical quality controls and checks. Any difference between in situ values and the laboratory must therefore be explained via other processes and mechanisms.

3.4.1 Phosphorus

For TP and TRP, the resultant paired data is presented using scatterplots in Figure 6. In all cases, the ideal 45^{o} line is shown together with the actual linear fit. Results of the tests for whether or not the ideal and actual lines significantly deviate from each other are given in Table 2, together with a general fit measure in R^2. At the 95 % level of significance, only the laboratory and in situ data for TP in sub-catchments 5 and 8 are in good agreement (as the *p*-values in Table 2 indicate the intercepts and slopes of their fitted lines are not significantly different to zero or one, respectively). Laboratory and in situ TP data in all three sub-catchments do however provide relatively high R^2 values, where for sub-catchment 2, the in situ TP tends to under-estimate laboratory TP at high values, pivoting the fitted line downwards at these values. Table 3 provides the ME, RMSE and NRMSE results for TP and TRP, where the negative ME value for TP in sub- catchment 2, indicates an overall under-estimation of laboratory TP by in situ TP, whilst in the other two sub-catchments, the reverse is true. Although sub-catchment 2 does not indicate the strongest 1:1 relationship between the paired

337 TP data, its TP data are most alike in terms of variation - as seen by the least scatter around the
338 fitted line, coupled with the lowest NRMSE value.

339 Corresponding results for TRP are not promising (Figure 5, Tables 2 and 3), where each
340 scatterplot depicts a poor correspondence between the laboratory and in situ TRP data, and
341 these poor relationships are statistically endorsed by the test results and the low R^2 values
342 presented in Table 2. Diagnostics presented in Table 3, provide little further insight into the
343 behaviour of the paired TRP data, except that in situ TRP will tend to under-estimate laboratory
344 TRP (as MEs are negative in two sub-catchments). Note however, that in situ TRP tends to be
345 less variable than laboratory TP, as shown by the scatterplots.

346 3.4.2 Nitrogen

347 Results for the differences between the in situ and laboratory NH_4-N data are quite complex.
348 From the scatterplots in Figure 7, and the associated tests in Table 2, a 1:1 relationship between
349 the paired NH_4-N data in sub-catchments 2 and 8 is clearly absent, although within sub-
350 catchment 2 the data are influenced by an anomalously high laboratory NH_4-N result. However,
351 the paired NH_4-N data do provide a high R^2 value in catchment 8, indicating a reproducible
352 relationship of sorts, albeit not one that is ideal. The most promising relationship for the paired
353 NH_4-N data is found in sub-catchment 5, where the R^2 value is reasonable and the NRMSE
354 value is much lower than that found in the other two sub-catchments.

355 Results for the differences between the paired NOx-N data, in contrast, are quite promising.
356 The scatterplots in Figure 7, overall, show a reasonable correspondence between the paired
357 NOx-N data, for all three sub-catchments, which is endorsed by very high R^2 values in Table
358 2. Although in all cases, these relationships cannot be viewed as 1:1 as indicated by the test
359 results in Table 2. For all cases, the in situ NOx-N data tends to over-predict the laboratory
360 NOx-N data.

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 26 January 2018

4. Discussion

4.1 Phosphorus

Direct comparison of laboratory and the in situ TP data shows no evidence of a significant difference although, at lower concentrations, the in situ data would appear to be *lower* than the laboratory values. Here, however, it is important to bear in mind that no direct comparisons were made on samples that were taken on discharge at the higher end of the concentration range. The modelled data confirm that there is a good match, in general, between in situ data and laboratory values with fitted lines not being significantly different to zero or one in sub-catchments 5 and 8. In sub-catchment 2, conversely, it would appear that in situ data were lower than laboratory values at *higher* concentrations which is confirmed by the negative ME value for this sub-catchment. Irrespective of this, all data showed good correlations with relatively high R^2 values, a fact that is confirmed by the good agreement shown by the chemographs in Figure 3 a-c. The data suggest that for TP, the PHOSPHAX in situ analysis provides reasonably good agreement with manual sampled laboratory analysed samples, and conversely that the manual samples do not suffer excessively from systematic, sampling or storage errors. However, it is noteworthy that the PHOSPHAX in situ data does produce a relatively 'smooth' chemograph which is in contrast to the laboratory data which is noticeably more 'noisy' and even contains a few anomalously high concentrations ('outliers') i.e. Figure 3a. This is probably a result of one or a combination of, three important issues regarding TP: a) data generated in situ is 'smoothed' by the analyser by rounding values to the nearest 10 µg P l^{-1}, b) sample container contamination at either the sampling stage or latterly during laboratory digestion, and c) laboratory analytical error. In the first case, the in situ values might actually be noisy, but this is not reflected in the smoothed data generated for download. In the second case, it is assumed that P of unknown origin (biological, tap water, chemical) could

386 have randomly, as opposed to systematically, contaminated some equipment leading to a high
387 result. In this scenario it is hard to imagine how this sort of error could cause a lower result
388 than expected. In the third, it could just be a random analytical artefact, which has resulted in
389 an unusually high (but could also cause an unusually low) result.

390 In contrast, the comparison of the TRP data were far less conclusive. Direct sample pair
391 comparison indicated a significantly lower concentration measured in situ than that measured
392 in the laboratory. Further, the larger data set generated by comparing modelled in situ and
393 manually sampled laboratory analysed TRP data shows very poor correspondence with
394 significant differences in both slope and intercept being >0 and <1 in every case, respectively,
395 indicating that the in situ data were consistently lower than that measured in the laboratory.
396 The low R^2 further confirms poor replication of data, a fact further confirmed by the
397 chemographs presented in Figure 3 d-f. It can be seen from Figure 6 d-f that the main cause for
398 poor correlation between the two data-sets is probably down to a combination of two factors;
399 a) the low resolution of the PHOSPHAX in situ data, rounding all numbers to the nearest 10,
400 and b) more importantly, that the vast majority of the PHOSPHAX in situ data is lower than
401 the machine's analytical limit of 50 µg P l^{-1}. That being said, in situ TRP concentrations have
402 trends (Figure 3 d-f) which are not so clearly represented in laboratory TRP data which again
403 although being above LOQ are extremely noisy.

404 One explanation is sample degradation between sampling and analysis. Ideally, samples should
405 be analysed immediately after collection to minimise degredation effects, but sample storage
406 is usually unavoidable prior to analysis. The concentrations of dissolved nutrient within water
407 samples can vary during storage as the result of a wide range of physical, biological and
408 chemical processes including sorption, hydrolysis, precipitation, complexation, and microbial
409 uptake and release (Jarvie et al., 2002b). This is particularly relevant for the samples collected
410 in this instance since they were unfiltered prior to analysis such that they were of the same

matrix as the sample collected by the PHOSPHAX. Rapid filtration of samples (typically >0.45 μm) is usually recommended in order to exclude microbial cells and inorganic particulate material, which can result in changes in physical or chemical forms of P through processes such as microbial uptake or adsorption in unfiltered samples (Lambert et al., 1992; Jarvie et al., 2002b; Worsfold et al., 2005). Biological processes and sorption to particulate matter can be rapid; Lambert et al. (1992) reported that concentrations of 'dissolved' P decreased substantially over a four-hour period in unfiltered lake water samples. Another possible effect of the unfiltered matrix is that sample particulates could be causing noise in the laboratory TRP analysis, both through their physical presence in the flow cell and through biogeochemical alteration of the sample in reaction to analytical reagents (Jarvie et al., 2002b), although presumably this is also an effect that happens in the PHOSPHAX analyser.

4.2 Nitrogen

Results for the differences between the in situ and laboratory NH_4-N data are quite complex but the 1:1 relationship between the paired NH_4-N data were in general poor. However, the paired NH_4-N data do provide reasonable R^2 values in sub-catchments 5 and 8. This variation in the responses needs to be examined more carefully. From the chemographs in Figure 4 a-c, all three in situ sondes produced similar responses, with rising and falling concentrations matching rises and falls in discharge. This would seem to indicate that the sondes were detecting a genuine chemical response. However, all the in situ data reported are well below the accuracy of the sonde at this concentration (Figure 7 a-c). This could be as a result of other factors affecting the sonde other than NH_4-N. The ion selective electrode is subject to effects caused by changes in temperature and interference from ions, which are similar in nature to the analyte. While the changes in temperature, or ions such as sodium and chloride, might only be slight in response to field drainage, they could be enough to cause the small responses recorded here which have a maximum range of about 1 mg NH_4-N l^{-1} and which were always below the

436 recommended accurate working concentration for the instrument. That said, in sub-catchment
437 8 which had the highest recorded NH_4-N values both by the sonde and the laboratory, the
438 chemical response in NH_4-N *is* mirrored by the laboratory grab samples, giving the highest R^2
439 of 0.83. Laboratory concentration values were also in the main below LOQ, but were much
440 closer to analytical limits than that of the sonde, and at their peak, slightly exceeded it. This
441 would seem to indicate that the sonde response in sub-catchment 8 would appear to be genuine
442 even if the absolute NH_4-N concentration is suspect. If this is the case, then we can maybe
443 assume that the responses recorded in sub-catchments 2 and 5 are also genuine, even if their
444 absolute values may not be. Laboratory values from these two sub-catchments were, however,
445 well below LOQ so cannot be used to back up this conclusion. Interestingly, laboratory data
446 from sub-catchment 5 (which recorded the lowest NH_4-N concentration from any of the three
447 sub-catchments) does mirror the response of the sonde to a degree (R^2 = 0.67), while the values
448 from sub-catchment 2 show no similarity at all. This paradox is confusing as if the loss of
449 response from sub-catchment 2 was due to sampling and unfiltered storage losses because of
450 the low NH_4-N concentration (i.e. (Kotlash and Chessman, 1998; Lentz, 2013)) then that would
451 surely have occurred in the even lower concentrations of sub-catchment 5. Further storm period
452 analyses are required to help resolve this paradox.

453 The NOx-N data, in contrast, show good similarity, which although not significantly similar,
454 have a very high R^2 (Table 2) and in all cases, the in situ modelled NOx-N data tends to over-
455 predict the laboratory data. The reason for this is clear from the chemographs in Figure 4 d-f,
456 whereby the trends in both sets of data are virtually identical (leading to high R^2), but whereby
457 modelled in situ values and laboratory values differ at lower concentrations. In all three
458 examples, pre- and post-discharge event values are near identical, but with the onset of
459 increased discharge, the NOx-N concentrations drop, with laboratory values dropping further
460 than modelled in situ values. In all cases, none of the recorded values are below the instruments

working capabilities so should be considered reliable, and only a few values are below the laboratory LOQ. The reason for this discrepancy is unclear and is the result, or a combination of, either the sensor underestimating NOx-N at increased discharge, or the laboratory analysed grab samples having a lower measured NOx-N at high discharge.

Here it useful to bear in mind that as the measurement is based on the evaluation of (invisible) UV light, the colour of the medium has no effect. The sensor contains a two-beam absorption photometer with turbidity compensation. So perhaps this turbidity compensation is having a greater effect on reducing calculated NOx-N values in situ at times when turbidity is greatly increased (at high discharge).

5. Conclusions

An increasing number of studies are reporting the use of in situ analysers and sensors to collect high temporal resolution hydrochemical data. Whilst such data permit the use of exploratory data interpretation techniques such as hysteretic loops, much hydrochemical data are used to estimate time-variant or averaged concentrations in the context of environmental objectives or thresholds and to estimate nutrient loads. The comparison herein of nutrient species data collected using in situ analysers or sondes and manually collected laboratory analysed samples confirms the following:

- PHOSPHAX in situ TP data would appear to be reliable, most likely as the determined concentrations are nearly always more than the instrument's lower limits. Discrepancies between laboratory and in situ data appear to increase as the PHOSPHAX lower measurable limit is approached.
- PHOSPHAX TRP measurements, in the context of the field drainage described here, are unreliable as the concentrations were nearly always below the LOQ for

485 the instrument. This is reflected in the poor agreement between laboratory and
486 instrument data. This poor agreement is largely due to the laboratory data being
487 very 'noisy' despite being above laboratory LOQ and may reflect
488 sampling/storage issues related to unfiltered sample matrix. Despite this, trends in
489 the concentration were discernible using the in situ data, although validation of
490 these trends requires more field work.

491 • The NH_4-N laboratory analysed data showed that concentrations were nearly
492 always below LOQ for the laboratory and as such were well below measurable
493 limits for the YSI sonde and electrode. This suggests that this analytical system is
494 not appropriate for this type of environmental setting. Despite this trends in NH_4-
495 N concentration were discernible from the sonde, although whether these are
496 analytical artefacts or genuine remains uncertain.

497 • Concentration of NOx-N were always higher than LOQ for both the in situ
498 NITRATAX sonde and the laboratory analysis. The two set of data show good
499 agreement, and exhibit similar classical NOx-N chemographs. However,
500 differences in the NOx-N are not linear and appear at lower concentration/higher
501 Q, with the in situ data giving lower concentrations than the laboratory measured
502 values. This may be an effect of the NITRATAX considering turbidity interference
503 at higher Q.

504

505 ## 6. Summary

506 PHOSPHAX TP and NITRATAX NOx-N data show good agreement with laboratory data
507 in this environmental setting. However, PHOSPHAX TRP and YSI NH_4-N data were less
508 reliable as concentrations were below the instrumental limits. Both these instruments

generated data with repeatable trends in concentration, but trends that were not reflected in the laboratory data which, in turn, was noisier. It is unclear whether the instrument trends were genuine, or why they were not present in the laboratory data which is itself very variable.

7. Acknowledgements

The authors would like to thank the Stapledon Memorial Trust for the Travelling Fellowship which enabled this work to be carried out. The work was also funded by the Biotechnology and Biological Sciences Research Council (BBSRC) grants BB/J004308 (The North Wyke Farm Platform) and BB/P01268X/1 (Soil to Nutrition). The authors a grateful to Jess Evans for her assistance with statistical support and to Verena Pfahler for her help with the sampling.

8. References

Bende-Michl, U., and Hairsine, P. B.: A systematic approach to choosing an automated nutrient analyser for river monitoring, J. Environ. Monit., 12, 127-134, 2010.

Bende-Michl, U., Verburg, K., and Cresswell, H. P.: High-frequency nutrient monitoring to infer seasonal patterns in catchment source availability, mobilisation and delivery, Environ. Monit. Assess., 185, 9191-9219, 2013.

Bieroza, M. Z., and Heathwaite, A. L.: Seasonal variation in phosphorus concentration-discharge hysteresis inferred from high-frequency in situ monitoring, J. Hydrol., 524, 333-347, 2015.

Campbell, J. L., Rustad, L. E., Porter, J. H., Taylor, J. R., Dereszynski, E. W., Shanley, J. B., Gries, C., Henshaw, D. L., Martin, M. E., Sheldon, W. M., and Boose, E. R.: Quantity is Nothing without Quality: Automated QA/QC for Streaming Environmental Sensor Data, Bioscience, 63, 574-585, 2013.

Carey, R. O., Wollheim, W. M., Mulukutla, G. K., and Mineau, M. M.: Characterizing Storm-Event Nitrate Fluxes in a Fifth Order Suburbanizing Watershed Using In Situ Sensors, Environ. Sci. Technol., 48, 7756-7765, 2014.

537 Donn, M. J., Barron, O. V., and Barr, A. D.: Identification of phosphorus export from low-
538 runoff yielding areas using combined application of high frequency water quality data and
539 MODHMS modelling, Sci. Total Environ., 426, 264-271, 2012.

540 Fucik, P., Kaplicka, M., Kvitek, T., and Peterkova, J.: Dynamics of Stream Water Quality
541 during Snowmelt and Rainfall - Runoff Events in a Small Agricultural Catchment, Clean-Soil
542 Air Water, 40, 154-163, 2012.

543 Granger, S. J., Hawkins, J. M. B., Bol, R., White, S. M., Naden, P., Old, G., Bilotta, G. S.,
544 Brazier, R. E., Macleod, C. J. A., and Haygarth, P. M.: High temporal resolution monitoring
545 of multiple pollutant responses in drainage from an intensively managed grassland catchment
546 caused by a summer storm, Water Air Soil Pollut., 205, 377-393, 2010.

547 Harmel, R. D., Cooper, R. J., Slade, R. M., Haney, R. L., and Arnold, J. G.: Cumulative
548 uncertainty in measured streamflow and water quality data for small watersheds, Trans.
549 ASABE, 49, 689-701, 2006.

550 Harris, G., and Heathwaite, A. L.: Inadmissible evidence: knowledge and prediction in land
551 and riverscapes, J. Hydrol., 304, 3-19, 2005.

552 Heathwaite, A. L., and Dils, R. M.: Characterising phosphorus loss in surface and subsurface
553 hydrological pathways, Sci. Total Environ., 251, 523-538, 2000.

554 Heffernan, J. B., and Cohen, M. J.: Direct and indirect coupling of primary production and
555 diel nitrate dynamics in a subtropical spring-fed river, Limnol. Oceanogr., 55, 677-688, 2010.

556 House, W. A., and Warwick, M. S.: Hysteresis of the solute concentration/discharge
557 relationship in rivers during storms, Water Res., 32, 2279-2290, 1998a.

558 House, W. A., and Warwick, M. S.: Intensive measurements of nutrient dynamics in the
559 River Swale, Sci. Total Environ., 210, 111-137, 1998b.

560 Howden, N. J. K., Burt, T. P., Worrall, F., Whelan, M. J., and Bieroza, M.: Nitrate
561 concentrations and fluxes in the River Thames over 140 years (1868-2008): are increases
562 irreversible?, Hydrol. Process., 24, 2657-2662, 2010.

563 Inamdar, S.: Exports of dissolved ammonium (NH4+) during storm events across multiple
564 catchments in a glaciated forested watershed, Environ. Monit. Assess., 133, 347-363, 2007.

565 Jarvie, H. P., Neal, C., Williams, R. J., Neal, M., Wickham, H. D., Hill, L. K., Wade, A. J.,
566 Warwick, A., and White, J.: Phosphorus sources, speciation and dynamics in the lowland
567 eutrophic River Kennet, UK, Sci. Total Environ., 282, 175-203, 2002a.

568 Jarvie, H. P., Withers, P. J. A., and Neal, C.: Review of robust measurement of phosphorus in
569 river water: sampling, storage, fractionation and sensitivity, Hydrology and Earth System
570 Sciences, 6, 113-131, 2002b.

Jordan, P., Arnscheidt, J., McGrogan, H., and McCormick, S.: High-resolution phosphorus transfers at the catchment scale: the hidden importance of non-storm transfers, Hydrology and Earth System Sciences, 9, 685-691, 2005.

Kirchner, J. W., and Neal, C.: Universal fractal scaling in stream chemistry and its implications for solute transport and water quality trend detection, Proc. Natl. Acad. Sci. U. S. A., 110, 12213-12218, 2013.

Kotlash, A. R., and Chessman, B. C.: Effects of water sample preservation and storage on nitrogen and phosphorus determinations: Implications for the use of automated sampling equipment, Water Res., 32, 3731-3737, 1998.

Lambert, D., Maher, W., and Hogg, I.: Changes in phosphorus fractions during storage of lake water, Water Res., 26, 645-648, 1992.

Lentz, R. D.: Delayed Sample Filtration and Storage Effects on Dissolved Nutrients Measured in Agricultural Runoff, Commun. Soil Sci. Plant Anal., 44, 2952-2960, 2013.

Lloyd, C. E. M., Freer, J. E., Johnes, P. J., and Collins, A. L.: Using hysteresis analysis of high-resolution water quality monitoring data, including uncertainty, to infer controls on nutrient and sediment transfer in catchments, Sci. Total Environ., 543, 388-404, 2016.

Madrid, Y., and Zayas, Z. P.: Water sampling: Traditional methods and new approaches in water sampling strategy, Trac-Trends Anal. Chem., 26, 293-299, 2007.

McMillan, H., Krueger, T., and Freer, J.: Benchmarking observational uncertainties for hydrology: rainfall, river discharge and water quality, Hydrol. Process., 26, 4078-4111, 2012.

Mellander, P. E., Jordan, P., Shore, M., Melland, A. R., and Shortle, G.: Flow paths and phosphorus transfer pathways in two agricultural streams with contrasting flow controls, Hydrol. Process., 29, 3504-3518, 2015.

Mellander, P. E., Jordan, P., Shore, M., McDonald, N. T., Wall, D. P., Shortle, G., and Daly, K.: Identifying contrasting influences and surface water signals for specific groundwater phosphorus vulnerability, Sci. Total Environ., 541, 292-302, 2016.

Milne, A. E., Macleod, C. J. A., Haygarth, P. M., Hawkins, J. M. B., and Lark, R. M.: The wavelet packet transform: A technique for investigating temporal variation of river water solutes, J. Hydrol., 379, 1-19, 2009.

Murphy, J., and Riley, J. P.: A modified single solution method for determination of phosphate in natural waters, Anal. Chim. Acta, 26, 31-&, 1962.

Orr, R. J., Murray, P. J., Eyles, C. J., Blackwell, M. S. A., Cardenas, L. M., Collins, A. L., Dungait, J. A. J., Goulding, K. W. T., Griffith, B. A., Gurr, S. J., Harris, P., Hawkins, J. M. B., Misselbrook, T. H., Rawlings, C., Shepherd, A., Sint, H., Takahashi, T., Tozer, K. N., Whitmore, A. P., Wu, L., and Lee, M. R. F.: The North Wyke Farm Platform: effect of

606 temperate grassland farming systems on soil moisture contents, runoff and associated water
607 quality dynamics, Eur. J. Soil Sci., 67, 374-385, 2016.

608 Palmer-Felgate, E. J., Jarvie, H. P., Williams, R. J., Mortimer, R. J. G., Loewenthal, M., and
609 Neal, C.: Phosphorus dynamics and productivity in a sewage-impacted lowland chalk stream,
610 J. Hydrol., 351, 87-97, 2008.

611 Perks, M. T., Owen, G. J., Benskin, C. M. H., Jonczyk, J., Deasy, C., Burke, S., Reaney, S.
612 M., and Haygarth, P. M.: Dominant mechanisms for the delivery of fine sediment and
613 phosphorus to fluvial networks draining grassland dominated headwater catchments, Sci.
614 Total Environ., 523, 178-190, 2015.

615 Rode, M., Wade, A. J., Cohen, M. J., Hensley, R. T., Bowes, M. J., Kirchner, J. W.,
616 Arhonditsis, G. B., Jordan, P., Kronvang, B., Halliday, S. J., Skeffington, R. A., Rozemeijer,
617 J. C., Aubert, A. H., Rinke, K., and Jomaa, S.: Sensors in the Stream: The High-Frequency
618 Wave of the Present, Environ. Sci. Technol., 50, 10297-10307, 2016.

619 Skeffington, R. A., Halliday, S. J., Wade, A. J., Bowes, M. J., and Loewenthal, M.: Using
620 high-frequency water quality data to assess sampling strategies for the EU Water Framework
621 Directive, Hydrology and Earth System Sciences, 19, 2491-2504, 2015.

622 Webb, B. W., and Walling, D. E.: Nitrate behaviour in streamflow from a grassland
623 catchment in Devon, U.K., Water Res., 19, 1005-1016, 1985.

624 Worsfold, P. J., Gimbert, L. J., Mankasingh, U., Omaka, O. N., Hanrahan, G., Gardolinski,
625 P., Haygarth, P. M., Turner, B. L., Keith-Roach, M. J., and McKelvie, I. D.: Sampling,
626 sample treatment and quality assurance issues for the determination of phosphorus species in
627 natural waters and soils, Talanta, 66, 273-293, 2005.

628 Zeileis, A., and Grothendieck, G.: zoo: S3 infrastructure for regular and irregular time series,
629 Journal of Statistical Software, 14, 27, 2005.

630

631

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 26 January 2018

Hydrology and Earth System Sciences
Discussions

		Sub-catchment 2		Sub-catchment 5		Sub-catchment 8	
		n	range	n	range	n	range
TP µg P l^{-1}	In situ	64	40 - 300	62	50 - 380	44	50 - 770
	Lab	30	46 - 365	31	68 - 428	38	48 - 706
TRP µg P l^{-1}	In situ	65	20 - 70	63	0 - 60	45	0 - 60
	Lab	30	8 - 77	31	7 - 111	38	6 - 76
NO_X-N mg N l^{-1}	In situ	130	0.62 – 1.7	126	1.6 – 4.8	119	0.72 – 2.1
	Lab	30	0.11 – 1.7	31	0.66 – 5.1	38	0.24 – 2.1
NH_4-N mg N l^{-1}	In situ	130	0.12 – 0.32	126	0.04 – 0.14	119	0.55 – 1.5
	Lab	30	0 – 0.19	31	0.01 – 0.13	38	0.09 – 0.48

Table 1. Summary of values (min – max) measured in drainage from the three NWFP sub-catchments using both the in situ automated analysers and laboratory analysis of manually collected samples.

	Catchment	Intercept	*p*-value	Slope	*p*-value	R^2
TP	2	22.40	0.033	0.79	0.002	0.85
	5	-2.34	**0.881**	1.09	**0.293**	0.84
	8	20.45	**0.259**	1.04	**0.482**	0.86
TRP	2	23.48	0.003	0.46	0.006	0.18
	5	22.48	0.001	0.22	0.000	0.09
	8	19.08	0.003	0.41	0.000	0.21
NH_4-N	2	0.24	0.000	-0.15	0.003	0.01
	5	0.05	0.000	0.67	0.001	0.67
	8	0.46	0.000	2.17	0.000	0.83
NOx-N	2	0.63	0.000	0.54	0.000	0.98
	5	1.20	0.000	0.70	0.000	0.96
	8	0.80	0.000	0.60	0.000	0.98

Table 2: Summary of linear regression outputs for in situ versus laboratory data. The *p*-values that are bolded indicate intercepts or slopes that are not significantly different to zero or one, respectively, at the 95% level.

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 26 January 2018

Hydrology and Earth System Sciences
Discussions

Parameter	Sub-catchment	ME	RMSE	NRMSE (%)
TP	2	-8.07	32.13	39.4
	5	12.05	43.47	50.1
	8	30.98	67.62	42.2
TRP	2	3.27	18.19	110.6
	5	-12.68	26.13	117.1
	8	-4.83	20.55	101.1
NH_4-N	2	0.20	0.21	638.7
	5	0.03	0.04	88.5
	8	0.82	0.84	626.6
NOx-N	2	0.30	0.40	68.3
	5	0.47	0.72	43.8
	8	0.47	0.54	80.1

Table 3: Summary of goodness of fit statistics for in situ versus laboratory data.

Sub-catchment 2				Sub-catchment 5				Sub-catchment 8			
TP (µg P l^{-1})		TRP (µg P l^{-1})		TP (µg P l^{-1})		TRP (µg P l^{-1})		TP (µg P l^{-1})		TRP (µg P l^{-1})	
In situ	Lab	In situ	Lab	In situ	Lab	In situ	Lab	In situ	Lab	In situ	Lab
50	45	20	36	50	80	20	42	50	48	20	7
60	77	20	40	70	72	20	36	160	161	20	27
170	174	60	61	210	197	50	83	390	371	50	61
140	138	50	52	150	133	40	47	250	194	60	56
70	73	20	25	60	68	20	46	70	60	30	15

Table 4. Comparison of TP and TRP data obtained from in situ analysers and laboratory analysed manual samples of discharge sampled at the same time (i.e. genuine temporal pairs).

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 26 January 2018

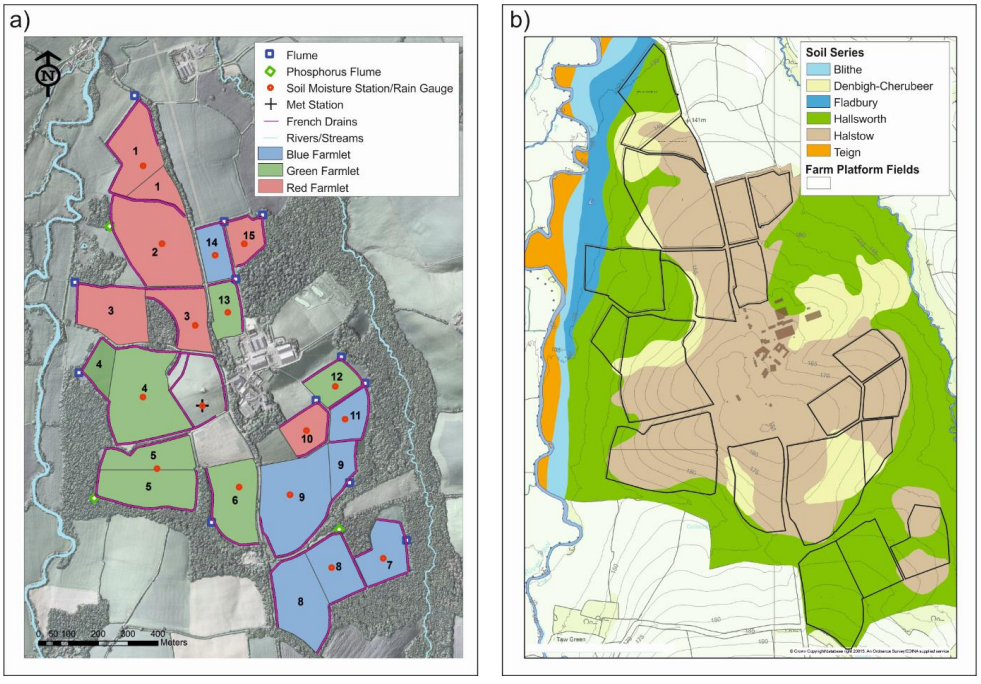


Figure 1: Maps of a) the North Wyke Farm Platform including infrastructure and b) soil series distribution.

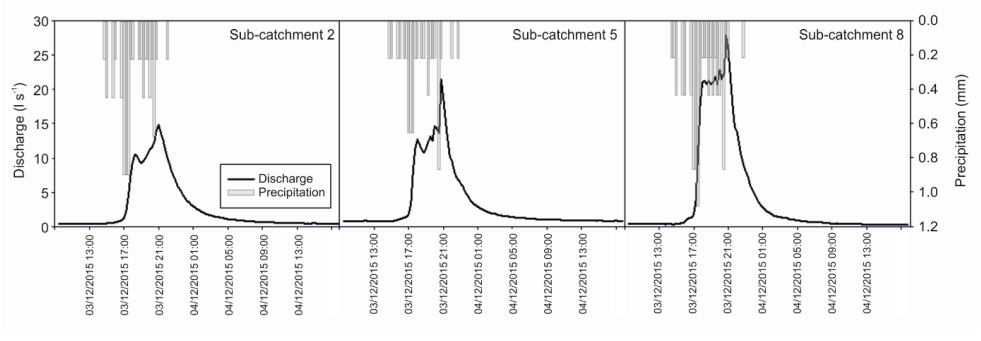
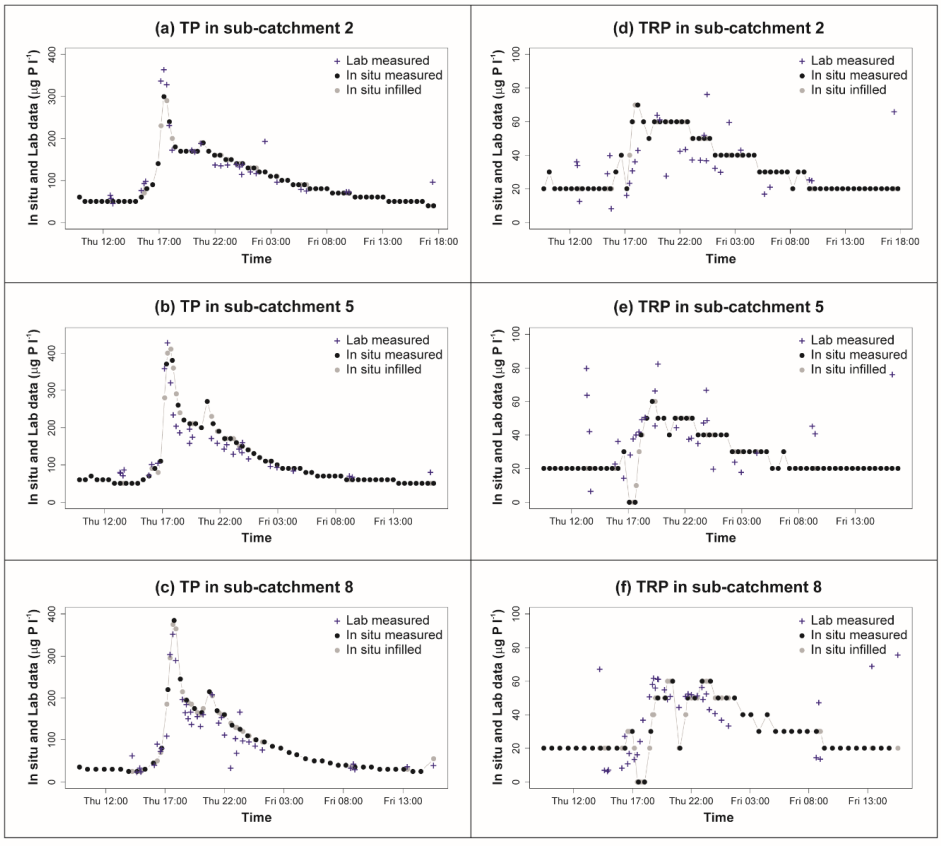


Figure 2: Discharge and precipitation for each sub-catchment.

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 26 January 2018

Hydrology and Earth System Sciences
Discussions
Open Access
EGU



666

667 **Figure 3:** Time series plots for Total Phosphorus and Total Reactive Phosphorus showing the
668 data measured in situ relative to that measured in the laboratory physical sample, and the
669 modelled 'in filled' data.

670

671

672

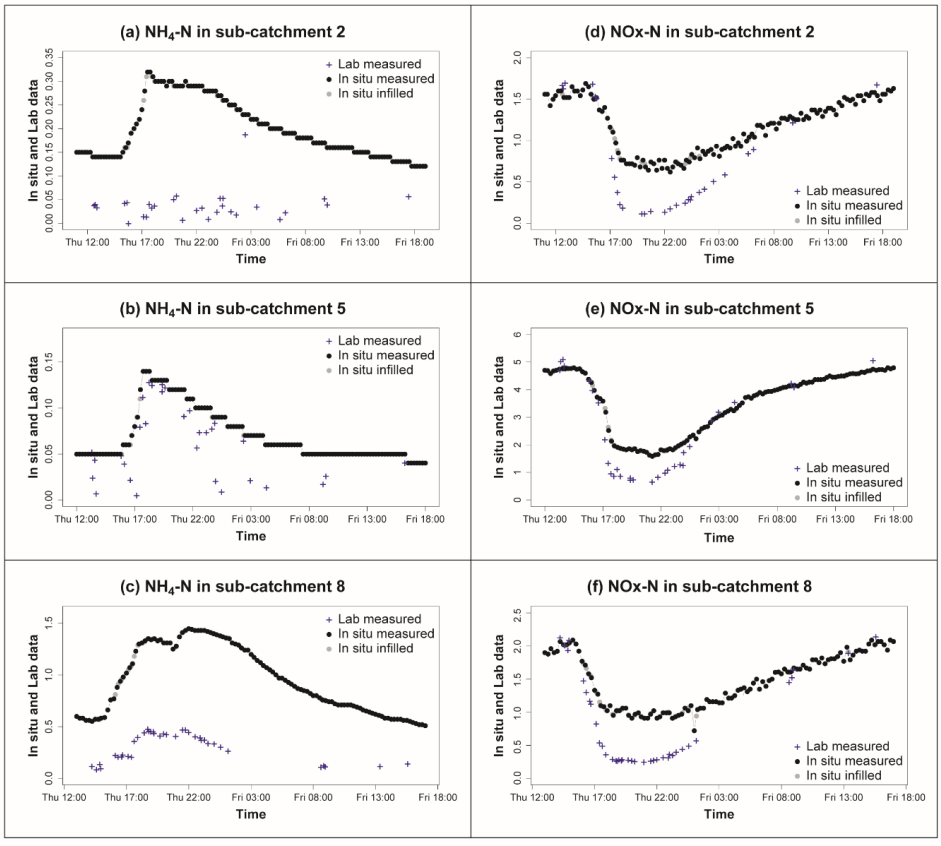
673

674

675

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 26 January 2018

Hydrology and Earth System Sciences
Discussions



676

677 **Figure 4:** Time series plots for NH_4-N and NOx-N showing the data measured in situ relative

678 to that measured in the laboratory physical sample, and the modelled 'in filled' data.

679

680

681

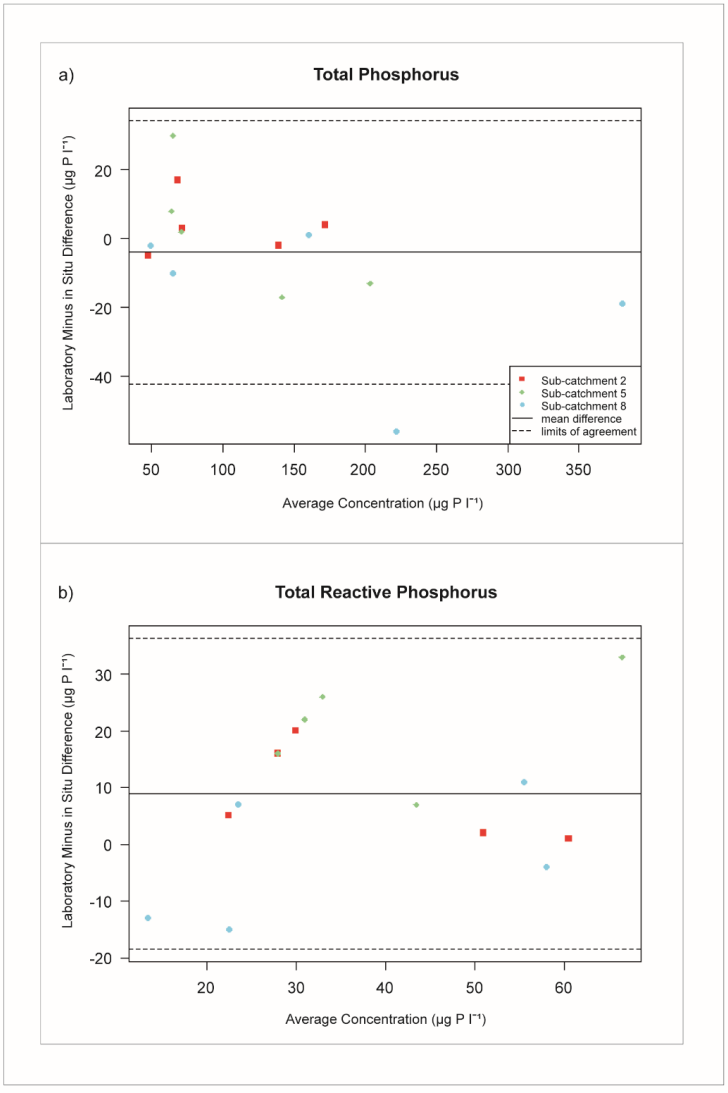
682

683

684

685

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 26 January 2018



686

687 **Figure 5.** Tukey mean-difference plots showing the average concentration of the two

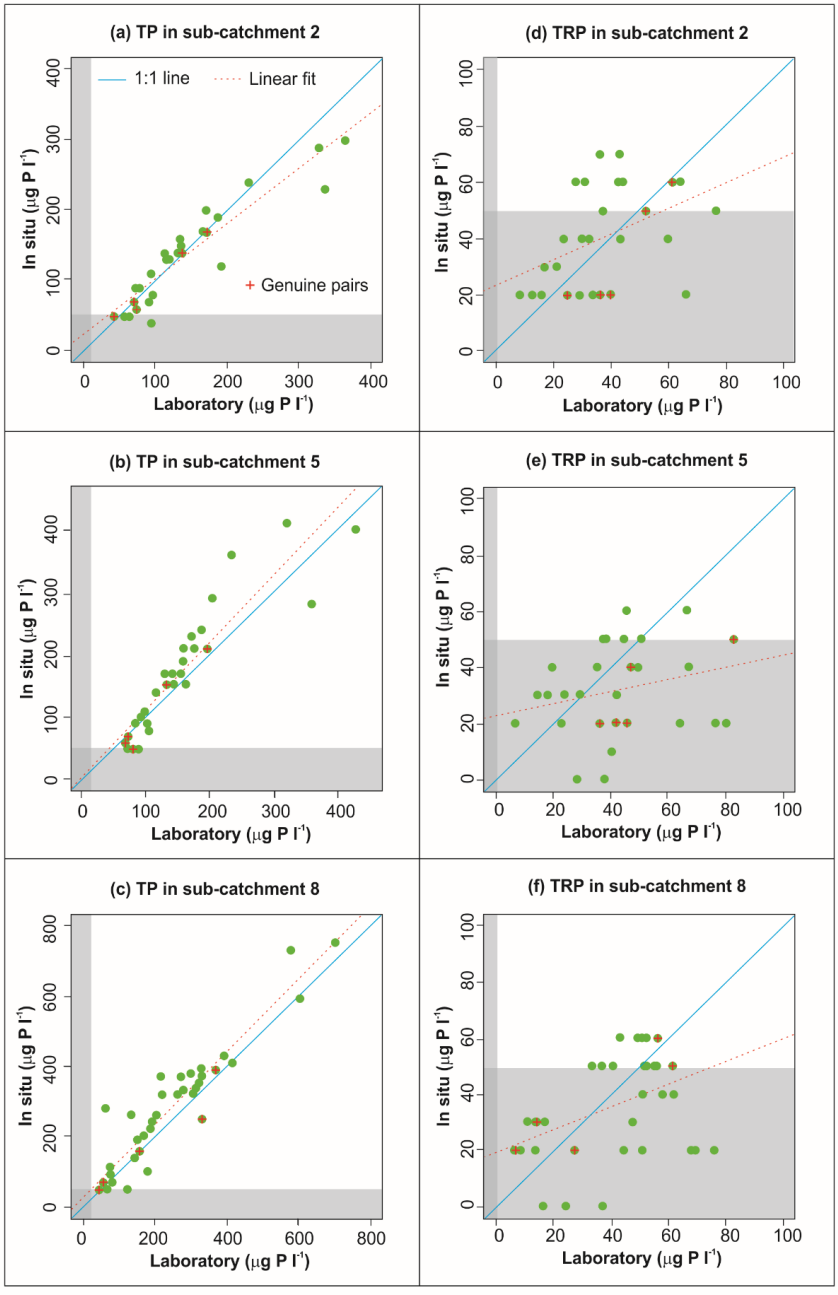
688 measurement methods against the difference between the two values (for TP and TRP only).

689

690

691

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 26 January 2018



692

693 **Figure 6:** Scatterplots for paired TP and TRP data. Shaded grey areas indicate areas below

694 limits of analysis for accurate determination.

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-684
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 26 January 2018

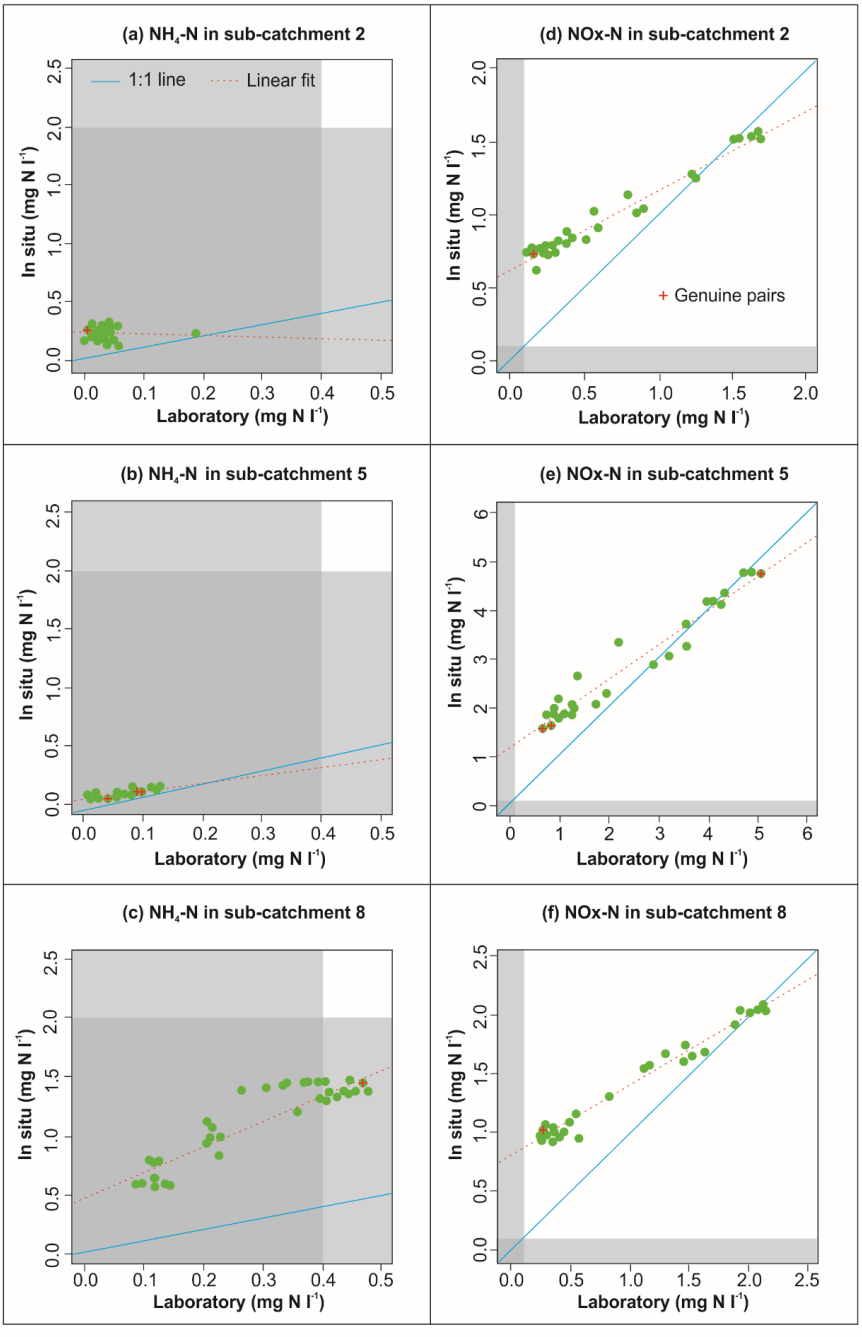


Figure 7: Scatterplots for paired NH_4-N and NOx-N data. Shaded grey areas indicate areas below limits of analysis for accurate determination.