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Hydrology and Earth System Sciences Discussions

Interactive comment on "From existing in situ, high-resolution measurement technologies to lab-on-a-chip – the future of water quality monitoring?" *by* A. J. Wade et al.

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The authors' response to the review comments are listed here and also contained in attached file loaded as supplementary material. This is done since the format of the attached file is clearer than this list of the reviewers' comments and the associated response. Figure 6 and 7 have been revised and drafts are also attached.

"From existing in situ, high-resolution measurement technologies to lab-on-a-chip – the future of water quality monitoring?" by A. J. Wade et al.

Authors' response to review comments. The authors thank the three reviewers for their thoughtful and constructive comments that have helped to enhance the paper. It is pleasing that the three reviewers found the paper a useful addition to the broader literature.

Comment/response to referee#1

Major remarks The majority of this paper offers good insights into the use of high frequency chemical monitoring technology in rivers and is a good example of use in lowland river settings. The paper is well written and generally well presented. I enjoyed reading the paper and seeing how the technology has been deployed and critically assessed and data interpreted with regard to process understanding and phosphorus load estimation. Response: The authors are really pleased that the paper was useful.

However, the title promises more. After reading, it's clear that the reference to lab on-a-chip technology is not part of the comparison and the material in section 5.5 is speculation rather than based on comparative deployment results. I think it detracts from the paper and reads a little like a grant application. The title could therefore be changed (and the hanging question mark removed) to reflect what the paper is about. This is an appraisal of in-situ high-resolution monitoring technologies and data insights in lowland rivers.

Response: The authors agree that section 5.5 is speculative. The section was included to start discussion on the need for novel, miniature sensors and the authors still think that such technology is much needed to progress water quality monitoring. The section will be rewritten, if a revised paper is invited, in accordance with the request of reviewer#1 (see response to the next comment). A proposed new title is 'Hydrochemical processes in lowland rivers: insights from in-situ, high-resolution monitoring'.

Lab-on-a-chip technologies are still open to question as is the use of extensive deployments of passive samplers. This will require much more research and development and it will be good to see critical comparisons, in ambient river systems, in the literature. Specifically, questions related to limits of detection, biofouling (if the mains powered

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and large Filtrax system was prone to biofouling here then I suspect that miniaturised ion-chromatography methods will be challenged) and deployment time should be compared against those methods that show a robust, accurate and sustained data run in complex and challenging river systems. I agree with some of the points on sustainability of bankside wet chemistry methods and that research to provide alternatives is a good objective. The whole of section 5.5 should therefore be condensed to a few referenced lines, and possibly with references to passive samplers, suggesting these (l-o-a-c and passive samplers) as a possible low cost, extensive monitoring solution but which will require testing across gradients of river systems alongside the wet chemistry platforms reported as an example in the manuscript. The manuscript is long anyway and this condensing will not affect the main messages.

Response: These are good points which on-going research is addressing, in particular the issue of biofouling. As noted in the response to the previous comment, section 5.5 was included to stimulate discussion and to note that miniaturised sensors are being developed. On reflection, the authors agree with the comment, but wish to keep the first two paragraphs of section 5.5 since this is felt to be useful discussion regarding the current state of the art in miniaturised water chemistry sensors. The section will be reduced in length and re-written to make the key points, noted by the reviewer in this comment, and to provide the main references.

Other comments Abstract The last three sentences of the abstract are irrelevant really – last section saying 'justified' is not...justified. Response: Agree – this claim is not demonstrated and therefore the last three sentences have been deleted from the abstract.

Claims of issues related to electricity supply and elsewhere with data processing are surprising – installation/deinstallation costs of new supplies, even in rural areas, are not generally prohibitive and water information systems are well able to cope with hydrometric time series at high resolution. Here and elsewhere, reference to daily sampling for annual load estimates is useful but consideration should also be given, here and

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where relevant, that the sub-daily sampling (here noted as 7hour potentials) will also pick up diurnal changes – not picked up by daily sampling.

Response: Lack of mains electricity is a key limitation as demonstrated by the problems at the Clatford site. The costs of installing a new mains electricity supply vary with the site, but even in lowland England the costs, which might involve additional cabling, transmission poles, transformers, negotiation of wayleaves, planning permissions etc, are likely to be large in comparison with available monitoring budgets. Sampling in more remote locations in upland UK would be even more expensive given the need for perhaps several kilometres of cable, and that much of the uplands are subject to various forms of statutory protection.

It is agreed that a benefit of sub-daily sampling will help identify diurnal patterns, but even seven hourly sampling does not always pick up these. A recently accepted paper, which has just appeared on-line and would not have been available to referee#1, demonstrates that even with a seven-hour sample frequency, complete diurnal patterns are missed for those determinands dependent on biological processes which differ between night and day (Halliday et al., 2012).

Halliday, S. J., Wade, A. J., Skeffington, R. A., Neal, C., Reynolds, B., Rowland, P., Neal, M., and Norris, D.: An analysis of long-term trends, seasonality and short-term dynamics in water quality data from Plynlimon, Wales, Sci. Total Environ., 434, 186-200. (2012)

Page 6461 line 18. Delete "the" Response: This will be done.

Page 6462 line 2. References should include (Fealy et al., 2011;Wall et al., 2011; Jordan et al. 2012; Mellander et al., 2012; Mellander et al. – in press; Mellander et al. - in press). Response: These are useful and will be added to a revised version.

Suggested refs: Mellander, P.-E., Jordan, P., Wall, D.P., Melland, A.R., Meehan, R., Kelly, C. and Shortle, G. (2012) Delivery and impact bypass in a karst aquifer

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with high phosphorus source and pathway potential. Water Research, 46 (7). pp. 2225 - 2236. Jordan, P., Melland, A.R., Mellander, P.-E., Shortle, G. and Wall, D. (2012) The seasonality of phosphorus transfers from land to water: Implications for trophic impacts and policy evaluation. Science of The Total Environment, doi: 10.1016/j.scitotenv.2011.12.070. Wall, D., Jordan, P., Melland, A. R., Mellander, P. -E., Buckley, C., Reaney, S. M. and Shortle, G. (2011) Using the nutrient transfer continuum concept to evaluate the European Union Nitrates Directive National Action Programme. Environmental Science & Policy, 14 (6). pp. 664-674. Fealy, R. M., Buckley, C., Mechan, S., Melland, A., Mellander, P. E., Shortle, G., Wall, D. and Jordan, P. (2010) The Irish Agricultural Catchments Programme: catchment selection using spatial multi-criteria decision analysis. Soil Use & Management, 26 (3). pp. 225-236. Melland, A.R., Mellander, P.-E., Murphy, P.N.C., Wall, D.P., Mechan, S., Shine, O., Shortle, G., Jordan, P. Stream water quality in intensive cereal cropping catchments with regulated nutrient management. Environmental Science & Policy, doi.10.1016/j.envsci.2012.06.006 – in press. Mellander, P.-E., Melland, A.R., Jordan, P., Wall, D.P., Murphy P. and Shortle, G. Quantifying phosphorus and nitrogen transfer pathways in agricultural catchments using high time resolution data. Environmental Science & Policy, 10.1016/j.envsci.2012.06.004 – in press.

It will be necessary, therefore, to change “of assessing streamwater quality has been limited to a handful of studies” to “of assessing streamwater P and N quality has been reported in a growing number of studies”. Response: Agree.

Page 6462 line 9 Should read “field-based spectrophotometric equipment similar in scope to that reported elsewhere (e.g. Wall et al., 2011)”. Response: Agree

Page 6462 lines 16-19 Delete. Response: The authors agree to this suggested deletion since a prototype device is not yet ready and no evidence of the benefits are presented in the paper. However, the authors wish to keep some discussion of the possibilities in section 5.5 to highlight what is possible with new technologies.

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Page 6462 line 24 “good” can mean many things here. Do you mean “complete, weekly” ? Response: The sentence will be revised to read ‘Of these sites, high-frequency water quality datasets were obtained for Enborne at Brimpton and The Cut at Bray.’

Page 6463 line 27 What did the study show? Response: The authors agree that the sentence does not describe the key findings of the study. The sentence will be changed to read ‘The sediment and phosphorus dynamics of the Enborne was thought to be controlled by diffuse inputs with subsequent in-stream processing (Evans and Johnes, 2004; Evans et al., 2004).’.

Page 6468 line 14 I believe the Sigmatax delivers sample to the ultra-sound chamber via positive pressure rather than by a vacuum. Response: On re-reading the Sigmatax manual this is correct, the sample is delivered via positive pressure. The text will be changed.

Page 6469 line 7 As the operational filter is 0.45 μm, need to mention at least this and why 0.15 μm was used. Response: The filter size in the Filtrax was 0.15 μm which is different from the usual 0.45 μm filter used prior to laboratory-based determination of soluble fractions. The filter in the Filtrax was built into a moulded unit and could not be changed. Text will be added to the revised version to note this.

Page 6472 line 20 Delete this sentence. You report on issues rather than justify the use of miniaturisation – which you don’t use in this study. Response: The authors disagree since the work at Clatford shows that, where power is not readily available, it would be useful to have an alternative sensor technology that could be sustained without access to mains power.

Page 6473 line 5 Consider a different word to ‘gleaned’ Delete last line of paragraph. Response: The sentence ‘The suitability of deploying laboratory-based instrumentation into the field is discussed, given the experiences gleaned from this study.’ will be changed to ‘The suitability of deploying laboratory-based instrumentation into the field is discussed, given the experiences of this study.'.

Page 6474 line 10 To end of sentence consider adding, "similar to findings for rural point source discharges reported in Northern Ireland rural streams by Jordan et al. (2007)." Response: the suggested extra words will be added.

Page 6474 line 14 and 16 Does the p value in the equation relate to 99% CI? Response - The p-value refers to the 95% confidence interval, which is already noted in the paper.

Page 6474 line 20 etc. Is it likely that combined storm overflows were part of high flow nutrient transfers? These need to be mentioned somewhere. Response: It is possible that Combined Sewer Overflows were part of high flow nutrient transfers but we have no data on these or sewage misconnections. A note will be added that further work is required to look at the importance of CSOs and sewage misconnections.

Page 6475 line 1 You infer that septic tank systems are a storm dependent transfer. Some reference to these as point sources also needs to be made. Response: The authors agree that septic tanks can act as multiple point sources and this will be referred to.

Line 6476 line 5 You need to complete this comparison by indicating that yours was made on higher resolution data and reasoning. Response: Agree. A note will be added.

Section 5.1.3 Some validation data of the Nitratax probe would be important for the readership (see Macintosh et al. 2011 which shows a calibration curve specific to two sites). Response: The Nitratax probe was tested before deployment using standard solutions between 15 and 185 mg NO3 l-1 in the laboratory and was also removed from the field periodically and re-checked. At 15 mg NO3 l-1 the standard deviation was 0.3 mg NO3 l-1 (rsd = 2.0%) and at 185 mg NO3 l-1 the standard deviation was 12 mg NO3 l-1 (rsd = 6.5%). This text will be added to the methods section.

Page 6477 line 19 "the lower Thames". Response: 'the' will be added.

Page 6478 line 10 “that the photosynthetic” Response: ‘that’ will be added.

Page 6479 line 28, 29 I thought that describing storm dynamics as nuanced was interesting. Maybe there are dissimilarities with other catchments in terms of storm transfers but it is important to note that use of high resolution, in-situ equipment elsewhere has been used in the recognition that this was the major process, and that point source signals were nuanced. Response: The high resolution, one-hour data show the difference in storm responses. An example is provided in Figure 6 where flow events can result in either concentration or dilution of TRP, likely dependent on re-suspension of the bed material, delivery of P from diffuse sources and dilution of point sources. As such, the term ‘nuanced’ here is used to describe the fact that different catchment behaviours in terms of TRP are evident during different storms. The dilution of TRP under high flows during winter suggests the point sources are the predominant control on the in-stream TRP dynamics. Figure 6 will be revised (attached) and will show turbidity to provide better evidence of bed resuspension and diffuse delivery, and the following text will be added.

The high-frequency TRP measurements for the rural Enborne reveal a complex system with subtle variations in dilution and concentration. This complexity in response can be seen in the one month period between 23rd January and the 22nd of February 2011 (new figure 6). At the start of the period flow was in decline following a high flow event at the start of January (new figure 6). Although there is a high degree of diurnal variability in the TRP concentration, it is clear that as flows decline there is a steady increase in the streamwater TRP concentration, with TRP and flow exhibiting a significant negative correlation between 23rd Jan and 9th Feb (= -0.86, $p < 0.001$, N = 426). This increase in concentration with declining flow suggests that even during this winter period, point sources of P still dominate the stream dynamics. When flow starts to increase on the 10th Feb there is an initial dilution in TRP concentration, which is followed by a small peak in concentration, then the TRP concentrations starts to decline as the flow declines (new figure 6). The initial decrease in concentration

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is due to the increased dilution capacity of the river as flow starts to increase. The increase in TRP concentration associated with this discharge peak corresponded with a small peak in turbidity, 25 NTU, and this was thought most likely due to mobilisation of sediment from the stream bed since the peaks in flow and turbidity occurred at the same time. After this initial flow peak there were further three flow peaks during this event (new figure 6). The second and largest flow peak, 5.74 m3 s-1, was associated with a large peak in TRP concentration, 0.17 mg P l-1, and a large peak in turbidity, 81 NTU. Again this peak in TRP concentration is likely to be caused by mobilisation of stream bed sediments and possibly also a mobilisation of P from diffuse sources under high flow conditions. After the concentration peak, TRP concentrations decline as the flow declines. The third flow peak of this event also caused a peak in TRP concentration, 0.10 mg P l-1, however although turbidity increased, the timing was not completely consistent with the flow and this peak in TRP concentration is thought more likely to represent the delivery of P to the stream from diffuse sources. The last flow peak of the period does not cause an increase in TRP, instead the TRP concentration remains in decline following the preceding flow peak (new figure 6). This suggests an exhaustion of P supply from diffuse sources during this event such that the delivery of water causes a dilution in the P being supplied from the catchment point sources. The propensity of this system to switch between point- and diffuse-source domination, dependent on the flow conditions, highlights the complexity involved in managing the system and designing effective P reduction strategies.

Page 6480 line 28 Jordan et al., (2007) only suggested that the data could be used to constrain models. Response: Re-reading Jordan et al. (2007) the authors agree and so this note will be deleted.

Page 6481 lines 2 and 3 I wasn't sure how you differentiated 24h from daily sampling. Also, while it is useful to show how the daily sampling appeared adequate to be integrated into annual loads, to be balanced, some discussion is needed here or elsewhere to contextualise to other systems - i.e. is there a take home message on general reso-

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lution or are you implying that sample resolution for load will depend on system? How will this be determined, etc. See also previous comment on pattern recognition with sub-daily samples. Response: The 24h refers to a frequency of the resampled data but this equates to daily sampling and the term '24h' will be changed in the text to 'daily' to help avoid confusion. The sentence 'This was due to an exhaustion of material entering the river during storm events for phosphorus (Fig 6).' will be replaced with the following text:

Recent studies have demonstrated that a high proportion of nutrient load is delivered to agricultural river systems during storm events, therefore low frequency sampling regimes may provide a biased sample dependent on whether or not high flow events have been captured (e.g. Jordan et al., 2005; Cassidy & Jordan, 2011; Jordan & Cassidy, 2011). In these cases, sub- daily sampling is necessary to fully quantify nutrient delivery. In the case of the River Enborne, the predominant source of TRP is STWs and therefore TRP delivery and in-stream load is not controlled by the occurrence of high flow events, unlike the more agricultural systems studied by Jordan et al. (2005).

Page 6481 line 18 sentence structure suggest, "in the field for P and also for NO3,..." Response: Agree, the wording will be changed.

Page 6483 line 4 Change "done" to "undertaken" Response: this is a personal preference by the reviewer.

Page 6483 line 5 Change to: "provide a temperature controlled environment" Response: The text will not be changed since the distinction is needed between providing warmth so the instruments can function, though the data may need temperature correction, and 'temperature controlled' which refers to having a more precise control over the temperature such that no temperature correction is necessary.

Page 6484 line 7 Do these issues also refer to Nitratax? Again, some comparison and performance data would be useful. Response: The Nitratax uses UV absorbance and the temperature tolerance is 2 to 40 oC. The minimum streamwater temperature

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in the River Enborne was 0.2 oC and the first percentile of the distribution was 1.3 oC. Thus, there may be an effect at the lowest temperatures measured. Streamwater temperatures below 20C were measured for a total of 109 hours, during the early mornings of November and December 2010, throughout the duration of the sampling programme, but otherwise a temperature effect is not expected. Further work is needed to determine the magnitude of the temperature effect on the nitrate concentrations during extreme cold periods. A note will be added to the paper. Section 5.5 See above. Reduce to a few referenced lines and incorporate. Not only is the section unjustified, it appears as an annex to the main thrust of the paper – which is really interesting. Therefore, amend last sentence of conclusion. Response: The authors were trying to provide a case for further research into novel, miniaturised sensors. The authors take the point that all three reviewers have made and accept, that while such technologies are much needed, section 5.5 is not well justified. The section will be shortened to note the main issues and suggested main lines of enquiry but no more. It is felt this is reasonable for the discussion section of the paper.

Figure 1 It wasn't clear on my print-out where the Kennet catchment was Response: Figure 1 will be re-drawn and possibly merged with Figure 2.

Figure 6 The discharge and TRP charts need to have the same axes and start from zero for clarity and comparison. Response: Figure 6 will be replaced and new text added. Please see the response above (Page 6479 line 28, 29).

Comment/response to referee#2

This is a good paper presenting the "goods and bads" of high frequency sampling of stream water chemistry, and introducing where to go next. The implementation of in situ automatic samplers and analyzers has been done carefully, and the authors have done an excellent job testing the quality of the data acquired in the field. The paper reads well, yet some sections need to be revised/shortened for improving clarity. Response: The authors are pleased that the paper was useful.

The introduction is somehow overlooking a bunch of studies performed during the last decades in which high frequency monitoring during storm events has been performed for understanding hydrological flow paths and sources of nutrients in pristine and non-pristine catchments. These storm-based studies have been useful for increasing load estimation accuracy and for understanding catchment functioning. The authors have undoubtedly a point when saying that continuous high-frequency monitoring is going one step further because it allows answering a set of new and interesting questions such as complex daily cycles during base flow conditions as well as pulses of industrial pollution. However, some reference to these storm-based studies should be made.

Response: Without the specific citations of the storm-based studies it is difficult to know which work the reviewer would like to see referenced. The work of Davies et al., 1992; Evans and Tranter, 1998; Deletic and Maksimovic, 1998 will be cited as these report studies of storm event hydrochemistry in upland and lowland contexts.

Section 2 explains in detail the different urban areas (with their corresponding STW) for each of the three studied catchments. However, the map in Figure 2 does not show the location of many of these towns/counties (?). It does not seem very useful to the reader knowing the name of these towns, especially when many of them cannot be localized in the map. It would be more useful (and the text will be more synthetic) if focusing on the PE of the STWs without giving too much detail on the specific names. Following with section 2, Figure 1 does not seem very informative. I would suggest deleting Figure 1 and enlarging Figure 2 so that key names can be found in the map.

Response: Figure 1 and 2 will be revised as suggested and possibly merged.

It is a bit confusing to refer to the same sampling point with two different names (either Enborne or Brimpton, Kennet or Clatford, Cut or Bracknell). This is especially confusing for the River Cut because the chemical sampling station was at Bray (or Bray Marina, not sure), the streamwater level was recorded at Bighams, but the stream discharge considered in the study was measured at Binfield. Wouldn't it be more simply to use only one name for each of the three rivers? Response: Having re-read the text, it seems that it is necessary to refer to the catchment or the sitename, depending on the context, but the text will be changed to maintain consistency.

In section 4, some info on detection limits and analytical errors would be acknowledged. Be consistent with the subtitles in sections 2 and 3: either “The River X” or “The X”. Response: The detection limits for the Phosphax are 0.01 mg P l-1 for TRP and TP, for the Nitratax 0.3 mg NO3 l-1 and for the Micromac Systea, 0.025 mg P l-1. A note will be added to the Methods section. The subtitles will be made consistent between sections 2 and 3. There are some issues that need to be improved regarding the interpretation of P and N temporal patterns. First, the authors are interpreting daily cycles without a “pristine” or “reference” site not affected by human activities. Thus, they need to be cautious when interpreting daily cycles because the contribution of natural vs human activity on daily cycles cannot be disentangled. Response: We have data from more pristine sites which do not show diurnal patterns with these characteristics (Biogeochemistry, submitted). The tone of the text is careful to highlight that caution is taken when interpreting the data.

Second, the authors refer several times to a two-peak daily cycle exhibited by Q, TRP, and nitrate which they interpreted as an indication of the STW dominance of water and nutrient inputs to the stream. However, such two-peak daily cycle is only clear for discharge (figure 5) and maybe (only some days) for TRP at the Cut. It is not exhibited by TRP at the Enborne and there is no data shown for nitrate. The authors need to analyze these daily cycles more thoughtfully to make a more meaningful discussion of these patterns. Response: The authors agree that the current Figure 7 does not show this diurnal cycling in either TRP or nitrate in a convincing manner. TRP and nitrate diurnal dynamics are complex, but two peak diurnal cycles are observed in TRP in both the Enborne and Cut and in NO3 on the Enborne, at certain times (redrawn Figure 7). The text will be revised to note the complexity in the cycling and the redrawn figure 7 added to highlight that two-peak daily cycling is evident in Q, TRP and NO3 during

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specific periods.

Please, revise the order and the content of the figures. Figure 5 does not fit with its related text. Figure 10 is introduced before Figure 9. Response: This will be done in a revised version of the paper.

Specific points P6462-5. Nitrate instead of NO3. Response: This will be changed.

P6463-6. Which was the recording frequency for these data? Response: The frequency is hourly. A note will be added to the text.

P6464-11. Do not refer to Figure 1 because it does not show these features. Response: Figure 1 and 2 will be revised and the text changed for consistency with the mapping.

P6464-11. Marlborough is not shown in the map (Fig. 2). Response: Figure 1 and 2 will be revised.

P6464-14. Fyfield is not shown in the map (Fig. 2). Response: Figure 1 and 2 will be revised.

P6464-18. Binfield is not shown in the map (Fig. 2). Response: Figure 1 and 2 will be revised.

P6464-19. Do you know the BFI for the river Cut. Response: The BFI is 0.46. This will be added to the text.

P6464-25. Ascot is not shown in the map (Fig. 2). Response: Figure 1 and 2 will be revised.

P6464-26. If Bray Marina and Bray correspond to the same site, delete Marina to be consistent. Response: They are the same site. 'Marina' will be deleted.

P6466-8. Which volume of water was pumped? Response: The pumping was intermittent as described in the paper. The volume of the flow-through cell was designed based on the pumping rate but the concentration is independent of this volume. Given this, the authors think this detail is not needed and no change will be made to the paper.

P6467-11. Is 39025 the EA ID? For Brimpton this is 7128 according to legend in Figure 2. Please clarify. Response: The EA ID is 7128 and the National River Archive gauge number is 39025. The legend will be changed.

P6468-1. Is 39037 the EA ID? For Marlborough this is 7113 according to legend in Figure 2. Please clarify. Response: The EA ID is 7128 and the National River Archive gauge number is 39037. The legend will be changed.

P6468-2. If there are no major tributaries and SWT, the specific discharge should be the same at the two points. However, groundwater lateral inputs may increase stream discharge along the 3 km transect. By how much increases the drainage area between these two points? These could give an idea of by how much stream discharge would increase between Kennet and Marlb. in relative terms. Response: The authors agree with this but since the data are not of sufficient quality to use, then this calculation is not needed.

P6468-3. If acronyms have been defined, make use of them through the text consistently: use STW instead of sewage treatment work. Response: Agree – this will be changed in a revised version.

P6469-14. Is 39052 the EA ID? For Binfield this is 7167 according to legend in Figure 2. Please clarify. Response: The EA ID is 7167 for Binfield and the National River Archive gauge number is 39037. The legend will be changed.

P6469-18. A good relationship between daily mean flow and flow level between the two points indicates a consistent hydrological response. However, it does not imply that stream discharge was similar between the two points. If there are no major tributaries and SWT, one may expect an increase in stream discharge proportional to the increase in drainage area between these two points. If such increase in drainage area is small in relative terms, the approach made by the authors would be appropriate; otherwise, the authors could be underestimating the load of P at the Bray site. This issue may not be relevant for this particular study since the annual loads are not compared among rivers, but it could be an issue for future studies. Response: The authors agree with this and perhaps the text was unclear. The text will be changed to clarify that there is a consistent hydrological response between the flow and level at Binfield and Bighams, but that the flow levels are not necessarily similar. Only the streamwater TRP and nitrate concentrations from the Enborne were used to estimate loads since the water quality and discharge measurements were made at the same site. No load estimates were made for The Cut given flow and concentration data were from two different sites.

P6469-24. What is CEH? Response: the Centre for Ecology and Hydrology. The acronym will be defined in a revised version.

P6470-3. Not for NH4 at Kennet (6467-21). Response: This is correct. The text will be changed.

P6470-25. Figure 5 does not show the agreement between hourly and weekly samples. Response: Figure 8 has been moved forward and the revised text will refer to this diagram. The figure order will be corrected.

P6472-7. Define Le and N. Response: definitions will be added and Le changed to L.

P6473-17. Bray? The authors used stream discharge measured at Binfield, didn't they (P6469-18). Response: 'Bray' will be changed to 'Binfield'.

P6474-12. Considering the fluctuation of P concentration in stream water between consecutive samples shown in Figure 6b, 1 ppb of P may be a too low concentration to be analyzed with precision. Could you add in M&M some information regarding the detection limit and/or the analytical error of the used instrumentation? Response: The detection limit for the Systea C Micromac, used on the Enborne, is 25 μg P l-1

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and, based on laboratory trials, the resolution is 5 μg P l-1. The analytical error of the Systea at 50 μg P l-1 was 3.3 μg P l-1. The detection limit of the Phosphax for both TP and TRP is 0.01 mg P l-1. The instrument was validated using standard solutions. A resolution of 0.01 mg P l-1 is shown in Jordan et al. (2005). The text will be changed to note the lowest value of the range was the detection limit of 0.01 mg P l-1 and not 1 ppb, and details of the validation of the instrument will be added to the methods section.

P6475-5. According to section 3.1, Tp was not measured at Enborne. Response: Correct, TP was not measured. The text will be changed.

P6476-25. According to Figure 7, there is no a two peak cycle in Enborne (at least, it is distinguishable by visual inspection only some days). The two peak cycle in the Cut is not apparent either. In my opinion, the one peak daily cycle at the Enborne (Fig 7b) would suggest that the two peak cycle for Q is not accompanied by a change in the input of P. Therefore, the two peak cycle for Q may not indicate the influence of the SWT on P (or N concentration, unless the P signature of the SWT would be undistinguishable from that in groundwater. Response: A redrawn figure 7 highlights the points made and the text changed to note that this behaviour is evident for specific periods.

P6476-24. Was this two peak diurnal cycle more evident for nitrate than for P? Were nitrate peak concentrations occurring at night or day time? Response: According to the new figure 7, a two peak cycle is evident for both TRP and nitrate on the Enborne .Much of the time nitrate peaks were in the daytime.

P6476-27. Please explain better how denitrification and aquatic vegetation activity would result in high nitrate peaks at midday? Response: This has been discussed at some length by the authors and this section of the paper will be deleted.

P6477-3. Why one would expect that alders prefer fixing N2 during the day when there is enough bioavailable inorganic N in stream water (and likely in groundwater)? N2

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fixation is energetically expensive. Response: Agree. This has been discussed at some length by the authors and the two sentences relating to Alder will be deleted as it is too speculative at present.

P6477-14. Please, check the order of figures in the manuscript. Response: This will be done in a revised manuscript.

P6479-11. Please, explain better for which sort of data analysis this aliasing effect occurs. Some readers of HESS may not be used to work in the frequency domain. Response: The issue of aliasing is noted and refers to frequency domain analysis. The short discussion will be removed since this is not the central to the paper. The interested reader is referred to the cited references.

P6480-2. Please, introduce INCA. Many readers of HESS may not have ever heard about this model. Response: The section on process-based models will be deleted to reduce the length of the paper. Further work with the models is needed. At present, this section is too notional.

P6487-9. Heterotrophic algae? Please clarify! Response: Heterotrophic algae do exist but after some discussion the authors think this part of the discussion is too speculative and the reference to heterotrophic algae will be removed

Caption Figure 5. “occurring” instead of “occur”. Response: This will be changed.

Caption Figure 6. Add “flow and” after Enborne. Response: This will be done.

Figure 2. Enlarge the size of the legend to improve legibility. What is EPSRC? How was the river level calibrated at Bighams? Equivalent instead of Equivelent. Response: Only stage is known for Bighams. Figure 2 will be revised. The acronym EPSRC which stands for the Engineering and Physical Sciences Research Council will be expanded in the revised figures.

Figure 6. Maybe it would be more illustrative to plot Q vs concentration, the hysteresis loop will be more clearly seen than in the actual plot. Response: Figure 6 now (see

above) shows flow, TRP and turbidity to better illustrate the different responses.

Comment/response to referee#3 This is a well-written paper in which the authors present a novel and thought provoking study that I believe is of wide interest and worthy of publication. Unfortunately, the title of the paper is not appropriate. While the authors' results may motivate the need for new water quality monitoring technologies, I cannot see that this is the primary focus of the paper. The authors have presented a novel and important study of high frequency variability in nutrient dynamics in two urban UK rivers. This study considerably expands our knowledge base about short term variability in riverine nutrient concentrations. As the authors note, all previous research on high frequency variability in water quality time series has focused on rural catchments. Adding time series from urban rivers adds significantly to our overall understanding of riverine water quality and the greater than previously expected impact of sewage treatment works. Response: Thank you for the positive comments. The title will be changed (see response to reviewer#1).

The authors claim the high frequency time series display "seemingly chaotic" (p 6459 l 11) behavior. If by this, they mean 1/f spectral scaling, it would be most informative if they could present these results. It would be interesting to see if point source inputs such as are found on their study sites change the slope of the power spectra. Response: The term 'seemingly chaotic' was used to describe a time-series that appeared to contain random patterns that were driven by deterministic factors. It would be the subject of a further research article to assess if the data were chaotic according to explicit mathematical criteria, such as the Lyapunov exponent. Tests for chaos are known to be highly dependent on the noise content of the time-series and claims that time-series are chaotic in other academic disciplines, such as economics, have been controversial. The phrase has been removed, though it shall be interesting to follow-up with a study to establish if the time-series are chaotic, or otherwise. From what I can tell, the authors have made a thorough review of high frequency water quality monitoring programs in the UK and Ireland. However, they may also wish to refer

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to Ferrant et al. 2012 "Continuous measurement of nitrate concentration in a highly event-responsive agricultural catchment in south-west of France: is the gain of information useful?" Hydrological Processes for a French perspective. Response: This is a useful reference and has been added. The authors were unaware of this article since it does not yet appear on ISI Web of Knowledge and a specific search of Hydrological Processes had to be done to find it.

It would be helpful if the authors adopted consistent naming conventions for their sites. It is confusing to have the sites referred to as Cut, Bray or Cut at Bray and Enborne, Brimpton or Enborne at Brimpton. I realize that all site names are provided in the map in Figure 2 but it is inconvenient to have to keep referring to it. Response: The text has been reviewed and will be changed to help maintain consistency in the naming convention.

The discussion of the INCA models on p 6480 l 1-24 was confusing and perhaps unnecessary. My understanding is that INCA is a daily time step model. It seems unfair to expect a daily time step model to reproduce sub-daily phenomena. If a process-based deterministic model were run on an appropriate time step, do the authors believe it would reproduce the observed time series? It also seems a little odd to suggest using a complex, daily time step model like INCA to reproduce annual mean concentrations.

Would a simpler export-coefficient approach be more useful? Is there any evidence to suggest that the structure of current bucket type models precludes simulation of fractal noise sensu Kirchner et al. (2000) or can this failure be ascribed to inappropriate model parameterization? Response: The authors included the section on process-based modelling, using INCA as an example, to begin to consider how sub-daily data could be used in models. It is agreed that this theme is not well developed in this paper and therefore the section has been deleted to reduce the length of the paper and focus more on the description of the dynamics. Modelling experiments using the carbon version of INCA has shown that the slope of the regression line between wavelength and spectral power has a value of 2, which is expected for current 'bucket' models

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that assume a well-mixed reservoir (Kirchner et al, 2000). Further work would be necessary to determine if different model parameter sets would change this as part of an additional project.

I have a great deal of difficulty with sections 5.4 and 5.5 and suggest they be removed from the revised version. While it is refreshing to see an explicit recognition of the difficulties inherent in collecting high quality water chemistry data, it is not clear to me that this discussion is necessary in the peer-reviewed literature. While I agree with the authors that current monitoring technologies are less than ideal, and that so-called “lab on a chip” technologies may revolutionize water quality monitoring, I would like to see more firm evidence of “lab on a chip” technology being successfully deployed outside the lab. Response: The authors would like to retain section 5.4 in part, since it provides a summary of the issues and justifies why effort should be made to move the science on from deploying laboratory-based kit into the field and develop novel, miniaturised sensors. This section maybe of interest to scientists and engineers working on new sensor technologies to understand better the issues to be addressed and system specifications. Hopefully this discussion will help efficient deployment of resources in future. Section 5.5 will be re-written to be more focused (see response to reviewer#1).

If sections 5.4 and 5.5 were removed, the abstract could end with the statement on p 6459 l 24 that “These results highlight the utility of sub-daily water quality measurements”. Sections 2.2 and 3.2 could be deleted as it does not seem that any results from the Kennet at Clatford are presented. It seems that the Kennet site is only described to give context for the difficulties described in section 5.4, p 6482 l 21 – p 6483 l 4. Response: The last two sentences of the Abstract will be deleted. The description of the site at Clatford will be retained in a revised version because it is useful to note the issues encountered when there is no mains power.

Some of the most important results the authors present are in table 1. I would like it if they could focus more on these results and their implications for monitoring programs. Response: This is addressed in the response to reviewer#1. The authors now highlight

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that different sampling frequencies are required to estimate loads in different types of catchment. The following text will be added.

Recent studies have demonstrated a high proportion of nutrient load is delivered to agricultural river systems during storm events, therefore low frequency sampling regimes may provide a biased sample dependent on whether or not high flow events have been captured (e.g. Jordan et al., 2005; Cassidy & Jordan, 2011; Jordan & Cassidy, 2011). In these cases, sub- daily sampling is necessary to fully quantify nutrient delivery. In the case of the River Enborne, the predominant source of TRP is STWs and therefore TRP delivery and in-stream load is not controlled by the occurrence of high flow events, unlike the more agricultural systems studied by Jordan et al. (2005).

In my experience, the chemical flux estimates for many regulatory programs (i.e. OSPAR and the WFD) are based on monthly or biweekly chemical samples. Table 1 shows some of the difficulties that may result from fixed time sampling. It would be most informative if the authors could expand their analysis to present maximum and minimum estimated loads based on the different temporal resolution of sampling schemes. Presenting the maximum and minimum estimated loads from the 7 different weekly sampling possibilities and similar analyses for fortnightly and monthly resolution data would be extremely important for putting into context and providing possible estimates of uncertainty of loads based on fixed time sampling. Response: This is moving away from the main emphasis of the paper which is to introduce new insights into the hydrochemical functioning of the catchments rather than focus specifically on load estimation which has been done in detail by others (Rozemeijer et al., 2010; Jordan and Cassidy, 2011; Ferrant et al., 2012). An interesting next step would be for all those with sub-daily monitoring data to meet and address issues such as load estimation in a common way for a range of sites.

Minor concerns: I would rather the authors refer to nitrate as NO3- instead of NO3 and NH4 as NH4+ Response: This is a personal preference and therefore no change has been made.

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P 6476 l17 – should be “. . . Kennet where streamwater . . .” Response: This will be changed.

The authors made significant attempts to reduce algal growth in their sampling systems. Was there any evidence of biofilm growth or fouling? Response: There was significant biofouling on the pump intake and within the monitoring equipment hence the need for cleaning every fortnight. This will be noted in the text.

13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? – YES, sections 2.2,3.2,5.4 and 5.5 could be eliminated. Response: Sections 2.2 and 3.2 have been kept since section 5.4, it is argued, should be retained in some way. The authors agree that section 5.5 should be redrafted as suggested by reviewer#1 and this will be done.

Please also note the supplement to this comment:
http://www.hydrol-earth-syst-sci-discuss.net/9/C4240/2012/hessd-9-C4240-2012-supplement.pdf

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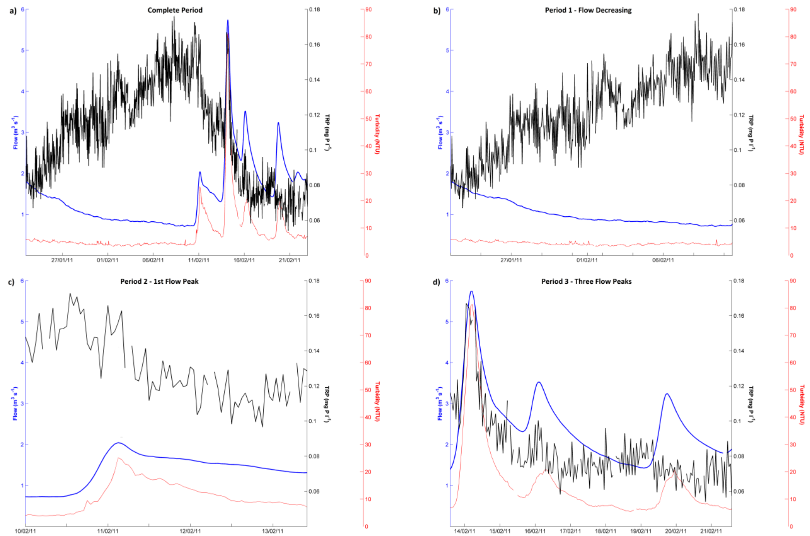

Figure 6 (*revised*): P dynamics on the Enborne for a one month period between January and February 2011. Figures show the complexity of the P response to flow events: a) Complete Period, b) P increasing as flow declines, c) P dilution and increase with flow peak and d) A three peak flow event with varied P response.

Fig. 1. Revised Figure 6

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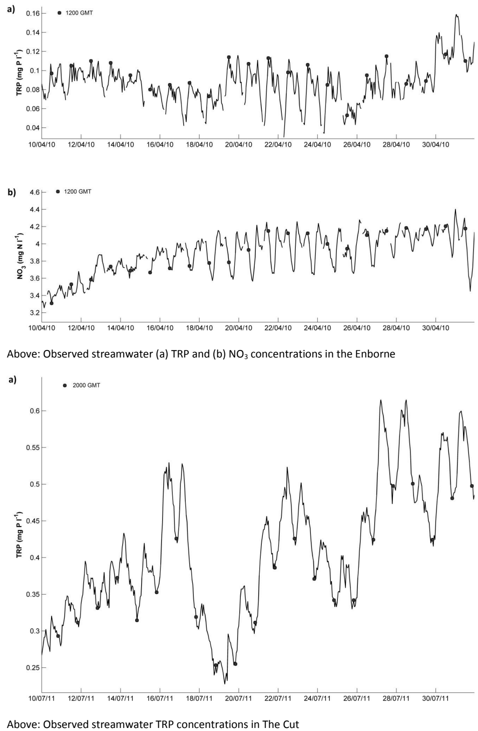

Fig. 2. Revised Figure 7

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