Referees comments are in italics, reply from author is in plain text

A Summary of the Manuscript's Content

The manuscript describes the monitoring of three streams in England during April 2012. The three streams are the Wylye, Blackwater Drain and the Morland and these drain catchments that contrast in terms of location, climate, soil type, geology and land cover. The data presented describe the changes in the flow and streamwater nitrate, ammonium, total phosphorus and total reactive phosphorus concentrations during a major storm event coming at the end of a major drought. The chemical data were collected using instrumentation deployed on the stream bank and therefore issues with sample degradation were avoided. The measurements were made every 30 minutes and are part of a much larger dataset being collected as part of the Demonstration Test Catchment programme. The streamwater concentrations were set in the context of data collected over one hydrological year by plotting the flows and concentrations on flow-duration and concentration duration plots. The results of a storm event hysteresis analysis were used to explore transport pathways and sources of inorganic nitrogen and total and total reactive phosphorus during the storm event, and the analysis was also used to indicate whether the diffuse nutrient sources were source or transport limited. It was concluded that source limitation did not occur in these agricultural systems when the frontal system passed in April 2012.

Evaluation

The article presents important datasets and provides interesting and useful insights into the hydrochemical dynamics during a storm. The subject of the paper is of definite interest to the readers of HESS and a broad international audience, and these new data add to our understanding of catchment hydrochemical functioning. Before the paper can be accepted, I feel there are a number of major issues that need to be addressed by the authors regarding the work, and therefore this review focuses on points of clarification, rather than an in-depth discussion of the results.

The authors thank the reviewer for these comments and we are pleased that you feel this paper is relevant for publication in HESS and that the data add to understanding of catchment functioning.

General Points

1. The title reflects the contents, though it seems unnecessary to include 'demonstration test catchments' at the end. If this is to be kept, then capital letters should be used: 'Demonstration Test Catchments'.

This was a typesetting error and has been corrected.

2. The abstract alone is sufficiently informative, even when read in isolation, however there is an (over)emphasis on describing the supporting research programme which is perhaps unnecessary and makes the abstract too long. The same issue occurs in the introduction.

We have removed superfluous information about the research programme from the Abstract and Introduction.

3. One of my main concerns is that I do not feel the overall aim of the paper is made clear. What do the authors hope to gain by studying the effects of the same frontal system moving over the three

catchments that could not be done by looking at all the extreme events in the data collected since 2011? If it is because of the highly unusual nature of the April 2012 event (coming at the end of prolonged drought), then the analysis needs to account for the different antecedent conditions, reported on page 15128, line 20 to page 15219, line 18. There appears to be an assumption that all three systems are at a similar baseline at the onset of the rainfall event on the 25 March 2012, but I am not convinced by this. For the Wensum, higher rainfall values were reported for March, 2012 than at the other two study sites. The authors note 'The Wensum DTC, by contrast, was already exhibiting relatively high flows before the first event (5.9% exceedance), due to heavy rainfall at the end of March and continued wet conditions in April 2012.' (page 15129, lines 10-12). The different baseline conditions need to be accounted for in the analysis and these differences make comparison difficult and must have an effect on the interpretation of the nutrient transport behavior in the dry-to-wet transition.

The authors agree that some of the more general sentences about the drought condition across the country give the impression that the catchments were all experiencing identical antecedent conditions before the storm event. These sentences have been removed. We did however include a discussion of antecedent conditions before the event with the flow duration curves. We have now, partly in response to other comments made by this reviewer and others, included the time-series data from the hydrological year 2011-2012 (Figure 2) and as part of this we have used an Antecedent Precipitation Index (API) as an indication of antecedent catchment 'wetness' throughout the water year, including a discussion of the API values before the storm (see section 3.1 and 3.2). It is correct that the Wensum had experienced wetter conditions in the run up to the storm and had also experienced a large event in March which we have pointed out as a possible explanation for the quick phosphorus exhaustion in the hysteresis discussion. Reference to antecedent conditions affecting storm response can be found: page 15 line 30 –page 16 line 2, page 17 line 3- page 18 line 1 for the Avon; page 16 line 28 -33, page 18 line 12-16 for the Wensum; page19 line 21-24 for the Eden.

4. As only one event is described in detail, it is difficult to know if the behavior reported in each of these systems is typical, or not. The flow-duration and concentration-duration curves show that the flow and chemical response was extreme within the year, however there is no sense of what the flow and streamwater concentration dynamics are like in general. Given the variation of chemical response expected and the extent of the dataset with measurements made since 2011, it appears a major limitation not to have explored the full dataset to comment on the range of storm responses to provide a comparison with this extreme event (see specific comment 9).

As mentioned above we have taken this comment on board by including time-series data for rainfall, discharge, API, nitrate and TP concentration data for the water year 2011-2012 (Figure 2). The storm period discussed in more detail is highlighted in grey so that the reader can see how it fits in to the context of the temporal dataset for each catchment. We feel this provides the reader with a good deal of information about the general hydrological regimes of the three catchments (section 3.1 and 4.1) and the antecedent conditions that may account for certain storm responses observed within the dataset (section 3.2 as well as comments mentioned above). We discuss this figure in Discussion (section 4.1), along with other relevant information for interpretation of the data such as geology, groundwater nitrate concentrations etc. that build a conceptual model of catchment functioning for

each site. We feel the inclusion of these data has strengthened the paper so we thank the reviewer for this helpful feedback.

5. I am not sure why the authors have modelled the rainfall event when they have tipping bucket gauges in each catchment. The data from the gauges do not appear to have been used other than in Figure 2.

This section has been removed.

6. The catchment descriptions are too brief. There is no overview of how the hydrology or hydrochemistry compares across the three study sites. This is important given the paper is about comparing the flow and chemistry response to a single storm event across the three different sites. Without a discussion of the normal hydrological regime of the individual catchments it is difficult to distinguish differences in storm response between the catchments.

We have increased the amount of information regarding geology and soils in section 2.1. We also believe that these concerns have been addressed with the inclusion of Figure 2 and relevant discussion in section 4.1, described above.

Much is made of the importance of fertiliser applications controlling the concentration changes, but there is only a limited description of the land use and no data on fertiliser application rates within the catchments.

This has been included in section 2.1 and Table 1.

There is no detail on point sources; the work seems to focus on diffuse sources only.
Does effluent, either from sewage treatment works or septic tanks, influence the observed chemical dynamics?

As these sites are on headwater streams there are no sewage treatment works. Septic tanks are only considered to be a significant source of nutrients in the Avon and this has already been included in discussion.

The cause of the nitrate rich baseflow in the Hampshire Avon is not really discussed. Is the resuspension of bed material important for explaining the phosphorus dynamics?

The authors would like to point out that groundwater contribution was already included in the Discussion but has been further discussed with the inclusion of borehole concentration data to strengthen arguments (page 9 line 8 – 9) and then in the Discussion section (page 13 line 11 – 16; page15 line 29 – page 16 line 14 for the Avon, page 13 line 23 – page 14 line 9 for the Wensum). The storage of P within the bed sediments has been added as a potential source in the Avon (page 17 line 18-19) but was already included in the discussion for the Wensum interpretation (page 18 line 6).

7. There seems to be some confusion as to whether the Blackwater, a tributary of the Wensum, is the study site or the Wensum itself. This is important because the geology seems to be quite different in the Blackwater from the rest of the Wensum. The references to the 'Wensum DTC', 'Eden DTC' and 'Hampshire-Avon DTC' rather than the name of the study site causes confusion because it is unclear if the authors are referring to the larger catchments of the Wensum, Eden and Hampshire-Avon or the smaller study areas where the sub-daily measurements have been made.

The authors thank the reviewer for this comment. The manuscript has now been edited to reflect the fact that the monitoring sites discussed are located in the headwater tributaries of the Avon, Wensum and Eden wider catchments and have been changed to the Wylye, the Blackwater and the Newby Beck.

8. I would recommend that a section is included on the quality assurance of the sub-daily data. How robust are these data compared to laboratory based analyses. Were corrections made for temperature effects or drift?

We have now included a section on QA/QC procedures (section 2.3) which we agree are essential for validating the high resolution data. We have included a comparison table (Table 2) between data collected using bankside analysers and grab samples analysed using standard laboratory procedures, which show the measurements are in good agreement.

9. The storm event responses are described in great detail but I'm not sure if all this detail is relevant. Could the paper be made shorter and more focused by reducing the level of detail in the results section and drawing out the salient points, and then placing the results in the context of other storm events measured since 2011? This would be very interesting.

We thank the reviewer for this comment and have taken this on board. We have shortened the description on the storm response and have, as mentioned above, included Figure 2 which shows the hydrological and hydrochemical regime for the three sites for a full water year in sections 3.1 and 4.1.

10. Given the focus of the paper is a comparison of the response across the three sites, it might be better to cut down the description of the individual storm responses and focus more on this comparison. In addition, I'm unsure what new has been learnt about storm event responses in these catchments, or how the findings fit into the context of the broader literature (e.g. Ferrant et al., 2012; Melland et al., 2012, Mellander et al, 2012a, b and the list of references given the paper). Please can the authors put the results into context? It would be excellent to see if these results confirm or contrast with other studies.

We thank the reviewer for this comment and have now cut down the individual descriptions as suggested and put the findings into the context of the broader literature throughout the discussion (page 15 line 1-19, page 16 line 14-18, page 17 line 8 – 12, page 18 line 1-3, page 18 line 22-25, page19 line24 – 27).

11. I feel the conclusions require further consideration as I do not believe that all the potential nutrient sources have been fully evaluated in the interpretation of the results. For example, there is little consideration of effluent from sewage sources or septic tanks, or of inputs of groundwater enriched by nitrate in the Chalk dominated catchments.

See comments above.

12. Table 3 is not necessary. Loads are presented in this table, but loads are not considered in the aims, discussion or conclusions.

The loads are in fact discussed in what was section 4.1, now section 4.3 and form an important part of the Discussion.

13. Figure 8. The results for total phosphorus in the Hampshire-Avon look odd in that the maximum concentration appears to be exactly 1 mg P l_{-1} and the measurements seem to remain constant at this concentration even though the flow decreases from approximately 1.7 to 0.7 $m_{3}s_{-1}$. Is this a data transcription error or is it suggesting exhaustion of supply (see specific comment 22)?

These points occur due to the 1 mg P L^{-1} limit set on the Phosphax instrument at this time. This has been made clear in the manuscript and the points have been removed from the hysteresis plot.

Specific Points

1. 15214, 23-28. Is the reference to the examples from Australia and Ireland relevant? The details regarding the Demonstration Test Catchments add to the length and it is unclear why these are needed in the context of this article.

This has been removed.

2. 15215, 3. 'Numerous authors' is rather vague. Please could you be more specific?

This sentence has now been removed.

3. 15215, 19. Did all three catchments experience drought stress and then flood conditions? What were the hydrological conditions in all three catchments prior to, and after, the storm?

See comment above regarding the inclusion of the time-series data.

4. 15217, 27. What does 'ARW' stand for? Please could you define acronyms on first use?

This whole section has now been removed.

5. 15128, 4. Please don't use colloquial terms such as 'nudging towards'. What is meant here – bias correction?

This whole section has now been removed.

6. 15128, 12. What is the definition of 'winter 2011-12'? Is this December 2011 to February 2012? I thought that March 2012 was also dry in some catchments. Please could you clarify the period that you are considering?

This sentence has been removed.

7. 15128, 20 to 15219, 18. These lines suggest that there were differences between the antecedent conditions in the three study sites. How did this affect the results? Does it really matter that you have captured the same weather front as this will manifest itself in different ways in the different catchments. The key is measuring the transition from very dry to wet conditions in a short space of time, but what will this tell us that other analyses of storm event responses haven't done already? Please could the authors explain?

See comments above.

8. 15219, 23-26. Could the high nitrate concentrations in the Wensum be due to the transport of groundwater, enriched with nitrate, from Chalk?
9. 15130, 15-29. Again I would suggest that nitrate enriched groundwater is an important source of nitrate in the Hampshire-Avon and Wensum, which are both predominantly Chalk catchments.

See comments above.

10. 15131. Be careful with precision here. Can you really quote runoff to 0.01 mm per hour?

The runoff values have now been reduced to 1 decimal place.

11. 15134, 4. Change 'NRL' and 'NFL' to 'N_{RL}' and 'N_{FL}'.

This has been done.

12. 15134, 6. What is meant be 'more hysteretic'? Do you mean a greater difference between the concentrations on the rising and falling limbs of the hydrograph?

Yes, this has been clarified (page8 line17-19).

13. 15135, 3. Are the dilutions caused by relatively clean water entering the system and diluting effluent inputs? The authors acknowledge that sewage will affect the ammonium concentrations, but why is sewage not important for nitrate and phosphorus?

This section of the text has actually been removed by means of reducing the detail on the individual storm responses. However, the dilution is largely of the nitrate-rich baseflow, as demonstrated by the similarity in concentration of the chalk groundwater and the stream baseflow concentrations. There are septic tanks in the catchment but no sewage works, the contribution of which have been acknowledged for P transfer (see comments above).

14. 15135, 4. Are the increased concentrations caused by the flushing of mineral N from the upper soil layers, or is it the input of groundwater enriched with nitrate?

This sentence has now been removed.

15. 15141, 1-13. Was the pre-storm period drier than 1997, or wetter?

Unfortunately we are not able to say as this information was not included in the Jarvie et al. 2002 paper.

16. 15142, 7-10. How can you be sure that you are separating the effects of transport- and source limitation? Please could a note be added to the methods section? Would it be useful to refer to the paper by Evans and Tranter (1998)?

This sentence has been removed.

17. 15143, 7-8. A hydrological year is not very long in terms of capturing a good representation of the full range of hydrological conditions. If you look at the series of storms in one hydrological year you will gain a better understanding of the dynamics, though you won't capture the full range of conditions.

We agree with the reviewer that one hydrological year will not represent the full range of hydrological conditions. However, as made clear in Figure 2 the high resolution bank side analysis in the three DTCs only commenced in 2011-2012 which means that we don't have historical records for all of these sites.

18. 15144. 25-27. I would suggest that to understand sub-hourly data you need long-term, low frequency data to determine the context of the sub-daily dynamics.

We agree with the reviewer, but, as mentioned above, but such data are often not available, especially if working in headwater streams which are not included in longer-term national monitoring studies.

19. 15145, 16. What is the evidence for transport limitation?

This sentence has been removed.

20. 15145, 17. Wensum – is it drainage, or groundwater nitrate?

This has now been more clearly explained in section 4.1 (page 13 line 23 – page 14 line 9). The groundwater concentration of the chalk in this part of the catchment is extremely low (<1 mg N L^{-1}) so cannot explain the peaks experienced during storms. We have provided concentration data for the tile drainage in the upper part of the catchment, some of the deeper drains flow all year round with summer concentrations of up to 10 mg N L^{-1}, which is a more likely explanation for the rise of

nitrate on the recession limbs of storms when the catchment is experiencing greater levels of saturation (demonstrated by the API values).

21. 15145, 26. No nutrient exhaustion, but TP in the Hampshire Avon maxed out at 1 mg P l^{-1}, does this indicate that there might be some exhaustion of supply?

This has been explained above.

22. Table 1. The geology is described, but not the soils.

This has now been added.

Is the elevation the mid-point of the catchment? Please could the elevation be specified as a range?

This is the elevation of the sampling point, which has now been specified in the table.

23. Figure 1. The catchment areas of the Eden, Wensum and Hampshire-Avon are shown on the map, but these are different from the study areas, which are much smaller.

We have now edited this figure to show a close up of each catchment, with the specific monitoring point and tributary discussed in this paper highlighted.

24. Figure 4. It would be better to present the flow-duration and concentration-duration plots on a normalized scale, so that the extremes can be seen more clearly?

Effectively, the x-axis is normalised so that the exceedences can be compared. The authors think it is more useful to keep the y-axis as it is to show the differences between the catchments in terms of flow or concentration values.

References

Evans, C. D. and Tranter, M. D. 1998. Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episode hydrochemistry, Water Resour. Res., 34, 129–137, doi:10.1029/97WR01881, 1998

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