Response to reviewer comments on manuscript number:

doi:10.5194/hessd-10-1-2013

Anonymous Reviewer 1: Hydrol. Earth Syst. Sci. Discuss., 11, C164–C167, 2014

General comments:

Harrington & Harrington provide a classical evaluation of hydrochemical time series with respect to nitrogen and phosphorus species being mobilized as result of event based and seasonal processes. The manuscript is concise and well structured. The used approach does not provide much novelty, but the presented findings add some interesting aspects concerning the importance of different N and P species, especially the particulate ones, in relation to the prevailing hydrologic conditions.

The authors wish to thank the reviewer for the positive review of our paper. Specific comments are addressed below. The novelty in the paper is primarily in the presentation of new information in relation to the river catchment, and in particular in the analysis of particulate nutrient concentrations during storm events.

One concern is that the sampling interval of 1 week may not be sufficient to capture the considerable temporal variability, in particular of P species, and to calculate annual loads and species balances. Two (of many) events were sampled at some higher resolution. The authors conclude from the data that flood events drive annual loads of P. As a consequence of their findings, they should more thoroughly discuss the representativeness of weekly samples and the resulting uncertainties. Furthermore, a more thorough consideration of the hydrological conditions during sampling could provide some more information about the processes responsible for P and N mobilization.

The sampling strategy employed was based around achieving a balance between the sampling frequency and the sampling duration. We acknowledge that the weekly sampling interval may not fully capture temporal variability of particular P species, hence our strategy of collecting more samples when possible for shorter durations during high flow events. This method was selected to support the objectives of the paper which were to review N & P inputs with an emphasis on specific high flow events. Other P (and N) inputs derived from other drivers would potentially be better understood by undertaking a study over a shorter duration at a higher sampling frequency, but for the purpose of this study we are satisfied with the chosen sampling strategy.

P loads are estimated based on the relationship with turbidity, and not on interpolation of the weekly samples (Section 4.3). Linear regression shows that turbidity is a suitable surrogate responsible for most of the variability within P species. To address the hydrological conditions we have added as requested additional information in Section 5.2 and also to Figure 4 as suggested below. This provides a more thorough consideration of the hydrological conditions.

Specific comments:

p. 110, l. 24: Reduction of temperature, productivity and the mass of benthic communities may result from increased sediment loads but you would expect the opposite as consequence of high nutrient concentrations.

The inclusion of nutrient concentrations in this sentence was not correct. We have removed the reference to nutrients in the sentence.

p. 114, l. 5: "Peak discharge" needs some statistical classification: Is that the highest discharge ever measured since 1956, the mean annual peak flow?

Peak discharge is defined as the mean annual peak discharge. Annual peak discharge was calculated for the entire record length and the mean value determined. We have defined this as the 'mean annual maximum discharge' and amended the text as follows:

'The mean discharge, for the 103 km^2 catchment contributing to the gauging station is 2.4m^3 s^{-1} with mean annual maximum discharge over 10 times the mean discharge.'

p. 115, l. 10: dt is not the whole interval of integration (t2-t1) but a time increment of (in the ideal case) infinitesimal length.

We have corrected the definition of *dt* in the text.

'where Lc is the load over a time period ($t_2 - t_1$), Q_t is the discharge at time t, C_t is the nutrient concentration at time t, and dt is a time interval of infinitesimal length. C is measured in mgL^{-1} and Q is measured in m^3 s^{-1} yielding Lc in g for the selected time period.'

p. 117, l. 15: The minimum proportion of TDN (20%) and maximum proportion of PN (84 %) do not sum up to 100 %. Is that a matter of rounding?

This was a typographical error. The corrected sentence is:

'The variation of TDN content was high with a range between 22 and 100% of the TN measurement. Correspondingly, PN constituted 24% of the TN concentrations of the samples, with a range from 0 to 78%.'

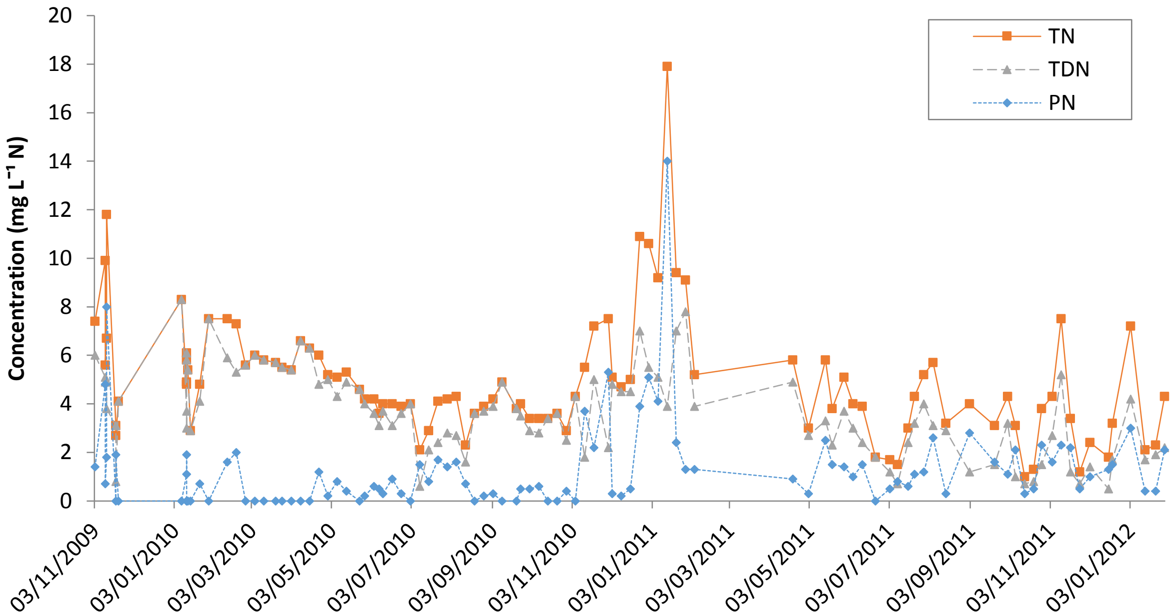
Figure 3: The authors have explained in the introduction that the method of differences to determine particle-associated species may be critical, in particular if adopted for low concentrations. This seems to be the case during some periods shown in Figure 3 when TDN are above TN concentrations. Please comment on these problems and the associated uncertainties.

As discussed in the paper, the source of error is complex, and an assessment of the uncertainty associated with such complex mechanisms is, we believe, beyond the scope of this paper. Nonetheless, it is important to recognise and manage the uncertainty risk. Our treatment of samples where the portion of dissolved concentrations is greater than that of the total concentration is to adjust the total concentration to be at least equal to the TDN value. This is the approach in the load calculation, and Figure 3 has now been revised to reflect this. We have also updated the title of the Figure to reflect more accurately the actual data shown on the chart. We have added a short paragraph to Section 3.1 as follows to address the reviewers comment.

‘Where the reported concentration of a dissolved species of a sample was larger than the corresponding total concentration, the total concentration was corrected to ensure that the concentration was equal to that of the filtered sample. This procedure was necessary for 23 TN results and 6 TP results with the average adjustment being 1.09 mg L^{-1} and 0.02 mg L^{-1} respectively. The testing method for both dissolved and total concentration determination is the same, and both were carried out using a subsamples from a single sample bottle and using the same blank. Consequently, we believe that the errors are related to the filtration process as discussed by Jarvie et al. (2002).’

Reference:

Jarvie, H.P., Withers, P.J.A., Neal, C.: Review of robust measurement of phosphorus in river water: sampling, storage, fractionation and sensitivity, Hydrology and Earth System Sciences, 6(1), 113–132, 2002.



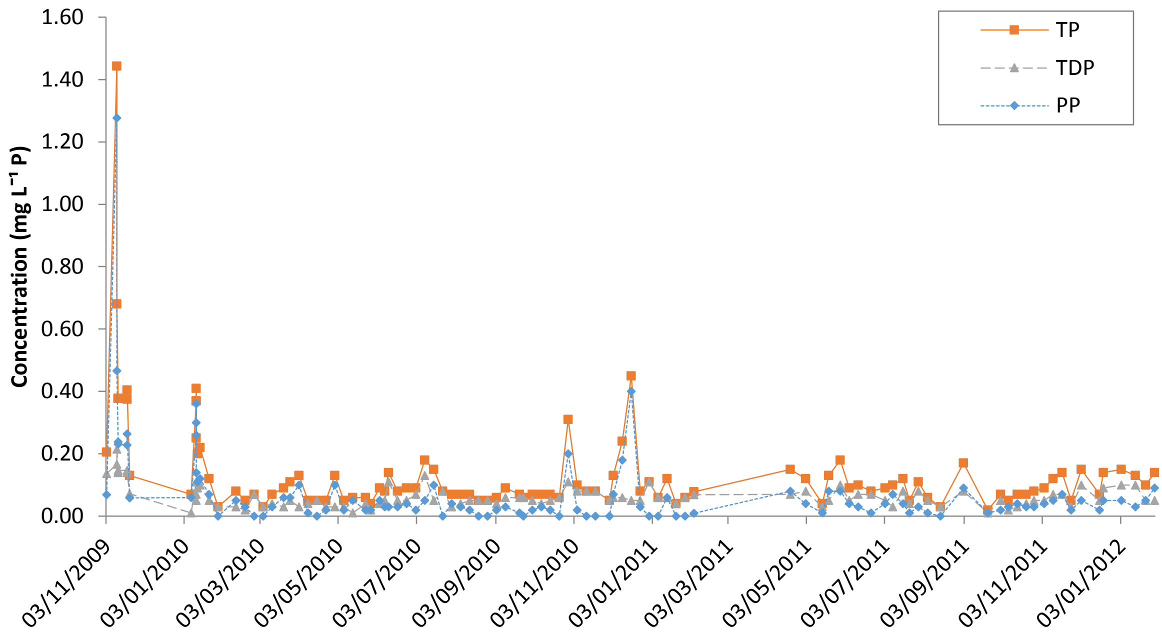


Fig. 3 concentrations of (a) nitrogen and (b) phosphorus during the sampling period

p. 117, l. 22: "….61 % of all samples being dominated by TDP" is unclear: Does that mean, that in 61 % of all samples TDP was higher than PP or that the mean proportion of TDP in all samples was 61 %?

We agree the sentence structure could be improved. We have rewritten it as:

'TDP dominates the TP measurement, with the mean TDP content of the samples being 61 %. The variation of TDP content was high with a range between 11 and 100% of the TN measurement. Correspondingly, PN constituted 39% of the TP concentrations of the samples, with a range from 0 to 89%.'

p. 118, l. 2: Are "nutrient parameters" concentrations or loads? In the former case: Why were "nitrogen parameters" (l. 12) calculated using Eq. 2 which yields a mass flux?

In l.2 we were referring to concentrations while in l.12 we refer to loads. We have amended the text to:

'Table 1 shows the result of a correlation analysis between the concentrations of the measured nutrient species. Both linear and power based regressions were investigated with the largest r^2 values reported. All 5 regressions were found to be statistically significant (p values< 0.001). SSC, TP, TRP, and PP were all found to have r^2 values (coefficient of determination) greater than 0.5 when regressed linearly against in-situ turbidity (Turbi). In particular, TP and PP were very well correlated with turbidity. Based on the correlation between P parameters and turbidity, P parameters were extrapolated from their respective regression curves with turbidity for the purpose of calculating P loads. Nitrogen loads were calculated using the method in Eq. (2).'

p. 119, first paragraph: Are nitrate concentrations given as NO3- or NO3–N? On p. 117 you state maximum concentrations for TDN of 8.3 mg/l, here you report maximum nitrate concentrations of 7 mg/l. If the latter corresponds to 1.6 mg/l NO3–N: Which N species is responsible for the remaining 6.7 mg/l TDN?

All nitrogen concentrations are reported in NO3-N. The maximum observed TDN concentration was 8.3mg/l. Nitrate, is defined as DIN and the maximum observed concentration of DIN was 7mg/l.

p. 120, ll. 19-20: Increases in total concentrations primarily driven by increases in particulate species? This is of course true for P, but for N the increases in PN are, according to Figure 4, rather weak and only slightly influence the TN concentrations. In my opinion, Fig. 4 rather stresses the difference in N and P, the latter being much more strongly transported associated with particles.

Our intention here was to highlight the initial increase in PN corresponding to the increase in Q which we feel is significant and important. We agree fully of course on the differences in hydrological dependency between TP and TN delivery. We have rewritten the sentence to clarify as follows:

'The dynamics between PN and TDN vary considerably at the intra event scale. Increases in PP and PN during the initial stages of a typical storm event of January 2010, lead to an overall increase in TP, but not TN which decreased.'

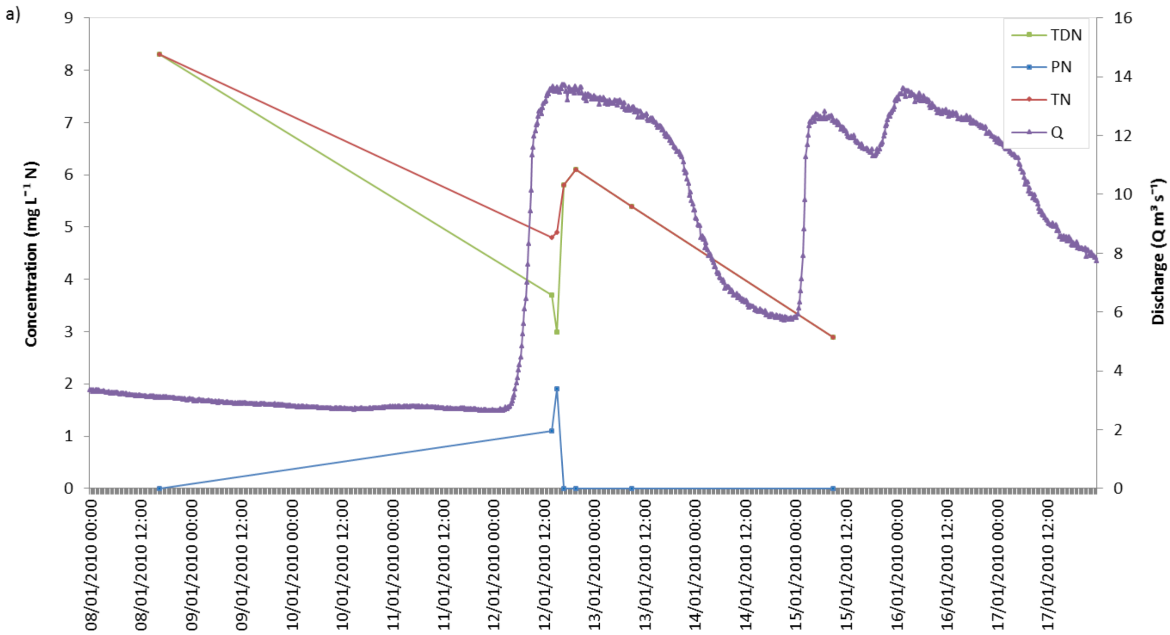
Figure 4: It would be helpful to show the whole hydrograph of the event instead of only a couple of discharges at the times of sampling. The characteristics of the event with the steepness of rising and falling limb and the timing of the peak discharge reveal loads of information about hydrological processes that should be further evaluated for the interpretation of N and P mobilization processes.

We have revised the Figures to show the whole hydrograph as suggested. We have also amended Section 5.2 to discuss the characteristics of the event in relation to N and P mobilisation as follows:

'The dynamics between PN and TDN vary considerably at the intra event scale. Increases in TP and TN during a typical storm event of January 2010 were found to be primarily driven by increases in PP and PN. The hydrology of the event is typical of many events observed on the River Owenabue (Harrington & Harrington, 2012). Maximum peak flow recorded during the event was approximately 13.7m^3 s^{-1}, compared to a discharge of 3.1m^3 s^{-1} at the beginning of the event. Initially, there is a sharp rise in flow rate starting after midnight on the 12th January. The flow rate peaks at approximately 14 m^3 s^{-1} after 12 hours and flows remained high into the 13th when they began to decline rapidly. Early on the 15th, flow rate began to rise rapidly again for a secondary peak.

In terms of nutrient delivery, the profile of both N and P is shown in Fig. 4 for the event. Initially there is a sharp decrease in TDN (Fig. 4a) which is partially offset by an increase in PN concentrations which are sufficiently large initially to reverse the overall downward trend in TN concentration. When the initial flush of PN passes, the TN concentration continues to decline. The decline in TN indicates that the nitrogen in the *river is being diluted by increased flows, which has also been reported by others (Salvia-Castellví et al., 2005). The most likely cause of the dilution is that the primary input to the river is from overland flow rather than through the sub-soil, where nutrient leaching would be higher.*

A similar, but stronger trend is found for TP during the same storm event (Fig. 4b). A significant increase in PP results in a significant increase in TP concentrations. The increase in PP is due to the mobilisation of suspended sediment during the initial period of the storm, whereas the sustained slightly elevated TDP concentrations most likely arise from the leaching of P from soils through sub-surface flow. The TP loads, and in particular the PP load is therefore mainly determined by infrequent storm based events, and particularly on the rising limb of the hydrograph of such events. The high correlation of PP with turbidity as presented in Table 1 is further evidence of the important relationship between PP and suspended sediment transport.'



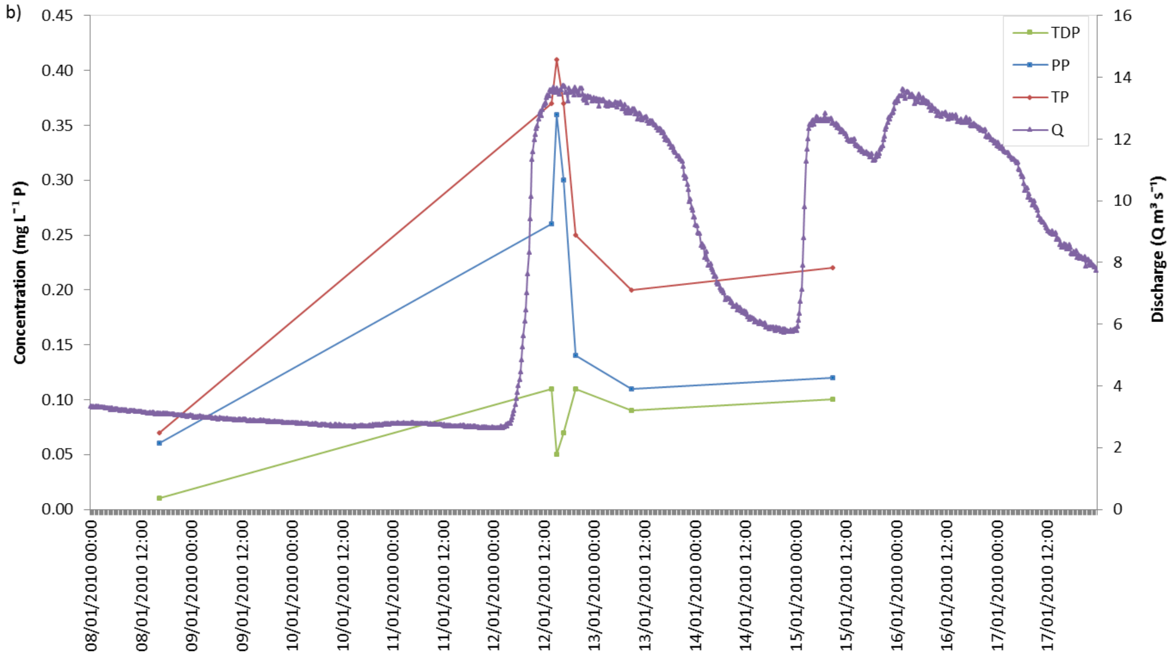


Fig 4. Discharge and **(a)** nitrogen and **(b)** phosphorus concentrations during a strom event from January 2010.

p. 121, l. 1: The fact that TN is diluted raises the question where this diluting component stems from. The authors answer this question partly in l. 7, using increased P concentrations as tracer for a soil-derived runoff component. This is quite interesting as it could mean that soils were more or less depleted in N during the period of the event. Further, this would contradict the expectation that high nitrate concentrations in winter are due to the flushing of soils. This point could be discussed more deeply here.

The reviewer raises a number of very interesting aspects in relation to the reduction in TN concentrations during the storm event. The reviewer may be correct in that the dilution effect may indicate that soils were depleted in N during the event from high ground water levels. Higher sustained winter flow rates generally do result in higher N concentrations due to prolonged leaching, however at the storm event scale, we suggest that N leaching is not significant. Further detailed study, beyond the current scope would be required to investigate in detail the degree to which N leaching impacts winter loads during storm events and may be addressed in future work. To address the reviewers' comments however, we have amended the paragraph as shown above in response to the previous comment.

p. 121, l. 8: The authors state that TP loads are determined by infrequent events, which is reasonable. It raises, as already mentioned in the general comments, the question to which extent it is possible to derive annual loads and balances for individual species from weekly samples (as done in the following paragraph). As part of the discussion a table showing the range of discharges encountered during sampling would be valuable.

P loads were estimated based on the regression of P species against turbidity, rather than on an interpolation of the weekly samples as described on p116, l1. We have added the following paragraph in relation to the flow rates over which sampling was undertaken to Section 4.1. We feel this is concise, but should the reviewer/editor prefer a table we will be happy to provide the information in such a format:

'The minimum, average and maximum flow rates over which samples were collected were 0.27 m^3 s^{-1}, 3.22 m^3 s^{-1} and 16.66 m^3 s^{-1} respectively compared with the equivalent values of the continuous record during the monitoring period of 0.27 m^3 s^{-1}, 2.31 m^3 s^{-1} and 19.59 m^3 s^{-1}. This indicates that the sampling programme captures a large majority of the range of flow rates observed in the river.'

p. 122, ll. 1-9: These comparisons with other catchments are quite interesting, but it is not clear what the purpose of this is. It appears as if the authors try to justify their findings by showing that other scientists found similar results. It is, however, difficult to compare yields of catchments that are characterized by different climates, geology, hydrology, and land management.

Reporting of results in the context of other studies is of interest to other researchers allowing comparison of yields from catchments with varying characteristics. It is not intended as a means of justifying our results. It is intended primarily for informational purposes.

Technical corrections:

p. 113, l. 1: plural s in sediments missing

Thank you. We have corrected the error.

p. 114, l. 18: TRP = total reactive phosphorus?

Thank you. We have corrected the error.

p. 119. L. 16: This should read "N" parameter, I guess.

Thank you. We have corrected the error.

Response to reviewer comments on manuscript number:

doi:10.5194/hessd-10-1-2013

Anonymous Reviewer 2: Hydrol. Earth Syst. Sci. Discuss., 11, C231–C233, 2014

This is a highly correct paper on its results and conclusions, but with minor novelty apart of its local description of the case. The paper neglects stating the main question as well as the underlying hypothesis that guided the approach. Indeed, the reader is willing to quickly understand which are the main issues defining the specific study. This needs to be supplemented in the forthcoming revision.

We would like to extend our thanks to the reviewer for providing useful and detailed feedback on our paper. The main question of the paper was to investigate the relationships between flow rate, turbidity and nutrient delivery in the Owenabue catchment. Coupled with this we wished to investigate if particulate nutrient concentrations were associated with high flows or high turbidity events. Our result suggest that particulate nutrient concentrations are influenced by rapid increases in flow rate. To address the reviewer's comments, we have added the following paragraph to Section 1.

'In this paper, we investigate the relationships between flow rate, turbidity and nutrient delivery in the Owenabue catchment. Additionally, we analyse the contribution of particulate nutrient concentrations during high flow or high turbidity events and show that particulate transport of nutrient forms a significant portion of overall nutrient transport.'

A more detailed description of the hydrological pattern should be also appreciated, since hydrology (and in particular storm events) appear to be so much important for the nutrient dynamics.

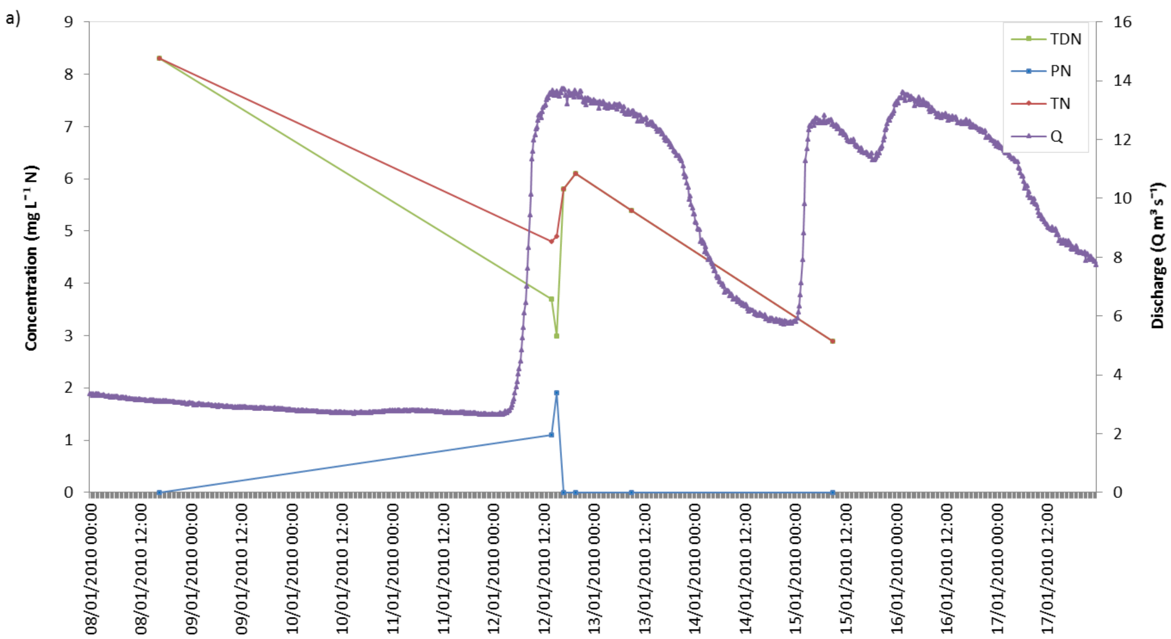
We have revised Section 4 to address the reviewers comment in relation to describing the hydrology. We have also updated Figure 4 (as recommended by the other reviewer) to show the hydrology associated with the event. Section 4 now reads as follows:

'Figure 2 shows the precipitation, flow hydrograph and turbidity signal for the monitoring period. Rainfall and river discharge are typically larger in the metrological Irish winter months of November to January and lower values are found for the July to September time period. Rainfall in 2011 (1014 mm) was greater than the annual rainfall in 2010 (859 mm) and both years were "drier" than the long term annual average (1208mm) following a very "wet" year in 2009 (1574mm).

Maximum total monthly rainfall over the monitoring period was 246.7mm in November 2009 while the lowest monthly total was 17.1mm in August 2010. The maximum daily discharge during the monitoring period was 16.3m^3 s^{-1} and was associated with high water levels due to prolonged rainfall during October and November 2009.Serious flooding was reported throughout the SWRBD during this period.

The River Owenabue exhibits a flashy hydrograph as seen in Figure 2 with suspended sediment concentrations and sediment associated nutrient concentrations responding quickly to high flow events. Typical events involve a rapid increase in flow rate early in the event, driven by the small catchment and steep catchment hill slopes. The time to peak of a typical event is of the order of hours. At the monthly scale, monthly discharge was observed to be greater than monthly rainfall for 8 months over the monitoring period, indicating that the catchment was regularly saturated. Detailed analysis of the catchment hydrology in relation to sediment transport is presented in Harrington & Harrington (2012).

The sampling programme resulted in a representative range of the flow regime being sampled. The minimum, average and maximum flow rates over which samples were collected were 0.27 m^3 s^{-1}, 3.22 m^3 s^{-1} and 16.66 m^3 s^{-1} respectively compared with the equivalent values of the continuous record during the monitoring period of 0.27 m^3 s^{-1}, 2.31 m^3 s^{-1} and 19.59 m^3 s^{-1}.'



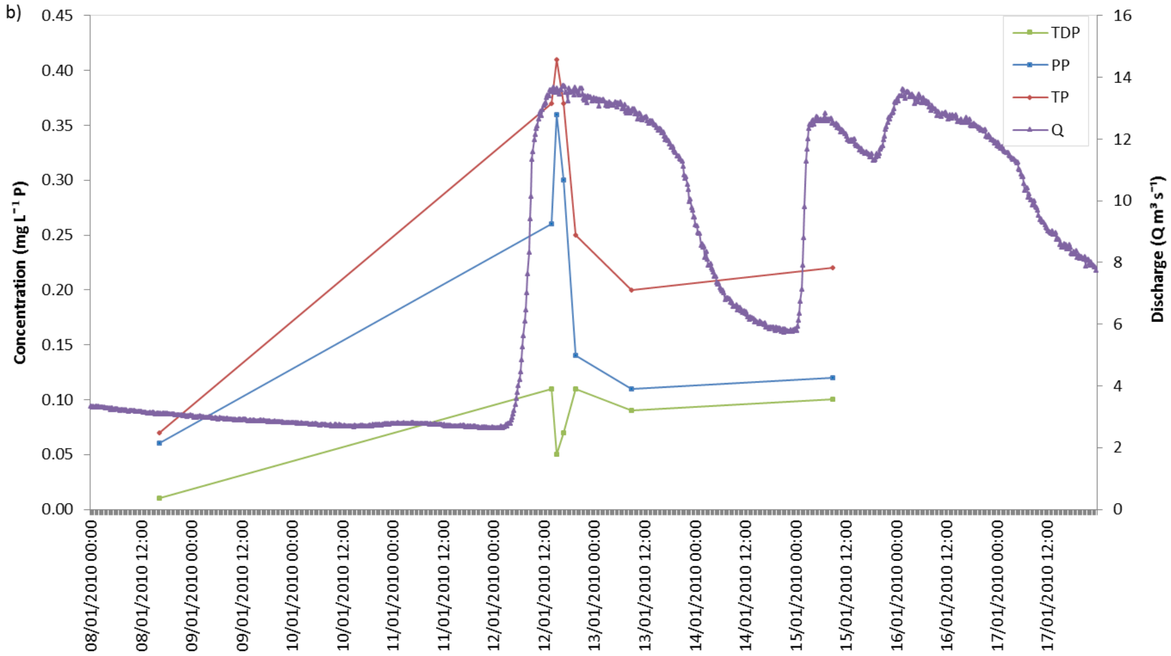


Fig 4. Discharge and **(a)** nitrogen and **(b)** phosphorus concentrations during a storm event from January 2010.

Finally, patterns need to be compared with others elsewhere; the comparison is by now restricted to very similar systems, and it remains unanswered whether the behaviour is or not singular.

Comparing the patterns across different catchment would be very interesting and informative. However, it is difficult to compare yields and patterns of sediment/nutrient dynamics in catchments that differ in terms of climate, geology, hydrology, and land use and management etc. Such a comparison would require a detailed study of the catchment characteristic of each catchment in the comparison and it is, we believe, beyond the current scope of this paper, but offers potential for future work.

The writing is sometimes unclear. I provide comments on specific sections of the paper.

110- L3 Why "enriching" nutrients?

We have removed the word 'enriching' from the sentence.

L12 Better "determination between

We have amended the sentence as shown below to clarify:

'High concentrations of phosphorus were associated with increased discharge rates and the coefficient of determination (r^2) between most forms of phosphorus and both discharge and suspended sediment concentrations were observed to be greater than 0.5.'

L22 Awkward sentence “a potential eutrophication risk to the river where phosphorus was found to be the limiting nutrient”

We have rewritten the sentence as follows:

‘While total nitrogen and total phosphorus levels were similar to other European catchments, levels of bio-available phosphorus were elevated indicating a potential risk of eutrophication within the river.’

L25 reducing temperature, productivity, density, the mass of bethnic communities. You mean that nutrients decrease productivity? and the mass of benthic (not bethnic) communities? This is certainly against usual knowledge.

The inclusion of nutrient concentrations in this sentence was not correct. We have removed the reference to nutrients in the sentence and corrected the spelling of benthic.

111-L13 non-point pollution to the surface- You mean surface waters?

Thank you, we have corrected the error.

113-L25 and ff. “The objective for the 2015 to 2021 reporting period is to improve river water quality. The poor status of the river can be attributed to the results of the macroinvertebrate tests rather than the physio-chemical testing”- This sounds contradictory. Probably you confuse the ecological status with the chemical status. The following sentence suggests you do not provide credibility to the biological status. In my opinion you need to refine this- the WFD is precisely requiring the different endpoints to be jointly considered.

The Owenabue (Owenboy) has six water body units. Two main water body units cover the catchment. The biological and other supporting element we refer to in the text are set out in the *‘Lower Lee Owenboy Water Management Unit Action Plan’* an appendix to Anon (2010). The table below is adapted from this source for the two main water body units.

	Biological Elements	**Supporting Elements**			
Member State Code	**Macroinvertibrates (Q)**	**Physio-chemical**	**Ecological**	**Objective**	**Date objective to be achieved**
SW_19_1584	P	H	P	GES	2021
SW_19_1968	M	H	G	GES	2021
P = Poor, M = Medium, G = Good, H = High, GES = ‘Good Ecological Status’					

Based on the above, we are satisfied with the paragraph in the paper relaying the current status of the Owenabue catchment in relation to the biological status compared to the physio-chemical status. We would be happy to discuss this further if necessary.

114-discharge by the staff of the Office of Public Work - this is not necessary

Noted and amended in the paper.

L15 Why Whatman GFC filters, 1.2m pore size were used? This is confusing regarding the comments at the introduction on the pore size. An explanation is required for this choice. Which were the fractions filtered and which were not- please describe in the text.

1.2 µm pore size filters were used to maintain consistency between the suspended sediment testing procedure and the particulate portion of nutrients. Dissolved nutrient parameters were based on the filtrate. We have amended the sentence as follows:

'Whatman GFC filters, 1.2 µm pore size, were used to filter the water samples to determine dissolved nutrient parameters. This provided analytical consistency between the suspended sediment analysis and the chemical analysis.'

L17 Define the method PhosVer3 Acid Persulfate Digestion/Photometric Method 8190. Stating that it is equivalent to USEPA Method 365.2 does not help much. Provide references.

L25- Equal for Cadmium Reduction Method 8171/Photometric

To address the above two comments we propose to amend P114 L17 to P118 L3 as follows:

'The nutrient parameters monitored were: total phosphorus (TP), particulate phosphorus (PP), total reactive phosphate orthophosphate (TRP), soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), total nitrogen (TN), particulate nitrogen (PN), total inorganic nitrogen (TIN), dissolved inorganic nitrogen (DIN) and total dissolved nitrogen (TDN).

Testing methodologies were as detailed in American Public Health Association (Eaton, 2005), namely persulphate digestion (TP, TDP, TN, TDN), ascorbic acid (TRP, SRP) and cadmium reduction (DIN, TIN). PN was calculated as the difference between TN and TDN and PP is the difference between TP and TDP. As an accuracy check, standard samples were included in the analysis of all chemical constituents.'

118 curves instead of cures.

Thank you, this error has been corrected.

120 L7 and ff- As stated, N:P stoichiometry is useful to predict P or N limitation, and this might be extensive not only to phytoplankton, but also for the other primary producers probably important in the river: biofilms, and even some plants. It is also clear that other factors are indeed important in affecting the primary producers' growth: hydrology, light, temperature needs to be included in the prediction of eutrophy, and references need to be included.

We acknowledge the role other factors play in the eutrophication of the river. We have not added detailed discussion, as we feel the focus should be on the importance of P in the context of the study and the WFD. We have however amended the paragraph as below to include the other producers as mentioned by the reviewer.

'N:P stoichiometry is widely used to define P or N limitation for plankton growth, which leads to eutrophication. A molecular N:P ratio greater than 16 (Redfield Ratio) indicates P to be the limiting nutrient, while N: P ratios lower than 16 indicate N to be the limiting nutrient. The mean N: P ratio of the Owenabue River for the entire study period was 43, indicating that plankton, biofilm and plant growth and thus eutrophication in the Owenabue River is controlled by P inputs, rather than N inputs. *This is important in the context of the WFD where rivers must achieve good status by 2015 and the Owenabue River has been identified as being at risk of not meeting this target based on both point source pollution from wastewater treatment plants and diffuse sources such as septic tanks which have a high P content.'*

Figures are in general of poor quality. Axes labels and numbering cannot be properly read. Figure 1 is tiny, and several others are hardly readable.

Thank you. We will discuss potential improvement of the figures with the Editor. We can provide the figures in editable format such as .docx or we can accommodate any other specific requirements.