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%.'

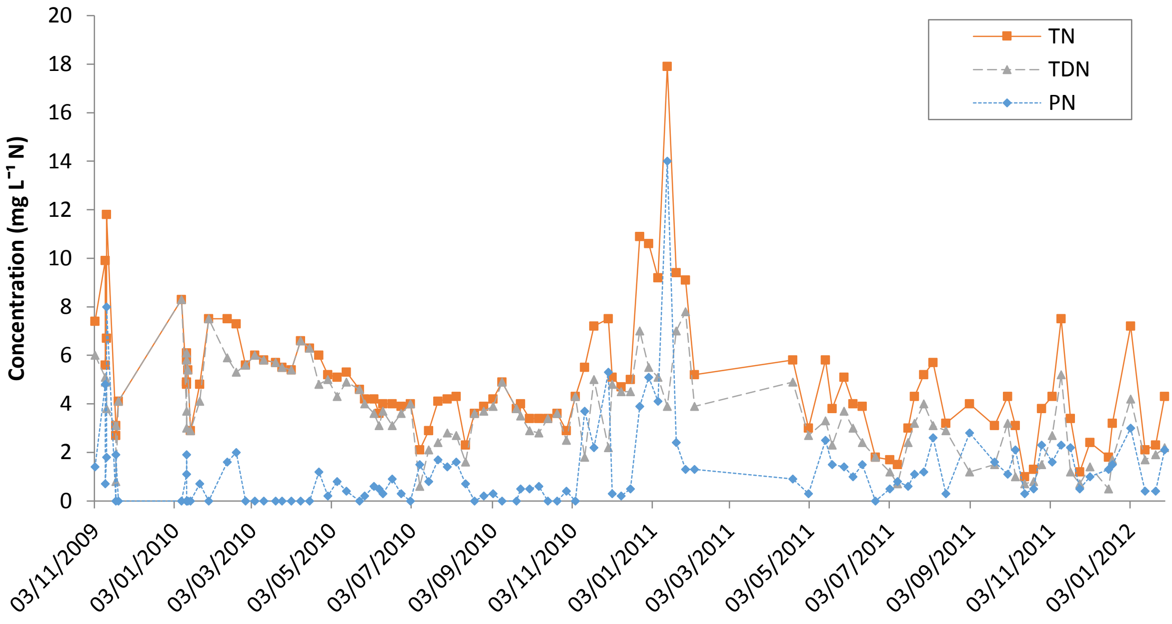
Figure 3: The authors have explained in the introduction that the method of differences to determine particle-associated species may be critical, in particular if adopted for low concentrations. This seems to be the case during some periods shown in Figure 3 when TDN are above TN concentrations. Please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



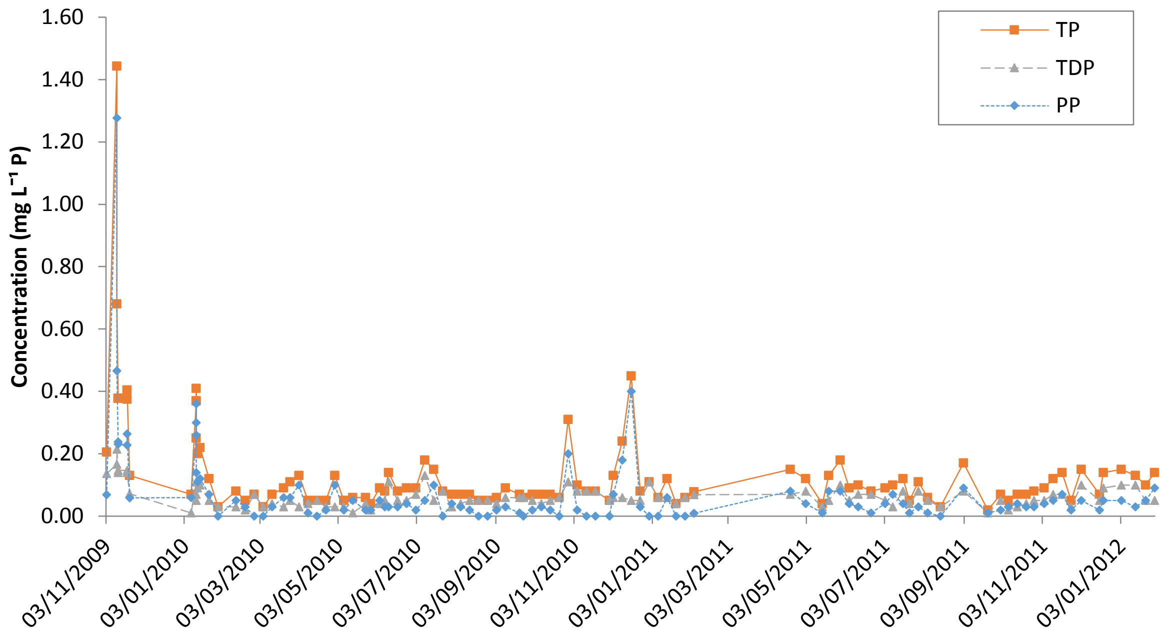


Fig. 3 concentrations of (a) nitrogen and (b) phosphorus during the sampling period

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.'

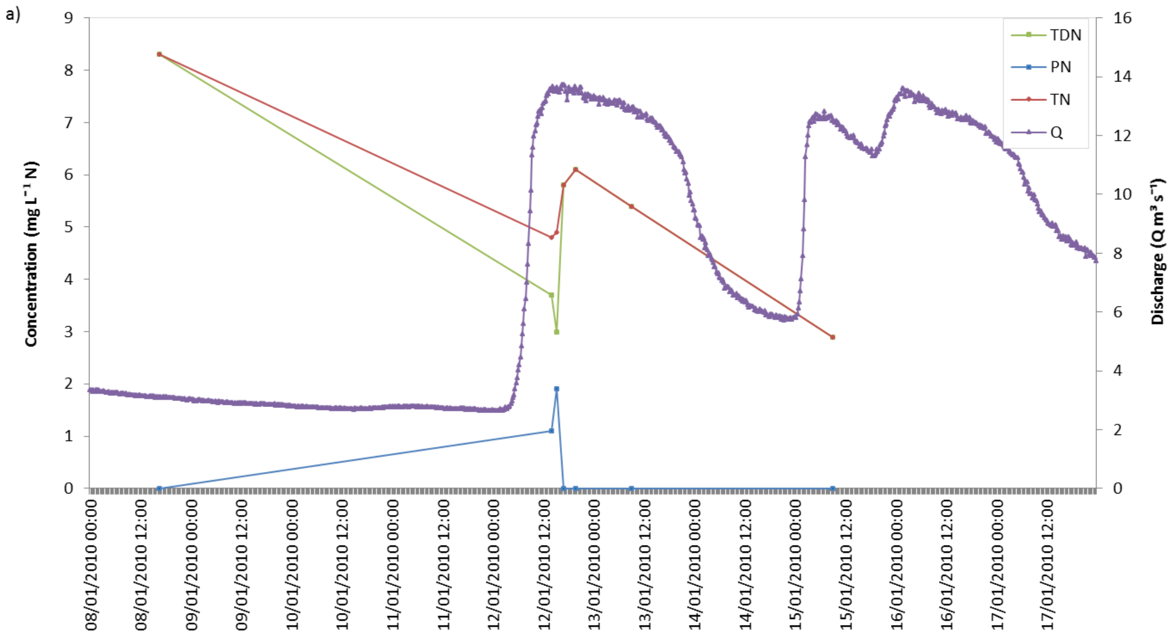
Figure 4: It would be helpful to show the whole hydrograph of the event instead of only a couple of discharges at the times of sampling. The characteristics of the event with the steepness of rising and falling limb and the timing of the peak discharge reveal loads of information about hydrological processes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



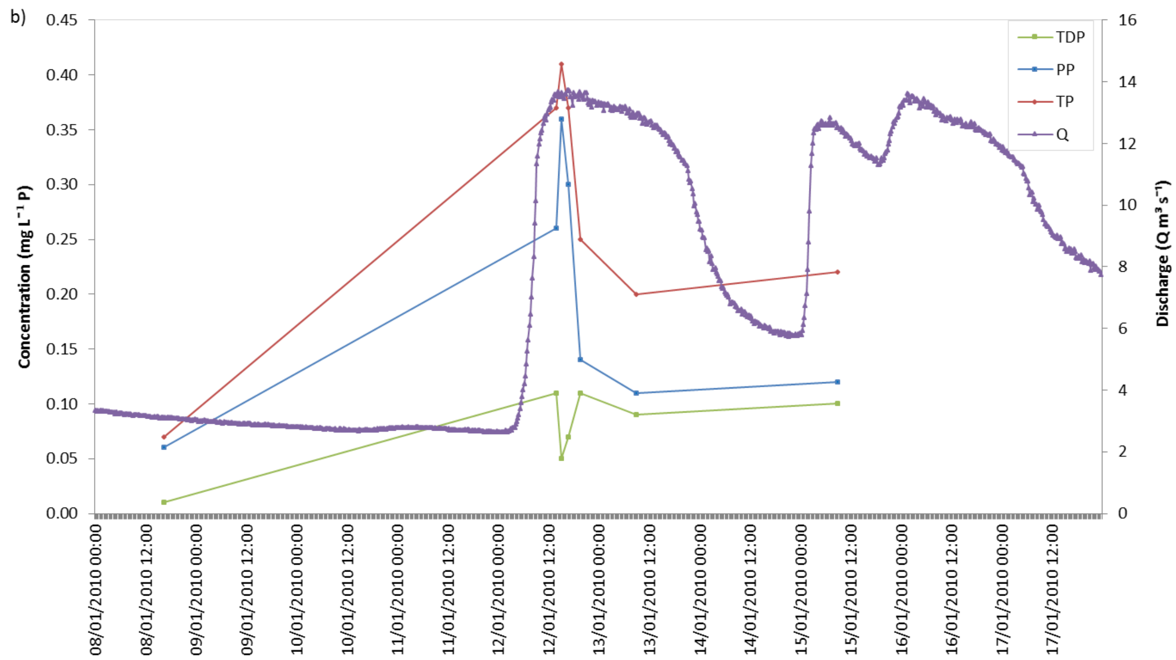


Fig 4. Discharge and **(a)** nitrogen and **(b)** phosphorus concentrations during a strom event from January 2010.

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.