Point-to-point Reply and Rebuttal to Anonymous Referee #1

Anonymous Referee #1

General comments:

This paper investigated the relationship between the dissolved organic carbon (DOC) concentration and river discharge or air temperature and addressed to estimate annual DOC yields from three mountainous watersheds in the subtropical region, Taiwan, in consideration of dynamics of river DOC during typhoon and non-typhoon periods. The data presented are precious because few studies have examined runoff characteristics of DOC in subtropical mountainous rivers during typhoon events. However, I can neither find scientifically something new in this paper nor understand what the significance of the paper is. It has been often described in several studies that temporal variations in DOC concentration appear to be related to river discharge, but the clear relationship between those variables cannot be found because DOC concentration varies depending on flow path, DOC sources, microbial activity (temperature), the magnitude and timing of storm events, land covers and topography as well as river discharge. This paper just follows existing knowledge by presenting the results of insufficient analyses on the relationship between the DOC concentration and the river discharge or air temperature.

We believe this is the first study implementing such long-term and intensive monitoring on DOC concentration in subtropical mountainous rivers. Besides, Taiwan is one of the Pacific Ocean's high-standing islands, the classical cases of SMRs that disproportionately deliver terrestrial material to the ocean. Furthermore, the global significance of freshwater on carbon cycle has been highlighted, particularly for the small streams (Biddanda, 2017; Hotchkiss et al., 2015). Therefore, Taiwan's case is worthy to be documented although several studies, mainly for temperate rivers, have been done for the DOC variation/transport by rivers.

In this study, we focus on the estimation of the amount of DOC being transported off the watershed as the basic but crucial information regarding the calculation of carbon budget within the watersheds. River discharge dominates DOC transport although DOC concentration varies depending on unidentified conditions. River discharge alone is a good predictor for DOC flux, revealing the flushing nature of rivers in Taiwan, which has been demonstrated by our previous studies for nitrate, phosphate, and other solutes (Lee et al., 2013; 2015). A 3-order magnitude increase of river discharge dilutes the solute concentration at less than 1-order magnitude (for the diluted solutes), revealing the hydrological control on the solute transport.

<References>

Biddanda, B. A. (2017), Global significance of the changing freshwater carbon cycle, Eos, 98, https://doi.org/10.1029/2017EO069751.

Hotchkiss, E., et al. (2015), Sources of and processes controlling CO2 emissions change with the size of streams and rivers, Nat. Geosci., 8, 696–699, https://doi.org/10.1038/ngeo2507.

Lee, T.Y., et al. (2013) Temporal variation of nitrate and phosphate transport in headwater

catchments: the hydrological controls and land use alteration, Biogeosciences, 10, 2617-2632, doi:10.5194/bg-10-2617-2013.
Lee, T.Y., et al. (2015) The sources of streamwater to small mountainous rivers in Taiwan during typhoon and non-typhoon seasons, Environmental Science and Pollution Research, doi 10.1007/s11356-015-5183-2.

Analyses on the relationship between the DOC concentration and the river discharge or air temperature in the former part of the paper are not reflected in the estimation of DOC yields by rating curves in the latter part. This is a problem because a scientific paper should be logical but the structure of this paper is not consistent. If the authors just tried to say that typhoon events export a large amount of DOC from the watersheds whereas they occur during a short period of the year, it would be enough to just calculate the annual and the typhoon DOC yields by using rating curves derived from relationships between the DOC flux and the river discharge during the typhoon and non-typhoon periods.

Yes, we focus on the estimation of annual DOC flux but we divide it into typhoon and non-typhoon periods owing to their different transport behaviors, i.e. C-Q relation. These are two different viewpoints from either the investigation of DOC concentration or flux calculation. It is important to understand the mechanism regarding the source of river DOC via the analysis of time-series DOC concentration although river discharge alone can well estimate the flux. We think these two viewpoints are indispensable but we will improve the flow of the manuscript to make it more logical.

According to the C-Q relations, we conclude that in-stream production may contribute to the river DOC in low-flow conditions during non-typhoon periods when temperature may play a role. With the increasing discharge during non-typhoon periods, the dilution could be attributed to the inputs from groundwater and deep soil water with lower DOC concentration. During typhoon periods, the elevated DOC concentration may result from the inputs of shallow soil water and overland flow, both have higher DOC concentration. Although we do not have direct in-situ evidence for these inferences, relevant references are cited to support our argument.
As for the flux calculation, the DOC concentrations vary within ~0.2-3 mgL^{-1} at the 4-order magnitude increase of river discharge, from ~0.1 to 1000 m^3s^{-1}. It indicates the unceasing supply of DOC from the watershed and hydrological control on DOC transport (Fig. 3), which are supported by our previous studies (for other solutes). Thus, rating curves with high R^2 could be derived and applied to estimate the DOC flux without the factor of temperature (Table 3).

The authors describe that the DOC flux is controlled largely by river discharge, but in Figure 6, it appears that the DOC flux varies up to an order of magnitude or more at a given discharge level. This means that a simple rating curve of F = aQˆb could not precisely estimate the annual DOC yield. I think these variations should be related to other factors, such as, air temperature and flow path. I am wondering whether the authors understand that the DOC flux under high flow conditions can be underestimated by using a rating curve (F = aQˆb) derived from the least square method (Ferguson, 1986). The authors should correct the bias of the estimation toward low flow conditions originating from the log transformation by using the moment-generating function. Or they should determine the parameters, a and b, by an iterative method, such as, Newton's method. Otherwise, they cannot accurately evaluate the proportion of the DOC yield during the typhoon periods to the annual DOC yield.

We do understand the underestimation led by the log-log linear regression method, i.e. F= aQˆb. We also understand it is particularly problematic while estimating the fluxes of sediment or particulate-associated solutes. For the dissolved solutes, it is relatively minor. Besides, the residuals of the log-log linear regression in this study do not follow the normal distribution, the requirement for the bias correction proposed by Ferguson (1986). We are very confident with the calculation because we are experienced in this issue and have published several articles regarding the solutes' fluxes from Taiwan rivers (Kao et al., 2005; Lee et al., 2009; 2013; 2014; Huang et al., 2012; 2016; Shih et al., 2016). Rating curve method, i.e. F= aQˆb, should be the best one when water samples from full range of river discharge are taken, as suggested by Copper and Watts (2002). The sampling frequency in this study is favorable for the rating curve method.

To demonstrate the minor effects of the "underestimation" on the DOC flux in this study, the bias correction factor proposed by Ferguson (1986) is calculated as shown in Table S1. The corrected DOC fluxes will increase 7-8% and 9-12% compared to our current estimations for the non-typhoon and typhoon periods, respectively, for the three studied watersheds. We do not think it is essential to implement the correction owing to the violation of the assumption regarding the normal distribution of the residuals and subtle influence on our stories in this study.

<References>

Kao, S.J., Lee, T.Y., and Milliman J.D., 2005. Calculating highly fluctuated suspended sediment fluxes from mountainous rivers in Taiwan, Terrestrial, atmospheric, and oceanic sciences, 16(3): 653-675.

Lee, T. Y., Huang, J. C., Carey, A. E., Hsu, S. C., Selvaraj, K., and Kao, S. J., 2009. Uncertainty in acquiring elemental fluxes from subtropical mountainous rivers, Hydrol. Earth Syst. Sci. Discuss., 6, 7349–7383, doi:10.5194/hessd-6-7349-2009.

Lee, T.Y., Huang, J.C., Kao, S.J., Tung, C.P., 2013. Temporal variation of nitrate and phosphate transport in headwater catchments: the hydrological controls and landuse alteration. Biogeosciences,

10: 2617–2632, DOI:10.5194/bg-10-2617-2013.
Lee, T.Y., Shih, Y.T., Huang, J.C., Kao, S.J., Shiah, F.K., Liu, K.K., 2014. Speciation and dynamics of dissolved inorganic nitrogen export in the Danshui River, Taiwan. Biogeosciences, 11, 5307-5321, doi:10.5194/bg-11-5307-2014.
Huang, J.C., Lee, T.Y., Kao, S.J., Lin, H.J., Hsu, S.C., Peng, T.R., 2012. Land use effect and hydrological control on nitrate yield in subtropical mountainous watersheds, Hydrology and Earth System Sciences, 16(3): 699-714.
Huang, J.C., Lee, T.Y., Lin, T.C., Hein, T., Lee, L.C., Shih, Y.T., Kao, S.J., Shiah, F.K., Lin, N.H., 2016. Effects of different N sources on riverine DIN export and retention in a subtropical high-standing island, Taiwan. Biogeosciences 13: 1787-1800.
Shih, Y.T., Lee, T.Y., Huang, J.C., Kao, S.J., Chang, F.J., 2016. Apportioning riverine DIN load to export coefficients of land uses in an urbanized watershed. Science of the Total Environment, 560: 1-11, DOI: 10.1016/j.scitotenv.2016.04.055

Table S1. The bias correction factor proposed by Ferguson (1986)

Watersheds	Non-typhoon period	Typhoon period
PL	1.07	1.09
DYK	1.08	1.10
GGL	1.08	1.12

In the first place, I do not understand why the authors selected a rating curve method to estimate the annual DOC yield even though there are several methods for estimating element yields (e.g., Cooper and Watts, 2002; Johnes, 2007; Webb et al., 2000). Additionally, the rating curves during typhoon periods ignore the fact that the DOC concentration varies partly depending on river discharge because the b values are approximately equal to 1 ($C = F/Q = aQ^1/Q = a$).

As mentioned above, we are confident with the estimations derived from the rating curve method, given the intensive samples covering the full spectrum of river discharge according to our published papers. Method choosing is influenced by the C-Q relation and sampling frequency because there is not a single method which can be universally applied to estimate the flux for one solute. We are experienced in the flux calculation and have used four methods, i.e. linear interpolation, global mean, flow weighted, and rating curve, to estimate nitrate flux for Taiwan rivers (Huang et al., 2012). We have found that the rating curve method gives the most confident flux estimation if samples are taken at both high- and low-end river discharge (Lee et al., 2009). The fact that hydrology controls the solute flux always results in high R^2 for the rating curves as far as Taiwan rivers are concerned (Lee et al., 2013; 2014). We even proposed a bias correction method to correct the inherent underestimation of the rating curve method which is particularly serious for sediment flux (Kao et al., 2005).

The rating curve is utilized for the sake of flux estimation, not for the concentration. DOC fluxes for four typhoons in PL watershed are shown below to illustrate the relations among the observed and the estimated DOC fluxes. DOC fluxes estimated by the rating curve are fairly good (although underestimated) even if the variation of DOC concentration is ignored. Some other methods, e.g. global mean and flow weighted method, would calculate a “mean” DOC concentration during typhoon period. Besides, the corrected ones by Ferguson (1986) do not improve much, explaining why we did not correct our current estimation.

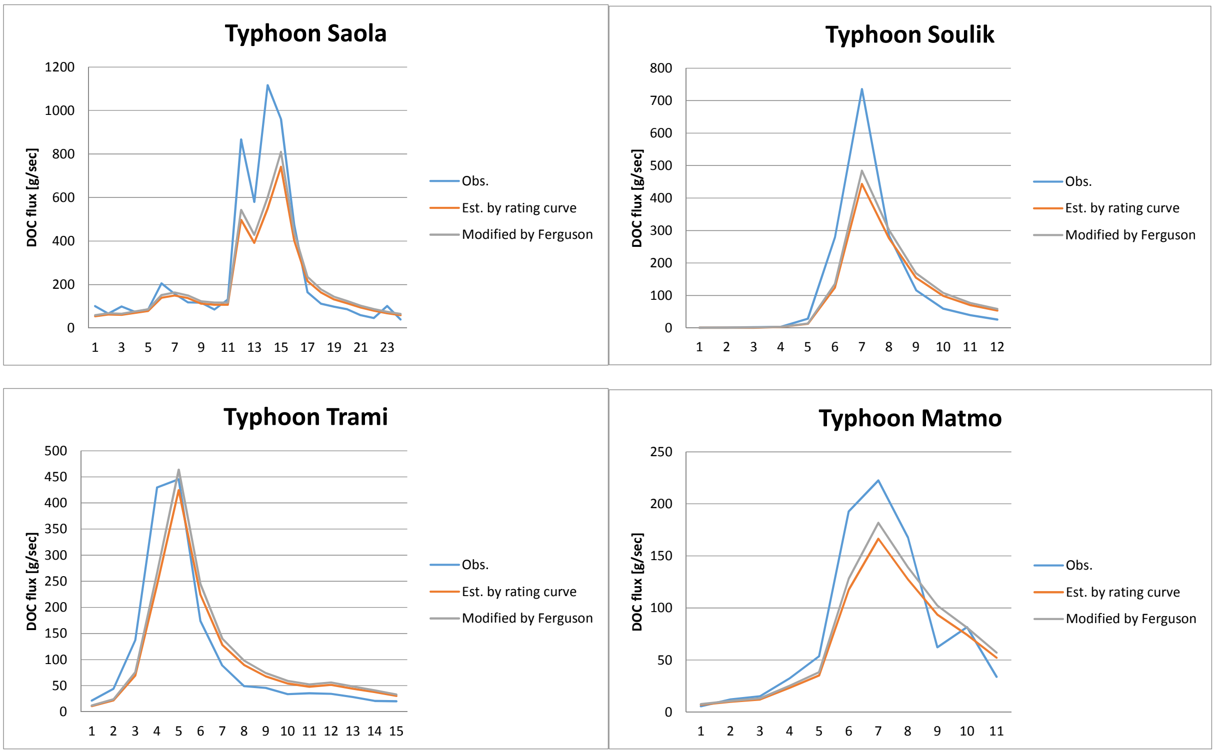

Figure S1. The observed, rating curve-estimated, and corrected DOC fluxes during four typhoons in PL watershed.

Specific comments:
Abstract and Introduction: The objectives of the study are not specific; the first objective described in L72 is not an objective of the study, but a methodology, and the second objective described in L73 is very ambiguous. Additionally, I do not understand why the annual DOC yields were evaluated in the three watersheds.

The objectives will be changed as: 1) to calculate DOC fluxes off the watershed during non-typhoon and typhoon periods and 2) to highlight the significance of subtropical SMR on delivering DOC by comparing the DOC yields with rivers worldwide.

The authors should describe what research gaps on the river DOC study are in the Introduction section, while they emphasize lacks of the river DOC study in subtropical regions.

I will improve the Introduction by highlighting the significance of this study on supplementing the lack of such long-term and frequent monitoring on river DOC in subtropical SMRs while small streams have demonstrated their global significance on carbon cycle.

Results: As a whole, analyses are not enough in this paper. The authors do not identify or detect the factors causing variations in DOC concentration that could not be explained by rive discharge alone, but just take a look at time series of DOC concentration and river discharge and the relationship between the DOC concentration and the river discharge (C–Q relation). The authors describe that DOC concentrations were higher during the rising limb of hydrograph than during the falling limb, resulting in a clockwise hysteresis loop. If this is the case, why didn't they separately analyze the C–Q relation between the rising and falling limbs of hydrograph at each typhoon event?

In this manuscript, we are focusing on the flux estimation. Although the C-Q relation shows a hysteresis loop, it does not significantly influence the flux estimation, as shown in Figure S1 above.

Additionally, the authors try to ascribe variations in DOC concentration to flow paths and available DOC sources that are linked to the degree of saturation in soils in the discussion section, but why didn't they explore associations between the DOC concentration and those factors using the data obtained? I think it is possible to analyze the associations in more detail using several hydrological indices, such as, rainfall intensity, rainfall duration, magnitude of typhoon, magnitude of direct runoff, runoff co-efficient, recession constant, antecedent rainfall, and antecedent moisture conditions.

First of all, the flux estimation is the main goal. The dynamics of DOC concentration could be referred to the previous studies. Second, typhoon samples were collected from only four typhoons. And three watersheds share the same weather station. We do not have adequate information to come up with certain general rules.

The authors plotted all of the DOC concentration data obtained during 2002–2014 against river discharge in Figure 3, but weren't there inter-annual variations in DOC concentration? If any, they should examine those variations to characterize dynamics of river DOC.

Yes, there were inter-annual variations in DOC concentration but not distinguishable, as shown in Table 1. DOC concentrations vary within the range of 0-3 mg L^{-1} with the annual mean at 0.79±0.33, 0.85±0.40, 0.79±0.35 mg L^{-1} for the PL, DYK, and GGL watershed, respectively. However, the variations of river discharge were much larger. We do not elaborate the changes of DOC concentrations since hydrology exerts the control on DOC flux which is the goal in this current study.

Why is there a blank period in data during 2006–2011?

There was no grant during this period.

I do not understand why the authors examined the relationship between the monthly average DOC concentration and the monthly-average air temperature in Figure 4, whereas they examined the relationship between the DOC concentration/flux and the river discharge at instantaneous values in Figures 3, 5 and 6.

As mentioned above, there are two different viewpoints from either the investigation of DOC concentration or flux calculation. As for the DOC concentration, it is found that at the monthly scale the DOC concentration is significantly influenced by river discharge and temperature (Table S2). We think this is also important information while the daily data are often unavailable. Monthly mean DOC, inferred from discharge (or rainfall) and temperature, could provide coarse estimations (but flux estimation method should be carefully selected in this case). As for flux calculation, daily (non-typhoon periods) even hourly data (typhoon periods) are essential, particularly for the SMRs. We think these two viewpoints are indispensable.

Table S2. The result of linear regression of monthly mean DOC [mg L^{-1}] against monthly mean river discharge [$m^3 s^{-1}$] and air temperature [℃].

Watershed	Intercept	River discharge coeff.	Air temperature coeff.	No. of data	R^2
PL	0.233	-0.0105*	0.0327*	81	0.48*
DYK	0.326	-0.0243*	0.0351*	81	0.52*
GGL	0.244	-0.0499*	0.0317*	79	0.44*

*indicates statistically significant at p-value < 0.01.

A hysteresis loop in the C–Q relation should strongly affect the relation of DOC flux to water discharge (F–Q relation) because the DOC flux varies up to an order of magnitude or more at a given discharge level as I described earlier. The high values of Rˆ2 of the F–Q relation in Figure 6 make no sense because F and Q variables are not independent.

As mentioned above, it is particularly problematic for estimating flux of sediment while its concentrations usually fluctuate a lot more (compared to DOC in this study) during typhoon periods. Figure S1 illustrates the time series of the observed and estimated DOC fluxes during typhoon periods. We do not think the hysteresis strongly affects the DOC flux because the estimated peaks of DOC fluxes fit the observed ones (except for Typhoon Saola).

From the viewpoint of flux estimation, the C-Q relation can be firstly used to construct C=aQˆb which is utilized to estimate DOC concentration at any unsampled time. The DOC flux can be further derived by multiplying the estimated DOC concentration by the river discharge. The DOC flux can be also estimated by the rating curve of F-Q relation. And both estimated DOC fluxes are identical, even though the rating curve of C-Q relation has poorer R^2.

Discussion: The authors just describe dynamics of DOC within forest watersheds, but hey should consider effects of agricultural lands on DOC concentration and yield, in addition to those of forests, because agricultural lands are distributed alongside rivers as shown in Figure 6. In general, water quality in rivers should be affected by nearby land covers and agricultural soils contain a large pool of organic carbon.

No influence of agricultural activities could be identified, which can be demonstrated by Figure S2 below. Here are some unpublished data, explaining how agricultural activities have no influence on river DOC. In the last two years of the monitoring program, water samples were taken from additional 16 sites (less frequent) within the three study watersheds. There is little correlation between the two-year mean DOC concentration and agricultural landuse proportion in the subwatersheds. Tea is the major crop, being fertilized mostly by synthetic nitrogen fertilizer. Bare soil is exposed between the rows of tea trees. We think the accumulation of organic carbon is little in most of the tea farms.

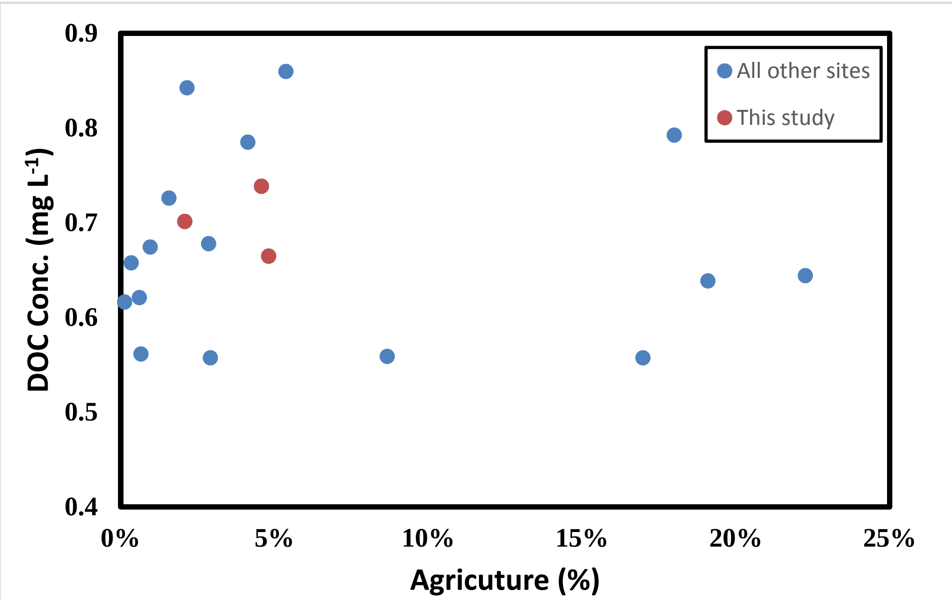

Figure S2. The relationship between the mean DOC concentration and the agricultural landuse proportion in the watersheds. Water samples were taken from the outlets of 19 sub-watersheds (including PL, DYK, and GGL) within the three study watersheds in this study.

I want to see a figure showing the frequency distribution (histogram) of DOC concentration and yield in the world rivers including this study sites because the authors describe that DOC concentration in this study is ranked in the lowest 1% whereas DOC yield is ranked in the top 30%.

Please see the following Figure S3 which will be shown in the revised manuscript.

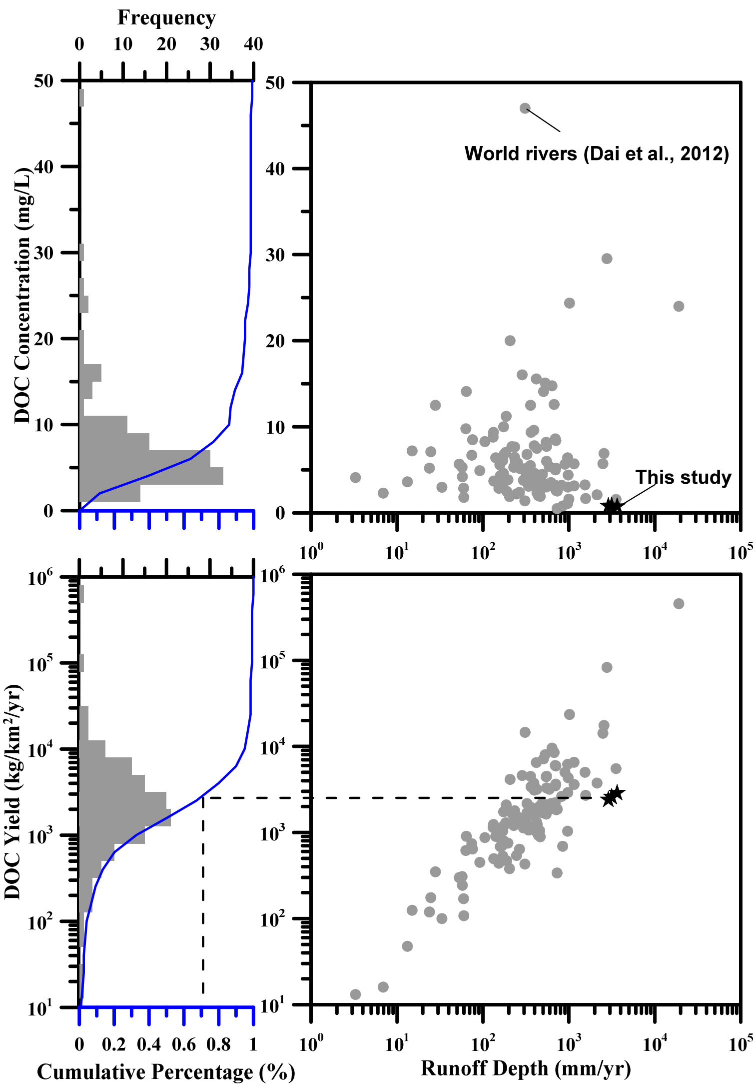

Figure S3. The frequency distribution of world rivers' DOC concentration and yield, and the scatter plot of DOC concentration and yield against the runoff depth.

Cited literature

Cooper, D. M., &Watts, C. D. (2002). A comparison of river load estimation techniques: application to dissolved organic carbon. Environmetrics, 13(7), 733-750.

Ferguson, R. I. (1986). River loads underestimated by rating curves. Water Resources Research, 22(1), 74-76.

Johnes, P. J. (2007). Uncertainties in annual riverine phosphorus load estimation: impact of load estimation methodology, sampling frequency, baseflow index and catchment population density. Journal of Hydrology, 332(1), 241-258.

Webb, B. W., Phillips, J. M., & Walling, D. E. (2000). A new approach to deriving 'best estimate' chemical fluxes for rivers draining the LOIS study area. Science of the total environment, 251, 45-54.