Monitoring strategies of stream phosphorus under contrasting climate-driven flow regimes

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Abstract

Climate and hydrology are relevant control factors determining the timing and amount of nutrient losses from land to downstream aquatic systems, in particular of P from agricultural lands. The main objective of the study was to evaluate the differences in P export patterns and the performance of alternative monitoring strategies in streams under contrasting climate-driven flow regimes. We compared a set of paired streams draining lowland micro-catchments under temperate climate and stable discharge conditions (Denmark) and under sub-tropical climate and flashy conditions (Uruguay). We applied two alternative nutrient sampling programs (high frequency composite sampling and low frequency instantaneous-grab sampling) and estimated the contribution derived from point and diffuse sources fitting a source apportionment model. We expected to detect a pattern of higher total and particulate phosphorus export from diffuse sources in streams in Uruguay streams, mostly as a consequence of higher variability in flow regime (higher flashiness). Contrarily, we found a higher contribution of dissolved P in flashy streams. We did not find a notably poorer performance of the low frequency sampling program to estimate P exports in flashy streams compared to the less variable streams. We also found signs of interaction between climate/hydrology and land use intensity, in particular in the presence of point sources of P, leading to a bias towards underestimation of P in hydrologically stable streams and overestimation of P in flashy streams. Based on our findings, we suggest that the evaluation and use of more accurate monitoring methods, such as automatized flow-proportional water samplers and automatized bankside analysers, should be prioritized whenever is logistically possible. However, it seems particularly relevant in currently flashy systems and also in systems where climate change predictions suggest an increase in stream flashiness.

1 Introduction

The global demand for phosphorus for fertilizers is projected to increase in the coming decades, although the existing global reserves will likely be exhausted within this century (Cordell et al., 2009). Nowadays, the global flow of phosphorus runs from mines through farms to aquatic systems, contributing to eutrophication and triggering aquatic ecosystem degradation (Carpenter et al., 1998; Elser and Bennett, 2011). Thus, humanity faces the challenge of sustaining food production while reducing the associated environmental costs

The biogeochemical processes inside a catchment, which determine the loss of phosphorus from the land to aquatic systems, are mainly dependent of climatic and hydrological regimes (Bormann and Likens, 1967). Streams located in areas with short duration-high magnitude rainfall events may respond with frequent and rapid changes in discharge (to be “flashy” streams sensu Baker et al., 2004) and may potentially have a higher risk of diffuse transfer of nutrients from land to water (Cassidy and Jordan, 2011; Haygarth et al., 1999). The importance of understanding hydrology-driven variations in nutrient discharge increases in the current climate change scenario where strong hydrological changes are expected in many different parts of the world.

Irrespective of the hydrological nature of the catchments, nutrient monitoring programs are frequently based on low frequency sampling at discrete intervals. This kind of sampling strategy complemented by interpolation methods are prone to very high uncertainties due to typical under-representation of high discharge, short-duration events (Defew et al., 2013; Jones et al., 2012; Jordan and Cassidy, 2011; Stelzer and Likens, 2006). A priori, the risk of missing the key moments when phosphorus is delivered to the streams is higher in flashy streams than in hydrologically stable ones. An approach to advance the understanding of how different monitoring schemes capture catchment phosphorus processes in contrasting climate-driven flow regimes is to compare monitoring performances in catchments under different climatic conditions and under different conditions of nutrient inputs.

The main objectives of our study were to evaluate the differences in stream P export patterns and the performance of alternative monitoring strategies in contrasting climate-driven flow regimes. We expected to detect higher total and particulate P exports in streams located in sites with higher frequency of extreme rainfall events and higher stream hydrological variability (flashiness). We also expected poorer performance of low frequency sampling programs under such conditions.

2 Material and Methods

2.1. Design rationale: Selection of case studies

We conducted a comparative study of concentrations and export of different P forms in two paired streams under two distinct climatic-hydrological conditions: temperate climate and stable discharge conditions (Denmark) and subtropical climate and flashy conditions (Uruguay). In both countries, the topography of the selected areas can be described as gently rolling plains (mean slope < 5%). Two main causes explaining the differences in flashiness between Denmark and Uruguay are precipitation patterns (annual average precipitation, 745 mm since 1990 in Denmark and 1300 mm in Uruguay, according to the Danish Meteorological Institute (DMI, 2015) and the National Institute for Agriculture Research, INIA, Uruguay (Castaño et al., 2011), respectively, and depth of soils and derived water storage capacity. The long-term continuous monitoring data in Danish catchments and the existence of published works evaluating alternative sampling strategies (e.g. Kronvang and Bruhn, 1996) decided us to use the temperate streams as the reference systems in our comparison.

In each area, two lowland non-experimental micro-catchments (< 20 km^2) were selected as typical productive systems to represent extremes of land use intensity (hereafter LUI) in each area.

As higher LUI catchments, we selected catchments where intensive farming comprising more than 90% of the total land area, with arable cropping systems, intensive use of fertilizers, and high density of livestock (Table 1). In the Uruguayan high-LUI catchment, the farming production system was based on forage crops, no-till practices associated with intensive application of mineral fertilizers over the soil surface (Derpsch et al., 2010), dairy cattle feeding all year round in open fields, and no effluent treatment facilities on milking plants. In Denmark, the high-LUI catchment included a rotation cropping system with winter cereals and confined pig farms with slurry storage facilities. In Denmark, most loamy agricultural fields are drained with subsurface tile drainage systems (Grant et al., 1996), and the manure originating from farming activities is reutilized with a demand on a 75% reuse of N in slurry.

The lower-LUI catchments were chosen so as to represent local more preserved conditions. The Uruguayan low-LUI catchment was dominated by the natural grasslands of the Pampa Biome (Allaby, 2006) and sustained low density cattle production (70% of total area and below 1 head by hectare; Table 1). In contrast, a mixture of deciduous and coniferous forests dominated the Danish low-LUI catchment (Table 1).

The subtropical high-LUI catchment had 170 inhabitants and the low-LUI catchment only 20 inhabitants (National Institute of Statistics, 2015). In the former, the sewage from only 10 households is treated in a facultative pond. All other households in both subtropical catchments had leaking septic tanks. The point sources in the temperate catchments were mainly scattered dwellings without connection to sewage treatment plants. The temperate high-LUI stream received stormwater outlets from a small village whose sewage water is pumped to a treatment plant with tertiary treatment outside the catchment.

Maps including land use for each catchment were included as supplementary material. Henceforth, we will refer to the temperate- Danish streams as “STABLE” and the subtropical-

Uruguayan streams as “FLASHY”, while LUI categorization of the intensive and extensive production catchments will be referred to as “high-LUI” and “low-LUI”, respectively.

2.2. Phosphorus monitoring

Similar gauging stations were established in all four micro-catchments. We applied two alternative nutrient sampling programs: low frequency instantaneous-grab sampling and high frequency composite sampling. Instantaneous-grab sampling of water was conducted fortnightly, and P exports were estimated by two daily step interpolation methods. High frequency composite sampling was undertaken using Glacier refrigerated automatic samplers (ISCO-Teledyne). The samplers collected an equal water volume every four hours, and the composite samples were also collected fortnightly. The final phosphorus concentration in the only sampler carboy thus represented a time-proportional average for the fortnightly sampling period. As the high frequency composite samples integrated more information (i.e. shorter time steps, with higher probability of capturing extreme events), we expected this method to provide better estimates of the ‘true’ exported P from the catchments. Based on this assumption, we evaluated the deviation relative to the estimation methods based on instantaneous-grab samples.

We analyzed the measurements and results from a two-year monitoring period (March 2010 to March 2012 in STABLE; January 2011 to January 2013 in FLASHY).

2.3. Meteorological and hydrometric monitoring

In all catchments, CR10X data loggers (Campbell Scientific Ltd.) collected data every 10 minutes. In the FLASHY streams, we used CS450 Submersible Pressure Transducers (Campbell Scientific Ltd.) for water stage monitoring as well as HMP45C temperature probes (Campbell Scientific Ltd.) and Rain-O-Matic Professional rainfall automatized gauges (Pronamic). In the STABLE catchments, water level was registered with PDCR 1830 pressure sensors (Druck), while meteorological information was obtained from the Danish Meteorological Institute monitoring network based on a 10 x10 km grid.

Periodic instantaneous flow measurements were taken using a C2-OTT Kleinflügel, transferring data to software for the calculation of instantaneous discharge (VB-Vinge 3.0, Mølgaard Hydrometri). Non-linear stable regressions between stage and discharge at each monitoring station (rating curves) were fitted. The rating curves were used to generate a 10 minutes discharge data series utilizing the software HYMER (www.orbicon.com). For comparisons, discharge data is reported as area-specific runoff.

2.4. Phosphorus analysis

All instantaneous-grab and composite water samples were analyzed for total phosphorus (TP), total dissolved phosphorus (TDP), and particulate phosphorus (PP). In addition, also soluble reactive phosphorus (SRP) and soluble non-reactive phosphorus (NSRP) were estimated from instantaneous-grab samples.

Instantaneous-grab samples for TDP and SRP analysis were filtered through 0.45 µm membranes. For TDP analysis, STABLE high frequency composite samples were filtered using 0.45 µm pore size membranes, while FLASHY-high frequency composite samples were filtered using Whatman GF/C (pore size 1.2 µm). To detect possible bias derived from the type of filter used, we performed a Kruskal-Wallis test on the proportional contribution of TDP to TP between FLASHY instantaneous-grab and high frequency composite samples and found no significant differences. Consequently, we consider grab and composite TDP samples to be comparable. Particulate phosphorus (PP) was estimated as the difference between TP and TDP. Soluble non-reactive phosphorus (SNRP) was also calculated as the difference between TDP and SRP.

All the samples were determined as molybdate reactive P by equivalent spectrophotometric methods, preceded by strong oxidation with a solution of potassium persulfate, boric acid, and sodium hydroxide following Valderrama (1981).

2.5. Data processing and analysis

Climatic and runoff patterns were explored in order to investigate the main parameters relevant for P temporal dynamics. As a proxy of catchment water balance, the runoff ratio (i.e. annual percentage of rainfall water exported as runoff) was calculated (Wu et al., 2013). Additionally, to quantify the variation in flow regime we calculated the Richards-Baker Index (hereafter R-B Index; Baker et al., 2004). The R-B Index allows for evaluation of the "flashiness" or the annual ratio of absolute day-to-day fluctuations of streamflow relative to total flow (Baker et al., 2004). Increasing its value with increasing flashiness, the R-B Index varies between 0 and infinity and assumes a value of 1 when the accumulated volume of daily oscillations has the same magnitude as the annually accumulated discharge. The relative contribution of baseflow to total stream flow was estimated from daily hydrographs using the automatic routine proposed by Arnold et al. (1995) as an indicator of the deeper groundwater contribution. Percent contribution of stormflow to total flow was estimated as complementary to the baseflow contribution (Table 2).

The statistical relationship between all phosphorus compounds from instantaneous-grab samples was analysed by Spearman rank order correlation. The temporal dynamics of P forms were followed for total P (TP), particulate P (PP), total dissolved P (TDP) and soluble reactive P (SRP), as minimum (min), median (med) and maximum (max) range and interquartile range (IQR). The statistical comparisons of P temporal dynamics between the four streams were conducted using Kruskal-Wallis tests (Zar, 2010), followed by a *post hoc* pairwise multiple comparison procedure when appropriate (Dunn, 1964).

Three different methods were used for the calculation of stream P export. The first method was based on multiplying the TP and TDP concentrations obtained from the high frequency fortnight composite samples by the accumulated discharge for the same time period (Kronvang and Bruhn, 1996). Missing data from the relatively short periods when the automatic samplers were not in operation (e.g. frozen in Denmark) were re-generated through linear interpolation of concentrations (Jones et al., 2012).

Secondly, we calculated exported TP and TDP from the low frequency instantaneous-grab data by two alternative methods of concentration interpolation: linear (Kronvang and Bruhn, 1996) and concentration-discharge relationships (Bowes et al., 2008). Daily real and interpolated concentrations were subsequently multiplied by daily accumulated discharge to obtain daily export estimates.

Concentration-discharge relationships (C-Q) were established based on instantaneous-grab samples for all four streams by applying the load apportionment model developed by Bowes et al. (2008). This simple modelling approach does not require GIS information on land use, catchment size, population, or livestock density and may act as a valuable and versatile tool for catchment managers to determine suitable catchment mitigation options (Bowes et al., 2008). Several authors have found similar relationships and used them to characterize P dynamics (e.g. Meyer and Likens, 1979), calculate P sources (e.g. Bowes et al., 2008), or to calculate P transport (e.g. Kronvang and Bruhn, 1996).

The Bowes et al. (2008) method assumes that the load of phosphorus from point and diffuse sources can be modelled as a power-law function of the river volumetric flow rate (Equation 1). The total load of P at the sampling point is then a linear combination of the loads from diffuse and point source inputs, as shown in Eq. (1).

$$\mathrm{PC} = dso\_PC + pso\_PC = A.Q^{B-1} + C.Q^{D\text{-}1} \tag{1}$$

where PC is phosphorus concentration, dso_PC is diffuse source originated PC, and pso_PC the point-source originated PC. Q is discharge (daily accumulated), while A, C, (proportionality constants) and B, D (exponents) are empirically determined parameters. Parameter estimation was conducted by using a nonlinear generalized reduced gradient method to select values that minimize the residual sum of squares. Parameter B was constrained to values lower than 1 (dilution effect over point contributions) and D values greater than 1 (at no flow, the diffuse inputs tend to be zero and to increase with increasing flow). Each established C-Q relationship was used for the calculation of daily mean concentrations and then multiplied by the daily discharge to achieve daily exports. The proportional annual contribution from point sources and diffuse sources was also calculated with this method.

For FLASHY catchments, we estimated the maximum P contribution from human inhabitants based on the composition of household wastewater (i.e. urine, faeces, and greywater) and biodegradable solid waste per person and year based on Vinnerås (2002). For STABLE catchments, we estimated the total annual load from scattered dwellings not connected to sewage treatment plants and stormwater outlets from validated models (Wiberg-Larsen et al., 2013).

The relative contribution of PP to total exported P was estimated based on data from low frequency instantaneous-grab sampling and linear interpolation, high frequency composite sampling, and flow-weighted concentrations (FWC) estimated from high frequency composite samples on a monthly basis. FWC estimation allows calculation of a flow-normalized comparison of P concentrations between catchments.

3 Results

3.1. Climate and hydrology

The climate characteristics of the study period can be considered typical years for both Denmark and Uruguay. During the study period, minimum, mean, median, and maximum air temperatures were between 8 and 12 °C lower in the temperate/STABLE catchments than in the subtropical/FLASHY catchments (Fig. 1). The annual average temperature in the temperate/STABLE catchments was around 8.8 °C and ranged between -7.0 to 20.4 °C. The corresponding figures for the subtropical/FLASHY catchments were around 17.5 °C and ranged between 3.7 to 32.2 °C.

In both climates, catchments showed similar intra-yearly distributed rain patterns, but with marked differences in frequency and intensity (Fig. 2). In the STABLE catchments, it rained almost 6 out of 10 days (58%), the rain frequency being nearly half in the FLASHY catchments (31%). Although there were more rainy days in the STABLE catchments, the daily average amount of rainfall was lower (3.4 mm d^{-1}) than in FLASHY catchment where it amounted to 10.7 mm d^{-1}. Only one event of 50 mm d^{-1} was registered in the STABLE catchments during the 2-year study period, while in the FLASHY catchments rainfall events > 50 mm d^{-1} occurred approximately 1.5% of the days, reaching extremes of > 100 mm d^{-1}. The annual rainfall was 1.44 times higher in the FLASHY than in the STABLE catchments (Table 2).

Most of the water flowing in the FLASHY streams was exported during stormflow conditions (stormflow contribution > 60.8%), while in the STABLE streams water was exported during baseflow conditions (stormflow contribution < 36.4%; Table 2). The STABLE/low-LUI stream showed a very different hydrological behavior than the other three streams in that a very high percentage of the rainfall was discharged (> 62 %), with high minimum flows and low temporal variability (Fig. 2 and Table 2).

The Danish streams exhibited stable hydrological behaviour characterized by low inter-annual variability of total discharge, and also low variability at daily scale (the R-B Index never reached values higher than 0.3; Table 2). In contrast, the Uruguayan streams could be classified as FLASHY systems, with an R-B index ranging around 1 (0.9-1.3; Table 2). The stream draining the high-LUI catchments was the most flashy (Table 2).

3.2. Phosphorus temporal dynamics

Total P concentrations were positively correlated with all other P fractions (PP, TDP, SRP, SNRP) in STABLE and FLASHY/high-LUI streams, whereas in the low-LUI streams TP only showed a significant relationship with PP in the STABLE and with TDP and PP in the FLASHY stream (Table 3). The relationships between TDP and SRP were weaker but significant ($p < 0.05$) in the low-LUI streams than in the high-LUI ones under both climatic conditions (Table 3). The contributions of PP to TP were relatively similar in the low and high-LUI catchments in STABLE, but in FLASHY the proportion of PP decreased with declining intensity of land use (Table 3). The strongest relationships between PP and TP were found in both STABLE streams and the FLASHY/low-LUI stream (Table 3). In contrast, in FLASHY/high-LUI, TDP, and particularly SNRP, showed the strongest relationship with TP (Table 3). Negative relationships were found solely for low-LUI streams, between PP and TDP, PP and SNRP for the STABLE stream and between SNRP and SRP for the FLASHY stream (Table 3).

Median TP concentrations calculated for the four streams differed significantly ($H = 107.8$; $p \leq 0.001$), being pronouncedly higher in the FLASHY/high-LUI stream than in any of the others (min = 271; med = 1.024; max = 4436 µg P L^{-1}; Fig. 3). All other paired comparisons of TP revealed no significant differences, except for the STABLE streams where the TP concentration was significantly lower in the stream draining the high-LUI catchment (median = 76 µg P L^{-1}) than in the low-LUI catchment (med = 108 µg P L^{-1}; Fig. 3). No differences were registered between the STABLE and FLASHY/low-LUI catchments (med = 100 µg P L^{-1}; Fig. 3).

A significant difference (H = 43.6; $p \leq 0.001$) in median PP concentrations was found between most streams (Fig. 3), with highest and lowest values being registered in the FLASHY high-LUI and low-LUI streams (median = 146 µg P L^{-1} and 25 µg P L^{-1}, respectively) and intermediate values in the STABLE streams (median = 52 µg P L^{-1} in the high-LUI, and 80 µg P L^{-1} in the low-LUI stream). Particulate P concentrations were highest in the STABLE low-LUI stream and *vice versa* in the FLASHY streams. As expected, the STABLE streams exhibited lower temporal variation in PP than the FLASHY streams (IQR= 23-37 and 53-227 µg P L^{-1}, respectively).

Furthermore, a significant difference in median TDP concentrations occurred (H = 133.3; $p \leq 0.001$; Fig. 3). *Post hoc* analysis revealed statistical equivalence only for the STABLE streams (median = 28 µg P L^{-1} and 23 µg P L^{-1} for low and high-LUI streams). Intermediate TDP concentrations were found in FLASHY/low-LUI and the highest concentrations appeared in the FLASHY/ high-LUI stream (median = 74 µg P L^{-1} and 756 µg P L^{-1} respectively; Fig. 3).

The median SRP concentrations also exhibited statistically significant differences between the streams (H = 141.2; $p \leq 0.001$; Fig. 3). SRP levels resembled TDP, with the lowest concentrations in the STABLE streams (median: 2 µg P L^{-1} in both), intermediate levels in the FLASHY/low-LUI stream (median: 45 µg P L^{-1}), and the highest levels in the FLASHY/ high-LUI (median: 659 µg P L^{-1}; Fig. 3). SRP in the STABLE streams never exceeded 23 µg P L^{-1}, and in the FLASHY/low-LUI stream it never exceeded 87 µg P L^{-1}. In contrast, the FLASHY/high-LUI stream never had SRP concentrations lower than 219 µg P L^{-1} and SRP reached a maximum concentration of 1,920 µg P L^{-1} (Fig. 3).

3.3. Modelling phosphorus inputs from diffuse and point sources

Graphical exploration of C-Q relationships for the FLASHY streams showed the typical pattern described by Bowes et al. (2008), with high TP concentrations at low discharges followed by steeply declining TP concentrations with increasing discharge (dilution associated with point source-originated P input), and a less pronounced increase in concentrations at higher discharges (associated with diffuse source-originated P inputs; Fig. 4). The C-Q relationships for the two STABLE streams did not show any dilution effect associated with point source inputs; therefore, the best fitting was obtained when considering only a diffuse input signal (Fig.

4; Table 4). The performance of the models evaluated with the Nash-Sutcliffe model efficiency coefficient was generally low (Moriasi et al., 2007), reaching a maximum value of 0.25 for the STABLE/low-LUI stream (Table 4).

When considering the relationships established for point source-originated TP for the FLASHY streams, we found a higher exponent (B) in the C-Q relationships for the high-LUI catchment (Table 4). As a consequence, the decrease in TP with increasing flow (the dilution effect) was less pronounced for the high than the low-LUI stream (at 1,000 L s^{-1} the FLASHY/high-LUI catchment reached 85 µg P L^{-1}, while the FLASHY/low-LUI dropped to 5 µg P L^{-1}, Fig. 4).

Considering only diffuse sources of TP, we found a higher coefficient (C) but slightly lower exponents (D) in the C-Q relationships established for the high-LUI than for the low-LUI catchments under both climate conditions (Fig. 4 and Table 4). However, the FLASHY/high-LUI stream always had higher TP concentrations from diffuse sources than the other streams (Fig. 4).

3.4. Estimation of phosphorus export

Comparing TP export estimates based on the high frequency composite sampling, we found an underestimation pattern when applying the low frequency sampling/linear interpolation method for both STABLE catchments and an overestimation for the FLASHY catchments (Table 6). This bias was always higher for the low than for the high-LUI catchments (Table 6).

The TP and TDP export from the FLASHY/high-LUI catchment was higher than in the other three catchments (Table 5). Moreover, for STABLE streams, the TP export was always higher from the low-LUI than from the high-LUI catchment (Table 5).

Also comparing with the high frequency composite estimates, the C-Q relationships used to calculate exported TP produced more accurate results than the linear interpolation for the two high-LUI catchments, irrespective of climatic region (Table 6). The largest and disproportionate deviations of exported TP were obtained when applying the C-Q model to the FLASHY/low-LUI catchment compared to the high frequency composite sampling estimates (364-400%; Table 6).

The contribution of PP to exported P was never lower than 65% of the annual exported TP in the STABLE catchments (Table 5). A contrasting pattern was recorded for FLASHY streams where the contribution of PP never exceeded 48% of TP, reaching values as low as 13.6% (Table 5). This pattern of a major contribution of PP in the STABLE catchments repeats itself in the estimations made with the low frequency instantaneous-grab samples, high frequency composite samples, and flow-weighted concentrations (Fig. 5). We found a tendency to a higher, though rarely significant, dissolved P contribution in streams draining high-LUI catchments (Fig. 5).

The estimated contributions of TP from point sources and diffuse sources indicated that most of the TP export from the STABLE catchments came from diffuse sources as point source contribution from human sources only reached a maximum of 18% of the exported P (Table 5), but it was still too low to be detectable in our established C-Q relationships as point sources (Table 4). Contrarily, in the FLASHY catchments point sources dominated the P export, always constituting more than 83% of the exported P, with human sources contributing < 8%, dairy cattle being the most probable source of the remaining P (Table 5).

4 Discussion

Our results show that climatic and hydrological variability affects the temporal dynamics of P in streams and that low frequency monitoring strategies may fail to adequately capture such dynamics.

As expected, we found strong concordance between climatic characteristics and stream hydrological regimes. Danish catchments have a lower rainfall that is more evenly distributed during the year, with rare or no extreme rainfall events (> 50 mm day^{-1}) and lower temperature (and therefore low evapotranspiration). These conditions resulted in stream flows characterized by higher stability (lower flashiness, R-B index = 0.1-0.3 in our study). In contrast, the Uruguayan streams exhibited a much higher contribution of stormflow to total flow and higher flashiness (R-B index = 0.9-1.3), reflecting the local climate and likely also soil conditions. As reference, reported data in the literature includes daily maximum values of R-B Index reaching 0.43 in mountain streams in Slovakia and Austria (Holko et al., 2011), 0.65 in 30 agricultural dominated catchments in seven Nordic and Baltic countries (Deelstra et al., 2014), 1.01 at 204 stations in Michigan temperate streams (USA) (Fongers, 2012), and 1.32 at 515 stations in catchments located in six US Midwestern States (Baker et al., 2004).

The calculated annual TP export values in all streams fell within the range reported in the literature for comparable micro-catchments, for instance streams with grassland-agriculture production in Ireland (0.89 to 3.98 kg P ha^{-1} y^{-1}; Campbell et al., 2015) Irish streams with catchment farming activities (0.12 to 0.83 kg P ha^{-1} y^{-1}; Melland et al., 2012), and Norwegian streams (0.5 to 5.8 kg P ha^{-1} y^{-1}; Kronvang et al., 2005a). The temporal variability of exported PP followed the hydrological variability in the streams (Fig. 2), but the amount of exported P and PP (the latter likely derived from diffuse sources) did not systematically increase with increasing variability. This was valid for both Uruguayan catchments where the highest and the lowest P loads were exported, and dissolved P forms always predominated over particulate forms. The pattern of P loads exported in relation to conditions of high hydrological variability was thus opposite to our *a priory* expectations (i.e. higher total and particulate P export from diffuse sources in connection with higher flashiness) (Table 5), likely due to other factors related to land use, less input of P with eroded stream bank material due to potential low content of P and maybe also less erosion (Kronvang et al., 2012) and particularly the presence/absence of point sources in the catchments.

Several factors may contribute to the predominance of dissolved P forms in the Uruguayan streams. The direct access of cattle to the stream channels is one of those reasons, being a practice that results in direct manure deposition in the water and trampling, and mobilization from stream bed sediments (James et al., 2007; Jarvie et al., 2010; Kronvang et al., 2012; Laubel et al., 2003; Sheffield et al., 1997; Trimble and Mendel, 1995). In the FLASHY/high-LUI catchment this contribution was exacerbated and further aggravated by the additional effects of the lack of slurry treatment in dairy facilities and the widespread no-till practices associated with the application of fertilizers over the soil surface (Sharpley and Smith, 1994; Sharpley et al., 1996). Some or all of these factors together may explain the high levels of TP, TDP, SRP, and SNRP, exceeding the maximum range found in 35 comparable Nordic⁄Baltic micro-catchments studied by Kronvang et al. (2007).

The contribution of TP from point sources was negligible in both STABLE catchment, but was always higher than 83% in the two FLASHY catchments irrespective of land use intensity. The magnitude of P point sources seems to have a much stronger influence on the hydrochemistry of the Uruguayan stream waters than do hydrological variability and flashiness *per se*. In contrast, the Danish pattern seems to be consistent with the well-documented reduced influence of P from point sources in northern Europe (European Environment Agency, 2005; Kronvang et al., 2005b). Apart from the climatic and hydrological differences between the analyzed catchments, the extremely high TP concentrations (as high as 4,436 µg P L^{-1}), P exports (as high as 5.20 kg P ha^{-1} $year^{-1}$), and the extremely high proportion of dissolved P (as high as 86.4%) estimated for the FLASHY/high-LUI catchment may have implications for the environmental regulations of farming production in Uruguay given the severe deterioration of water quality in our case study. Our results also provide insight into the future behavior of P in northern European temperate streams seen in the context of the predicted change in climate towards more extreme, warmer, and wetter conditions, probably giving flashier streams (Hanssen-Bauer et al., 2005).

The importance of understanding hydrology-driven variations in nutrient discharge will most likely increase in the near future. In our study, the performance of the different monitoring frequencies and P export estimation methods reflected the hydrological character or flashiness of the investigated streams. The performance of the low frequency sampling programs in estimating TP and TDP exports was low in comparison with the high frequency sampling program. Although the performance of the models evaluated with the Nash-Sutcliffe efficiency coefficient was generally low, the C-Q method did not have a comparatively poorer performance.

Although our study was limited to four representative catchments (due to logistic reasons), our results suggest that a clear interaction between climate/hydrology and land use intensity occurred. This was shown by a lower deviation in the exported P estimations of the low frequency sampling for the high-LUI than for the low-LUI catchments. However, the low frequency sampling and linear interpolation method performed equally poor for the FLASHY and the STABLE streams. Our results suggest that climate and hydrological conditions may promote/may yield a bias in P load estimations at low sampling frequency, with a tendency towards underestimation for the hydrologically STABLE streams and overestimation for the FLASHY streams (Table 6). These results are in accordance with the findings of Richards and Holloway (1987) that the loads of P from diffuse sources (whose water concentration increases with runoff) tend to be underestimated, while the loads of P from point sources (whose concentration decreases with runoff) tend to be overestimated. This underlines the potentially high inadequacy of low frequency sampling programs to properly depict stream dynamics, which is consistent with previous findings (e.g. Jones et al., 2012).

Research into P dynamics in subtropical streams is in its initial phase. The expected intensification of agricultural production in many regions of the world, such as in southern South America, highlights the need for appropriate stream monitoring programs. Accurate estimation of P temporal dynamics and exports can help explain the linkages between climate, hydrology, land use, and water quality. Based on our findings, we suggest that the evaluation and use of more accurate monitoring methods, such as automatized flow-proportional water samplers and automatized bankside analysers, should be prioritized whenever is logistically possible. However, it seems particularly relevant in currently flashy systems and also in systems where climate change predictions suggest an increase in stream flashiness.

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Table 1. Site coordinates (datum WGS84), name and catchment size, dominant soils and land use. Danish catchments are part of Gudenå River basin, and the Uruguayan streams are part of the Santa Lucía Chico River basin. Source: (*) World Reference Soil Database classification, European Commission and European Soil Bureau Network (2004); (#) SOTERLAC database, ISRIC Foundation, (www.isric.org). STABLE: low flashiness Danish streams; FLASHY: Uruguayan flashy streams; low and high-LUI: low and high land use intensity.

Id	Name & size	Coordinates	Dominant soils	Land use (area %)
STABLE low-LUI	Granslev 740 ha	56°17'2"N 9°53'51"E	Haplic Luvisols (*)	Forest (59); arable farming (29); pasture/meadow (7);
STABLE high-LUI	Gelbæk 1180 ha	56°13'29"N 9°48'41"E	Gleyic Luvisols (*)	Arable farming (92); forest (2); urban (1); other (5)
FLASHY low-LUI	Chal-Chal 1880 ha	33°49'31"S 56°16'55"W	Luvic Phaeozem & Eutric	Extensive pasture (~70); arable farming (~30)
FLASHY high-LUI	Pantanoso 840 ha	33°54'13"S 56°00'23"W	Eutric Regosols (#)	Arable farming and dairy farms (90); extensive pasture (7); urban (3)

Table 2. Yearly accumulated rainfall and runoff in mm (direct measures), runoff ratio (percentage of rainfall water exported as runoff), and R-B Index (Richards-Baker Index) of flashiness for each monitored year. Stormflow contribution: Percent contribution of stormflow to total flow was estimated for the complete data set (2 years). STABLE: low flashiness Danish streams; FLASHY: Uruguayan flashy streams; low and high-LUI: low and high land use intensity.

	STABLE low-LUI	**STABLE high-LUI**	**FLASHY low-LUI**	**FLASHY high-LUI**
Accumulated rainfall 1st year	770 mm	778 mm	1030 mm	1196 mm
Accumulated rainfall 2nd year	756 mm	766 mm	1010 mm	1405 mm
Total accumulated runoff 1st year	515 mm	223 mm	170 mm	235 mm
Total accumulated runoff 2nd year	472 mm	198 mm	294 mm	255 mm
Runoff ratio 1st year	66.9%	28.6%	16.5%	19.6%
Runoff ratio 2nd year	62.4%	25.9%	29.1%	18.2%
R-B Index 1st year	0.1	0.3	1.0	1.3
R-B Index 2nd year	0.1	0.3	0.9	1.2
Stormflow contribution (%)	11.8%	36.4%	60.8%	70.6%

Table 3. Correlation matrices of total (TP), particulate (PP), total dissolved (TDP), soluble reactive (SRP), and soluble non-reactive (SNRP) phosphorus from instantaneous-grab samples. Numeric values represent Spearman rank order correlation and were included only when significant ($p \leq 0.05$). ns: non-significant. STABLE: low flashiness Danish streams; FLASHY: Uruguayan flashy streams; low and high-LUI: low and high land use intensity.

	TP	**PP**	**TDP**	**SRP**	**SNRP**
TP	\	0.78	0.75	0.68	0.57
PP	0.81	\	ns	ns	ns
TDP	ns	-0.31	\	0.93	0.70
SRP	ns	ns	0.86	\	0.44
SNRP	ns	-0.34	0.56	ns	\

STABLE/high-LUI

STABLE/low-LUI

	TP	**PP**	**TDP**	**SRP**	**SNRP**
TP	\	0.63	0.90	0.67	0.84
PP	0.80	\	ns	ns	0.41
TDP	0.58	ns	\	0.83	0.81
SRP	ns	ns	0.56	\	0.40
SNRP	ns	ns	0.41	-0.37	\

FLASHY/high-LUI

FLASHY/low-LUI

Table 4. Estimated parameters for the load apportionment model fitted for each stream. RSS: residual sum of squares. NSC: Nash-Sutcliffe model efficiency coefficient. STABLE: low flashiness Danish streams; FLASHY: Uruguayan flashy streams; low and high-LUI: low and high land use intensity.

Source	**Parameter**	**STABLE low-LUI**	**STABLE high-LUI**	**FLASHY low-LUI**	**FLASHY high-LUI**
Point	**A**	0	0	1915	2550
	B	-	-	0.140	0.501
Diffuse	**C**	7.145	20.677	3.658	399.000
	D	1.58	1.40	1.64	1.15
Global	**RSS (10^3)**	42.5	460	253	36362
	NSC	0.25	0.12	0.12	0.10

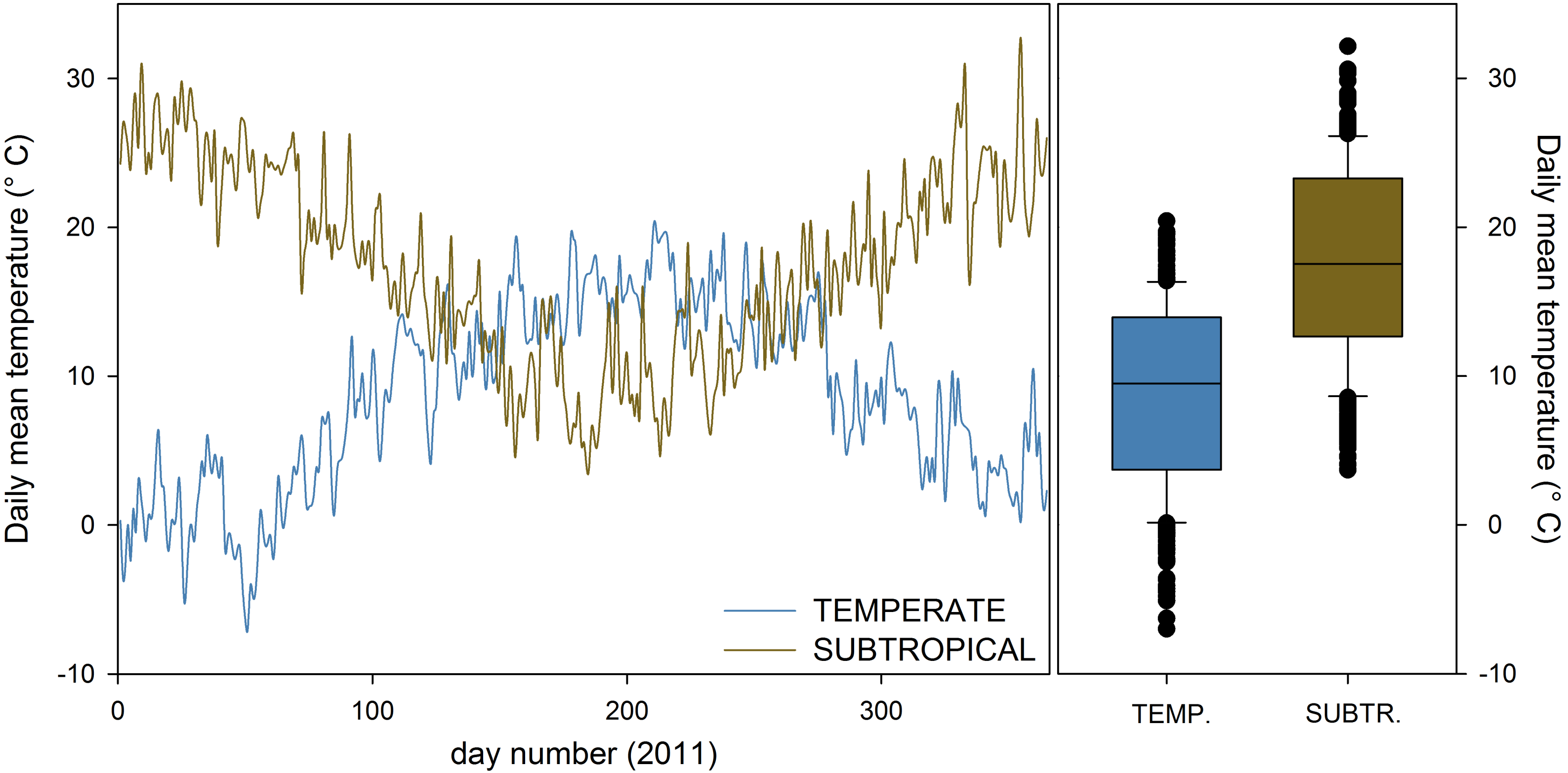
Table 5. Alternative estimations of annual total phosphorus (TP) and total dissolved phosphorus (TDP) exported from the four catchments expressed as kg P ha^{-1} year^{-1}. Estimation strategies: “COMP”: high frequency composite sampling. “LFS-LI”: Low frequency sampling and linear interpolation. “C-Q”: low frequency sampling and concentration-discharge relationships interpolation. % PP: percentage TP exported in particulate form. “% hs” under COMP represents the percentage of annual exported P from human sources. “% ps” under C-Q represents the percentage of the total annual exported load from point sources *sensu* the model. STABLE: low flashiness Danish streams; FLASHY: Uruguayan flashy streams; low and high-LUI: low and high land use intensity.

		STABLE/low-LUI			**STABLE/high-LUI**			**FLASHY/low-LUI**			**FLASHY/high-LUI**		
		COMP	**LFS-LI**	**C-Q**	**COMP**	**LFS-LI**	**C-Q**	**COMP**	**LFS-LI**	**C-Q**	**COMP**	**LFS-LI**	**C-Q**
1st year	**TP**	1.09 (12.5% hs)	0.64	0.61 (0% ps)	0.34 (10.5% hs)	0.29	0.34 (0% ps)	0.13 (6.9% hs)	0.25	0.52 (89.7% ps)	2.28 (7.5% hs)	2.36	2.86 (83.1% ps)
	TDP	0.17	0.20	\	0.08	0.10	\	0.08	0.13	\	1.97	1.83	\
	% PP.	84.4	68.6	\	76.5	66.9	\	38.5	48	\	13.6	22.5	\
2nd year	**TP**	0.74 (17.7% hs)	0.47	0.54 (0% ps)	0.35 (10.4% hs)	0.25	0.33 (0% ps)	0.25 (3.6% hs)	0.27	0.91 (83,6% ps)	5.20 (4.2% hs)	5.76	5.19 (86.5% ps)
	TDP	0.10	0.11	\	0.07	0.06	\	0.14	0.21	\	4.07	4.7	\
	% PP.	86.5	76.4	\	80	76.9	\	44	22.2	\	21.7	18.4	\

Table 6. The percentages summarizes the relative fit of alternative estimation methods in relation to the reference annually exported load estimated by the composite sampling programme (see Table 5 for references). 100% represents the same annual P exported in kg ha^{-1} year^{-1}. Values below 100% (italics) represent underestimation (less than 90%) relative to the estimation of composite sampling. Values over 110% (bold) represent overestimation relative to the estimation of composite sampling. STABLE: low flashiness Danish streams; FLASHY: Uruguayan flashy streams; low and high-LUI: low and high land use intensity.

		STABLE		**STABLE**		**FLASHY**		**FLASHY**	
		low-LUI		**high-LUI**		**low-LUI**		**high-LUI**	
		LFS-LI	**C-Q**	**LFS-LI**	**C-Q**	**LFS-LI**	**C-Q**	**LFS-LI**	**C-Q**
1st year	**TP**	*58.7%*	*56.0%*	*85.3%*	100.0%	**192.3%**	**400.0%**	103.5%	**125.4%**
	TDP	**117.6%**	****	**125.0%**	****	**162.5%**	\	92.9%	\
2nd year	**TP**	*63.5%*	*73.0%*	*71.4%*	94.3%	108.0%	**364.0%**	**110.8%**	99.8%
	TDP	110.0%	\	*85.7%*	\	**150.0%**	****	**115.5%**	\

Fig. 1. Left: Mean daily air temperature variation for a temperate (Danish) and a subtropical (Uruguayan) catchment in 2011. Right: boxplots of the same data. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers above and below the box indicate the 90th and 10th percentiles. Black dots display outliers.



Daily mean temperature (° C)
30
20
10
0
-10
0
100
200
300
day number (2011)
TEMPERATE
SUBTROPICAL
TEMP.
SUBTR.
Daily mean temperature (° C)

Fig. 2. Accumulated daily rainfall and specific runoff hydrographs for the four monitored streams. For each variable a fixed scale was used to aid visual comparison. R-B Index (Richards-Baker Index) of flashiness.

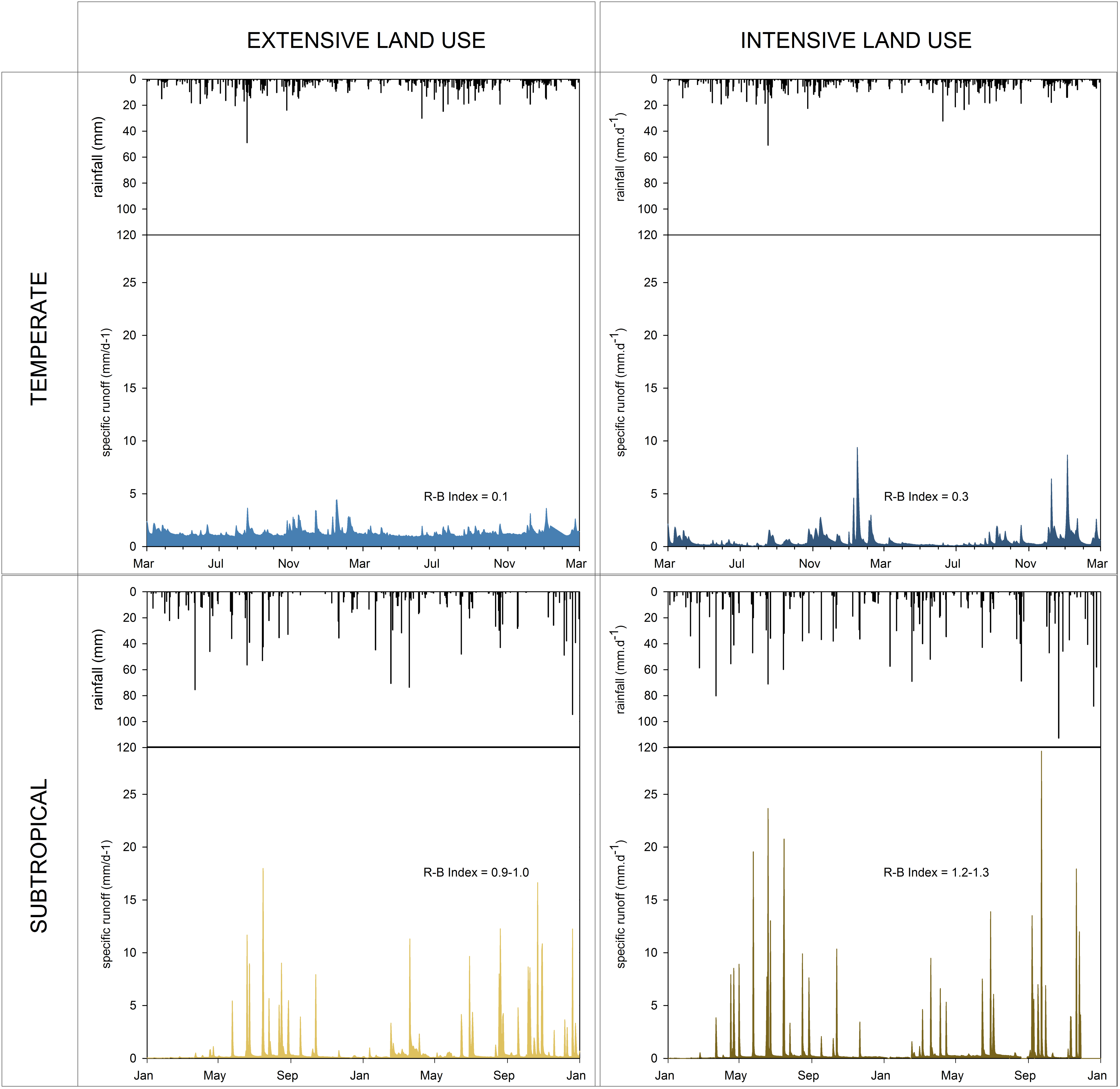

EXTENSIVE LAND USE
INTENSIVE LAND USE
TEMPERATE
SUBTROPICAL
rainfall (mm)
rainfall (mm.d^{-1})
specific runoff (mm/d-1)
specific runoff (mm.d^{-1})
0
20
40
60
80
100
120
25
20
15
10
5
0
R-B Index = 0.1
R-B Index = 0.3
R-B Index = 0.9-1.0
R-B Index = 1.2-1.3
Mar
Jul
Nov
Mar
Jul
Nov
Mar
Jan
May
Sep
Jan
May
Sep
Jan

Fig. 3. From top to bottom: temporal variation of total (TP), particulate (PP), total dissolved (TDP), and soluble reactive phosphorus (SRP) concentrations from grab samples for all the monitored catchments. Log_{10} scale was selected on the vertical axe to improve vizualisation. The phosphorus concentration is always expressed as µg P L^{-1}. Right: boxplots are based on the same data. Letters A, B, and C are used to display statistical groups according *post hoc* paired comparison analysis. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers above and below the box indicate the 90th and 10th percentiles. Black dots display outliers. STABLE: low flashiness Danish streams; FLASHY: Uruguayan flashy streams; low and high-LUI: low and high land use intensity.

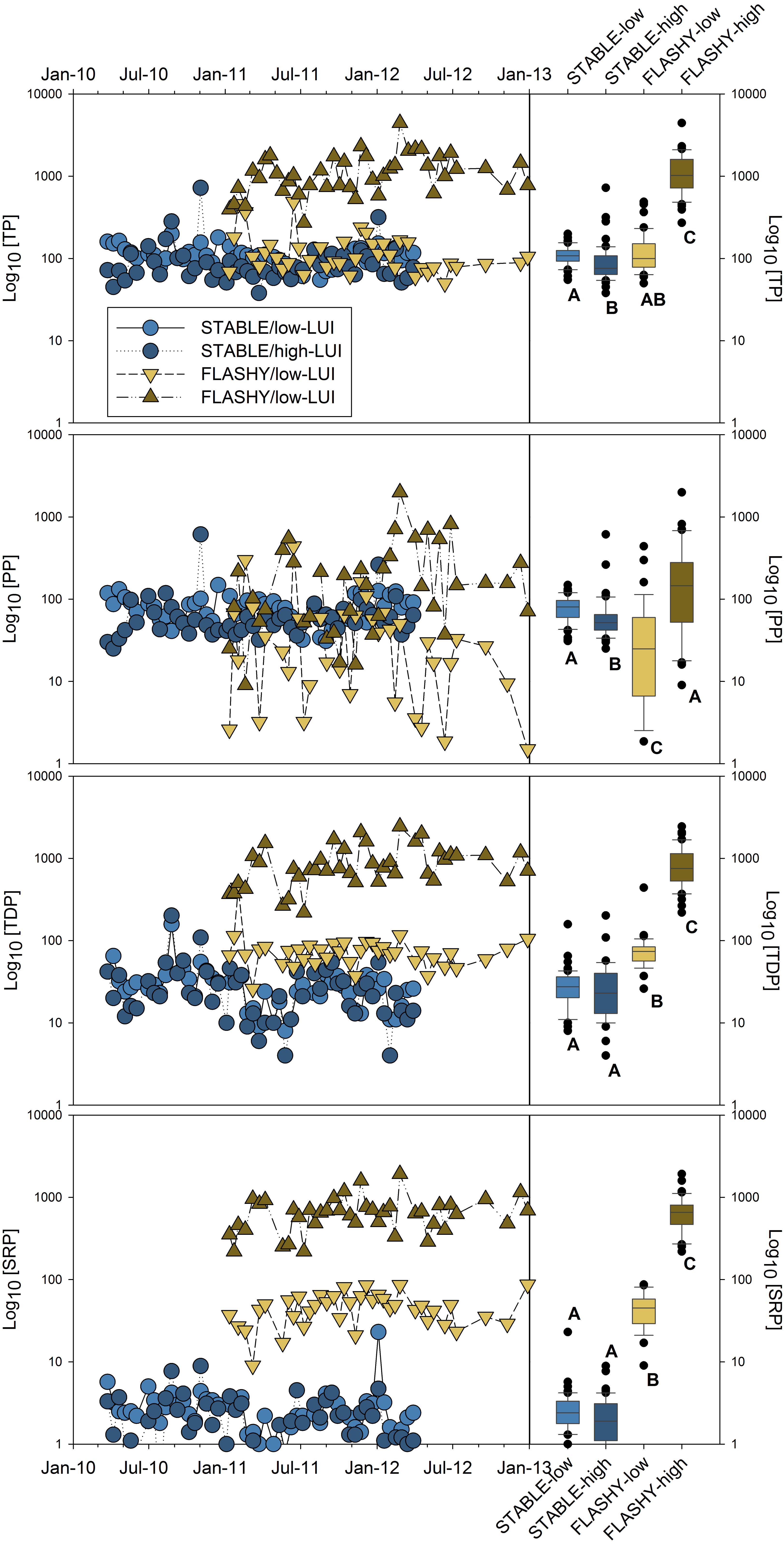

Jan-10
Jul-10
Jan-11
Jul-11
Jan-12
Jul-12
Jan-13
STABLE-low
STABLE-high
FLASHY-low
FLASHY-high
Log10 [TP]
Log10 [PP]
Log10 [TDP]
Log10 [SRP]
10000
1000
100
10
1
STABLE/low-LUI
STABLE/high-LUI
FLASHY/low-LUI
FLASHY/low-LUI
A
B
AB
C
A
B
C
A
A
A
B
C
A
A
B
C

Fig. 4. Scatterplots of total phosphorus (TP) concentrations of instantaneous-grab samples relative to discharge from the four streams. The dots connected by lines represent the predicted values according to the load apportionment model (see Table 4). For STABLE catchments, only the diffuse originated term of the model is included. Lowest graphs display the predicted TP concentration of all catchments from point (left) and diffuse sources (right) for a range of 0 to 1000 L s^{-1}. Note the Log_{10} scale for TP. STABLE: low flashiness Danish streams; FLASHY: Uruguayan flashy streams; low and high-LUI: low and high land use intensity.

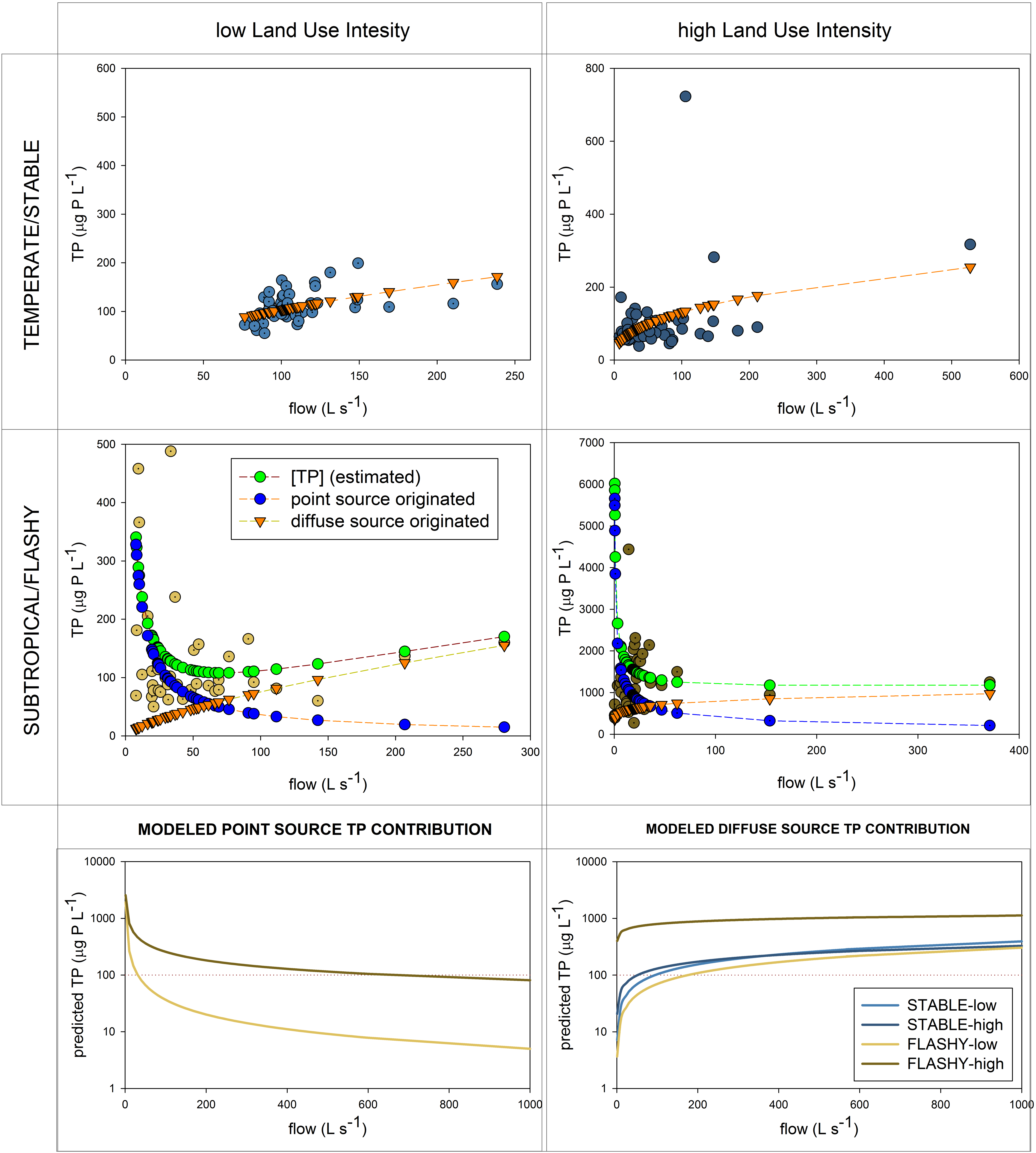
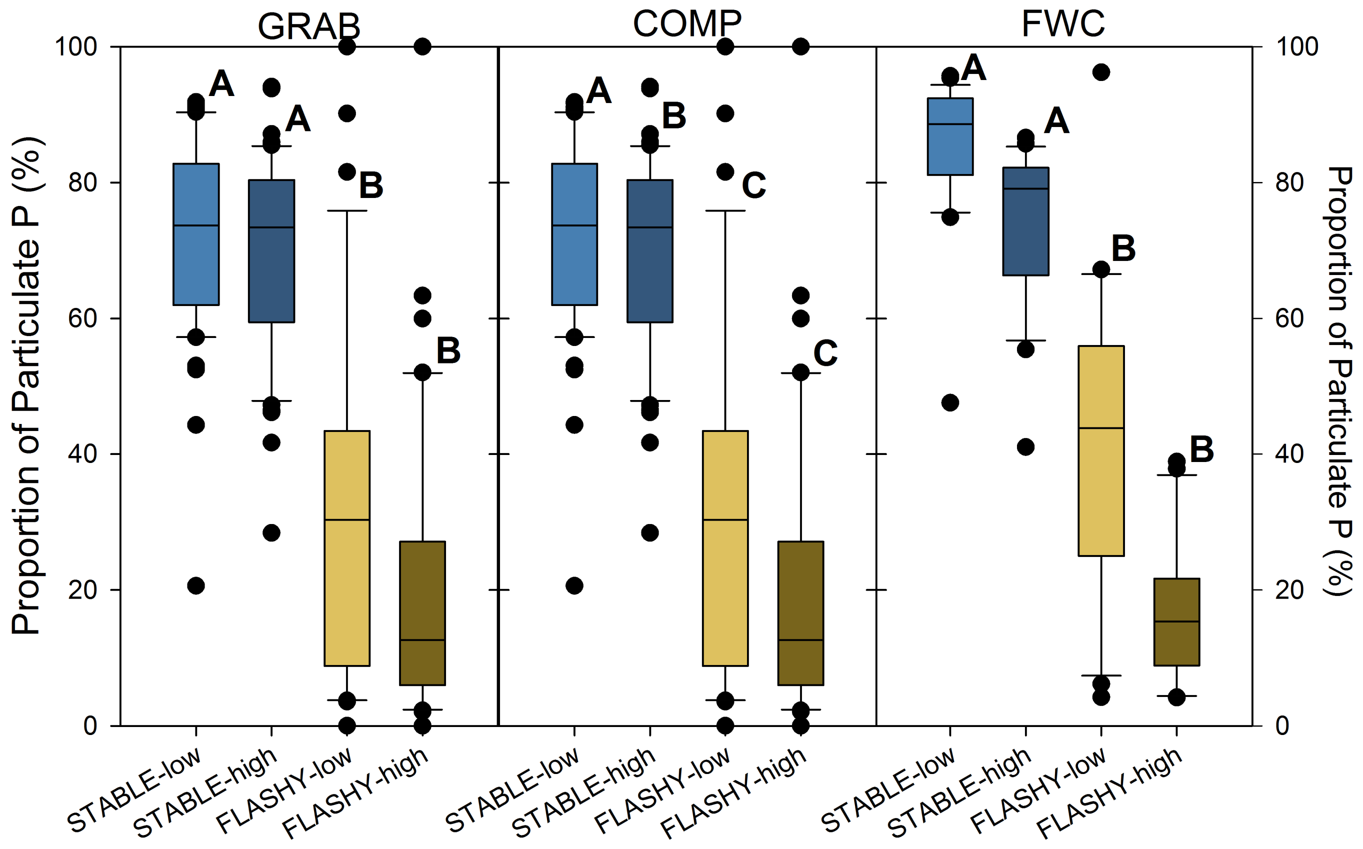

low Land Use Intesity
high Land Use Intensity
TEMPERATE/STABLE
SUBTROPICAL/FLASHY
TP (µg P L^{-1})
flow (L s^{-1})
0
50
100
150
200
250
300
400
500
600
700
800
1000
2000
3000
4000
5000
6000
7000
[TP] (estimated)
point source originated
diffuse source originated
MODELED POINT SOURCE TP CONTRIBUTION
MODELED DIFFUSE SOURCE TP CONTRIBUTION
predicted TP (µg P L^{-1})
1
10
100
1000
10000
STABLE-low
STABLE-high
FLASHY-low
FLASHY-high

Fig. 5. Contribution of particulate phosphorus (PP) to exported total phosphorus (TP). Left boxplots are based on instantaneous-grab sampling and linear interpolation estimation, centre boxplots are based on composite data, and the right boxplot on flow-weighted concentrations. Letters A, B, and C are used to display statistical groups according *post hoc* paired comparison analysis. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers above and below the box indicate the 90th and 10th percentiles. STABLE: low flashiness Danish streams; FLASHY: Uruguayan flashy streams; low and high-LUI: low and high land use intensity.


GRAB
COMP
FWC
Proportion of Particulate P (%)
0
20
40
60
80
100
A
A
B
B
A
B
C
C
A
A
B
B
STABLE-low
STABLE-high
FLASHY-low
FLASHY-high