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Phosphorus dynamics in lowland streams as a response to climatic, hydrological and agricultural land use gradients

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Abstract

Climate and hydrology are relevant control factors for determining the timing and amount of nutrient losses from agricultural fields to freshwaters. In this study, we evaluated the effect of agricultural intensification on the concentrations, dynamics and export of phosphorus (P) in streams in two contrasting climate and hydrological regimes (temperate Denmark and subtropical Uruguay). We applied two alternative nutrient sampling programmes (high frequency composite sampling and low frequency instantaneous-grab sampling) and three alternative methods to estimate exported P from the catchments. A source apportionment model was applied to evaluate the contribution derived from point and diffuse sources in all four catchments studied. Climatic and hydrological characteristics of catchments expressed as flow responsiveness (flashiness), exerted control on catchment and stream TP dynamics, having consequences that were more significant than the outcome of different TP monitoring and export estimation strategies. The impact of intensification of agriculture differed between the two contrasting climate zones. Intensification had a significant impact on subtropical climate with much higher total (as high as 4436 μg P L^{-1}), particulate, dissolved and reactive soluble P concentrations and higher P export (as high as 5.20 kg P ha^{-1} year^{-1}). However, we did not find an increased contribution of particulate P to total P as consequence of higher stream flashiness and intensification of agriculture. The high P concentrations at low flow and predominance of dissolved P in subtropical streams actually exacerbate the environmental and sanitary risks associated with eutrophication. In the other hand, temperate intensively farmed stream had lower TP than extensively farmed stream. Our results suggest that the lack of environmental regulations of agricultural production has more severe consequences on water quality, than climatic and hydrological differences between the analysed catchments.

1 Introduction

Land use is intensifying worldwide (Foley et al., 2005), particularly in many developing countries that are undergoing a process of agricultural expansion and intensification (Alexandratos and Bruinsma, 2012). It has been suggested that agriculture can promote regime shifts in freshwater ecosystem by directly and indirectly altering different components of the hydrological cycle (Gordon et al., 2007). In particular, the impacts of agriculture on water quality depend on several control factors such as cropping system, livestock type and density, use of fertilizers, tillage operations, among others (Moss, 2008; Sharpley et al., 1994). Moreover, climate, hydrology and soil types in the catchment are important for determining the timing and amount of nutrient losses from agricultural fields (Haygarth and Jarvis, 2002; Kronvang et al., 2007).

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 potentially have a higher risk of diffuse transfer of nutrients from soils to water (Cassidy and Jordan, 2011; Haygarth et al., 1999). Additionally, modifications in land use and management may lead to an increase or decrease in flashiness (Baker et al., 2004). Nutrient monitoring may, therefore, need to employ different sampling frequencies in stable or highly flashy streams, to accurately capture and describe the temporal dynamics of nutrient concentrations in the aquatic ecosystems (Cassidy and Jordan, 2011).

Accurate estimation of phosphorus (P) dynamics and mass delivered to lotic systems is crucial to determine causal relationships with catchment activities, mass balances, temporal trends, environmental impacts and develop models (Kronvang and Bruhn, 1996). Irrespective of the hydrological nature of the catchments, nutrient monitoring programmes are frequently based on low cost/low frequency sampling at discrete intervals. Comparisons of monitoring and calculation methods to estimate exported P have been reported in a vast series of papers (e.g. Aulenbach and Hooper, 2006; Jordan and Cassidy, 2011; Kronvang and Bruhn, 1996; Preston et al., 1989; Raymond et al., 2014; Robertson and Roerish, 1999). Among others, monitoring strategies vary from low frequency instantaneous grab sampling and linear interpolation of concentrations between sampling days (henceforth LFS-LI; Kronvang and Bruhn, 1996) through rating curve estimations of nutrient loads (Stenback et al., 2011) and composite or serial sampling (Defew et al., 2013; Harmel et al., 2003), to near-continuous monitoring stations including bankside analysers (Cassidy and Jordan, 2011; Outram et al., 2014).

We conducted a comparative study of hydrology and the concentrations and export of different P forms in paired lowland micro-catchments ($< 20\,\text{km}^2$) having different agricultural land use intensity and covering two distinct climate-hydrological conditions (temperate and stable discharge regime in Denmark and sub-tropical and flashy conditions in Uruguay). We applied two alternative nutrient sampling programmes (high frequency composite sampling and low frequency instantaneous-grab sampling) and three alternative methods to estimate exported P from the catchments. The main objective of the study was to evaluate the direction and magnitude of the effects of agricultural intensification on the concentrations, dynamics and export of P in streams under contrasting climate and hydrological regimes. Three questions were addressed: (i) How do alternative P monitoring programmes capture the differences in climate-hydrology between the two kinds of land use? (ii) Do streams in intensively farmed micro-catchments have higher P concentrations and exports than those in extensively farmed catchments, beyond climatic-hydrologic differences? and (iii) Is there a synergistic interaction between agricultural intensification and climatic-hydrological variability in water P dynamics?

2 Material and methods

2.1 Catchment selection

Based on of our prior knowledge about the different hydrologic regimes of temperate streams (higher hydrological stability) and subtropical streams (higher hydrological variability), four comparable low order streams draining lowland micro-catchments were selected in Denmark (Europe; Gudenå River basin) and Uruguay (South America; Santa Lucía Chico River basin). Two streams draining catchments with contrasting land uses were selected in each climate. Intensive agriculture with arable cropping systems was the predominant land use (more than 90 % of total area) in one of the two catchment types (Table 1). In the Uruguayan intensive catchment, the agricultural production system was based on forage crops, dairy cattle feeding all year around in open fields and no effluent treatment facilities on milking plants, while in Denmark the intensive catchment included a rotational cropping system with winter cereals and confined pig farms with effluent storage facilities. Moreover, the intensive catchment in Denmark mostly consisted of arable fields drained with subsurface tile drainage systems (Grant et al., 1996). The extensive land use catchments were chosen to best represent local conditions. The Uruguayan extensive catchment was dominated by the natural grassland of Pampa Biome (Allaby, 2006) as a basis of a low density cattle production (70 % of total area and below 1 head by hectare; Table 1). A mixture of deciduous and coniferous trees dominated the Danish extensive catchment (Table 1). The subtropical intensive catchment had 170 inhabitants and the extensive catchment only 20 inhabitants (Instituto Nacional de Estadística, 2015). The former catchment featured a facultative lagoon that receives effluents from 10 households. All other households in both subtropical catchments had leaking septic tanks. The point sources for temperate catchments corresponded mainly to scattered dwellings without connection to sewage treatment plants. The temperate intensive stream received the stormwater outlets pouring from a small village, but their sewage water is pumped to a treatment plant with tertiary treatment outside the catchment.

Henceforth we will refer to the temperate-Danish catchments as “TEMP” and the subtropical-Uruguayan catchments as “SUBTR”, while catchments with intensive and extensive land use will be referred as “INT” and as “EXT”, respectively. Measurements and results from a two-year monitoring period were analysed (March 2010 to March 2012 in TEMP, and January 2011 to January 2013 in SUBTR).

2.2 Field measurements

Similar gauging and monitoring stations were established in all four micro-catchments in order to register meteorological data, stream hydrology and phosphorus (P) concentrations.

In all catchments, CR10X data loggers (Campbell Scientific Ltd.) were configured to register data every 10 min. In the SUBTR streams we used CS450 Submersible Pressure Transducers (Campbell Scientific Ltd.) for water stage monitoring as well as temperature probes HMP45C (Campbell Scientific Ltd.) and rainfall automatized gauges Rain-O-Matic Professional (Pronamic). In the TEMP 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 km × 10 km grid.

Instantaneous periodic flow measurements were conducted during the project development period using a C2-OTT Kleinflügel transferring data to software for 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. Rating curve was used for calculation of 10 min and daily discharge utilising the software HYMER (www.orbicon.com). For comparisons, discharge data is reported as area-specific runoff.

Two alternative water sampling strategies were implemented for nutrient analysis. High frequency composite sampling was undertaken using Glacier refrigerated automatic samplers (ISCO-Teledyne). The samplers were programmed to collect an equal water volume every four hours, and the composite samples were collected following a fortnightly sampling programme. The final phosphorus concentration in the sampler carboy represents a time-proportional average for the complete sampling period. Complementary low frequency instantaneous grab sampling of water was conducted at every fortnightly visit to the stations.

2.3 Laboratory analysis

Sediments decanted in composite and grab sample bottles were resuspended before aliquots were taken for total phosphorus (TP) analysis. Grab samples for total dissolved phosphorus (TDP) and soluble reactive phosphorus (SRP) analysis were filtered using 0.45 µm membranes. For TDP analysis, TEMP-composite samples were filtered using 0.45 µm membranes, while SUBTR-composite samples were filtered using Whatman GF/C (pore 1.2. µm). To detect possible symptoms of bias derived from type of filter used, we performed Kruskal–Wallis test to evaluate statistical differences for the proportional contribution of dissolved forms to TP (TDP/TP) between SUBTR grab and composite samples. In this sense, no significant differences were found in the comparison between TDP/TP values estimated from grab and composite samples for the SUBTR-INT stream (median for composite data = 86.7 %; for grab data = 87.7 %; $H = 0.128$, 1° of freedom; $p = 0.720$) and for the SUBTR-EXT stream (median for composite data = 69.1 %; for grab data = 69.7 %; $H = 1.580$, 1° of freedom; $p = 0.209$). 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 in case of total forms. Samples from the Uruguayan streams were frozen at −20 °C and later analysed following the method proposed by Valderrama (1981). The water samples from the Danish streams were analysed within 48 h following Danish standards (Danish-Standards-Association, 1985a, b). All P concentrations are expressed as micrograms of P element per litre ($\mu g\,P\,L^{-1}$).

2.4 Data processing and analysis

2.4.1 Climate and hydrology

Climatic and runoff patterns were explored in order to investigate the main parameters relevant for P dynamics. As a proxy of catchment water balance, the runoff ratio (annual percentage of rainfall water exported as runoff) was calculated (Wu et al., 2013). Additionally, to quantify hydrological responsiveness, we calculated the Richards–Baker Index (hereafter R–B Index; Baker et al., 2004). The R–B Index allows evaluation of the "flashiness", or the annual ratio of absolute day-to-day fluctuations of streamflow relative to total flow, which is an important aspect of the hydrologic regime (Baker et al., 2004). Increasing its value with flashiness, the R–B Index ranges among 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. In the literature, maximum values reach 0.43 for mountain streams in Slovakia and Austria (Holko et al., 2011), 1.009 for Michigan streams (USA) (Fongers, 2012), and 1.32 for the catchments in the US Midwestern States (Baker et al., 2004). The baseflow index, considered as the deeper groundwater contribution to the stream flow, was estimated from daily hydrographs using the automatic routine proposed by Arnold et al. (1995).

2.4.2 Phosphorus dynamics

The statistical relationship between all phosphorus compounds were analysed by means of Spearman rank order correlation. The temporal dynamics of P forms were presented 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) and were graphically presented in scatter and boxplots. As the parametric test assumptions generally failed to be accomplished even with transformed data, the statistical comparisons were made using Kruskal–Wallis tests (Zar, 2010). When differences in the median values among treatment groups were greater than would be expected by chance, a post hoc pairwise multiple comparison procedure was applied to isolate the group or groups differing from the others (Dunn, 1964). Differences were considered statistically significant when the value of p was ≤ 0.05.

2.4.3 Modelling inputs from diffuse and point sources and estimation of export

Three different methods were used for stream P load calculations. The first method (COMP) was based on multiplying fortnightly TP and TDP concentrations from the time proportional composite samples by the accumulated discharge for the same time period (Kronvang and Bruhn, 1996). During the relatively short periods when the automatic samplers were not in operation (e.g. frozen in Denmark), missing data were regenerated through linear interpolation of concentrations for the whole period as in previous works (Jones et al., 2012). Secondly, we calculated daily TP and TDP exported from linear interpolation between the fortnightly grab samples to obtain daily concentrations (LFS-LI), which were subsequently multiplied by daily discharge (Kronvang and Bruhn, 1996). Lastly, concentration–discharge relationships (C–Q) were established based on grab samples for all four streams by applying the load apportionment model developed by Bowes et al. (2008). This alternative estimation strategy is based on the same low frequency data set as the LFS-LI. 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/decide on suitable river mitigation options (Bowes et al., 2008).

The Bowes' 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 (Eq. 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).

$$\mathrm{PC} = \mathrm{dso}_{\mathrm{PC}} + \mathrm{pso}_{\mathrm{PC}} = A \cdot Q^{B-1} + C \cdot Q^{D-1} \tag{1}$$

where PC is phosphorus concentration, $\mathrm{dso}_{\mathrm{PC}}$ is diffuse source originated PC and $\mathrm{pso}_{\mathrm{PC}}$ the point source originated PC, Q is discharge (daily accumulated), and A, C

(proportionality constants) and *B*, *D* (exponents) are empirically determined parameters. Parameters estimation was made using a nonlinear generalized reduced gradient method to select values that minimise the residual sum of squares in the Solver function in Microsoft EXCEL©. 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 zero and increase with increasing flow). Each established *C*–*Q* relationship was used as a model for calculation of daily mean concentrations and then multiplied by daily discharge to achieve daily and annual loads. The proportional annual contribution from point sources and diffuse sources was calculated with this method.

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

As composite samples integrate more information (i.e. shorter time steps, higher probability of capturing extreme events) and do not force temporal variation to arbitrary dynamics (as linear on LFS-LI approximation), we consider this method to provide better estimates of the “true” exported P from the catchments. Based on this assumption, we evaluated the uncertainty involved when utilising the two other load estimation methods: LFS-LI and *C*–*Q*. It should be noted that the concentrations obtained in composite samples are time-weighted averages for each time lapse/each sample sequence, while effective exported P estimates are directly dependent on an instantaneous combination of concentration and discharge (flow-weighted averages).

2.4.4 Total, dissolved and particulate phosphorus

The relative contribution of particulate (PP) and dissolved (TDP and SRP) P to total P was analysed for loads and concentrations in two ways. First, we calculated the percentage of the total amount of phosphorus exported in particulate forms for each hectare of catchment and monitored year (COMP and LFS-LI methods). Then, we estimated the contribution of PP to TP as grab, composite and flow-weighted concentrations (FWC) estimated from composite samples on a monthly basis as accumulated load divided by total flow for the considered period. FWC estimation allows calculation of a flow-normalised comparison of P concentrations between catchments.

3 Results

3.1 Climate and hydrology

During the study period, minimum, mean, median and maximum air temperatures were between 8 and 12 °C higher in the SUBTR catchments than in the TEMP catchments (Fig. 1). The annual average temperature in the TEMP catchments was around 8.8 °C and ranged between −7.0 to 20.4 °C. The corresponding figures for the SUBTR catchments was around 17.5 °C and ranged between 3.7 to 32.2 °C.

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

The TEMP streams exhibited a stable hydrologic regime at the annual (low inter-annual variability of total discharge) and daily scale (the R–B Index never reached values higher than 0.3; Table 2). In contrast, the SUBTR streams could be classified as flashy systems with an R–B Index ranging between 0.9 and 1.3 (Table 2). When comparing the hydrological regime of the streams within each climate, those draining the intensively farmed catchments had the most flashy characteristic (Table 2).

Most of the water flowing in the TEMP streams was exported during baseflow conditions (64–88 %), while in the SUBTR streams most was exported during stormflow conditions (29–39 %; Table 2). The TEMP-EXT stream showed a very different hydrologic behaviour than the other three streams in that a very high percentage of the rainfall was discharged (64–67 %), with high minimum flows and low variability (Fig. 2 and Table 2).

3.2 Phosphorus dynamics

Total P concentrations were positively correlated with all other P fractions (PP, TDP, SRP, SNRP) in the TEMP-INT and SUBTR-INT streams, whereas for extensive streams TP only showed a significant relationship with PP in TEMP and with TDP and PP in SUBTR (Table 3). The relationships between TDP and SRP were less strong but significant ($p < 0.05$) in the extensive streams than in the intensive ones under both climate conditions (Table 3). The contributions of PP to TP were relatively similar for the intensive and extensive agricultural land use catchments in TEMP, but in SUBTR the proportion of PP decreased with the intensification of agriculture (Table 3). Strongest relationships between PP and TP were found in both the TEMP and SUBTR-EXT streams (Table 3). By contrast, in SUBTR-INT, TDP, and particularly SNRP, showed the strongest relationship with TP (Table 3). Negatives relationships were found uniquely for EXT streams, between PP and TDP, the first and SNRP for TEMP stream and between SNRP and SRP for SUBTR stream (Table 3).

The median TP concentrations calculated for the four streams differed significantly ($H = 107.805$; $p \leq 0.001$), being significantly higher in SUBTR-INT stream than in any of the other studied streams (min = 271; med = 1024; max = 4436 $\mu g\,P\,L^{-1}$; Fig. 3). All other paired comparisons of TP revealed no significant differences, except for the TEMP streams where the TP concentration was significantly lower in the stream draining the intensively farmed catchment (median = 76 $\mu g\,P\,L^{-1}$) than in the extensively farmed catchment (med = 108 µg P L^{-1}; Fig. 3). No differences were registered between the TEMP and SUBTR-EXT catchments (med = 100 µg P L^{-1}; Fig. 3).

A significant difference ($H = 43.548$; $p \leq 0.001$) in median PP concentrations was found between most streams (Fig. 3), with higher and lower values being registered in the SUBTR-INT and SUBTR-EXT streams (med = 146 and 25 µg P L^{-1} respectively), and intermediate values in the TEMP streams (med = 52 µg P L^{-1} in the intensive, and 80 µg P L^{-1} in the extensive stream). The intensity of agricultural land use affected the PP concentrations differently, being highest the effect on the extensive stream in the TEMP climate, and vice versa in the SUBTR climate. The TEMP streams exhibited lower temporal variation in PP than the SUBTR streams (IQR = 23–37 and 53–227 µg P L^{-1}, respectively).

Furthermore, a significant difference in median TDP concentrations was traced between the streams ($H = 133.298$; $p \leq 0.001$; Fig. 3). Post hoc analysis revealed statistical significance for the TEMP streams only (med = 28 and 23 µg P L^{-1} for extensive and intensive streams). Intermediate TDP concentrations were found in SUBTR-EXT and the highest concentrations were revealed in the SUBTR-INT stream (med = 74 and 756 µg P L^{-1} respectively; Fig. 3).

The median SRP concentrations also exhibited statistically significant differences between the streams ($H = 141.157$; $p \leq 0.001$; Fig. 3). SRP levels resembled TDP, with the lowest concentrations in the TEMP streams (median: 2 µg P L^{-1} in both), intermediate levels in the SUBTR-EXT stream (median: 45 µg P L^{-1}) and the highest levels in the SUBTR-INT (median: 659 µg P L^{-1}; Fig. 3). SRP in the TEMP streams never exceeded 23 µg P L^{-1}, and in the SUBTR-EXT stream it never exceeded 87 µg P L^{-1}. By contrast, the SUBTR-INT stream never had SRP concentrations lower than 219 µg P L^{-1} and SRP reached a maximum concentration of 1920 µg P L^{-1} (Fig. 3).

3.3 Modelling phosphorus inputs from diffuse and point sources

A graphical exploration of concentration–discharge (*C*–*Q*) relationships for the SUBTR streams showed a typical pattern (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 TEMP 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 TEMP-INT *C*–*Q* relationship showed an outlier of a very high TP concentration that we could not explain. 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 TEMP-EXT stream (Table 4).

When considering the relationships established for point source-originated TP for the SUBTR streams, we found a higher exponent (*B*) in the *C*–*Q* relationships for the intensive catchment (Table 4). As a consequence, the decrease in TP with increasing flow (the dilution effect), was less pronounced for the intensive than extensive stream (at 1000 $\mathrm{L\,s^{-1}}$ the SUBTR-INT catchment reached 85 $\mathrm{\mu g\,P\,L^{-1}}$, while the SUBTR-EXT dropped to 5 $\mathrm{\mu g\,P\,L^{-1}}$, 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 intensive than for the extensive catchments under both climate conditions (Fig. 4 and Table 4). However, the SUBTR-INT stream always had higher TP concentrations from diffuse sources than the other streams (Fig. 4). All other *C*–*Q* relationships tested for TP, TDP or SRP produced poorer fits (results not shown).

3.4 Estimation of phosphorus export and sources

The TP and TDP export from the SUBTR-INT catchment was higher in comparison with the other three catchments (Table 5). Moreover, the TP export was always higher from the TEMP-EXT than from the TEMP-INT catchment (Table 5).

When comparing TP export estimates with the high frequency-composite sampling, we found a pattern of underestimation when applying the LFS-LI method for both TEMP catchments, and an overestimation for the SUBTR catchments (Fig. 5 and Table 6). The deviation of exported TP calculated based on COMP sampling and from grab samples using the LFS-LI estimation method was always higher for the extensive than the intensive catchments independent of climate (Table 6). The comparison of exported TP based on COMP sampling and the LFS-LI estimation showed that the difference was most pronounced for TP in the TEMP catchments, a pattern that could not be traced in SUBTR (Table 6).

The C–Q relationships used to calculate exported TP (compared with COMP estimates) produced more accurate results than LFS-LI for the two intensive catchments, irrespective of the climatic region (Fig. 5 and Table 6). The largest and disproportionate deviations of exported TP were obtained by applying the C–Q model to the SUBTR-EXT catchment compared to COMP sampling estimates (364–400 %; Fig. 5 and Table 6).

The field evidence showed a high contribution of PP to exported P, percentages never being lower than 65 % of annual exported TP in the TEMP catchments (Table 5). A contrasting pattern was recorded for SUBTR where the contribution of PP to TP never exceeded 48 % of TP, reaching values as low as 13.6 % (Table 5). This pattern showing a major contribution of PP in the TEMP catchments is repeats itself in the grab, composite and flow-weighted concentrations (Fig. 6). A tendency of a higher, though rarely significant, dissolved P contribution in streams draining intensively farmed catchments was found (Fig. 6).

The estimated contributions of TP from point sources and diffuse sources indicated that the most of the TP export from the TEMP catchments were derived from diffuse sources, as point source contribution from human sources only reached a maximum of 18 % of the exported P (Table 5). Contrary, in SUBTR catchments point sources dominated the P export contributing always more than 83 % of exported P, with human sources contributing < 10 % and the remaining delivered from livestocks (Table 5).

4 Discussion

4.1 Importance of climate and hydrology for P dynamics and sources

A clear difference was found in hydrological regimes between the TEMP and SUBTR climates, being the TEMP more stable than the SUBTR streams, which were classified as flashy (higher R–B Index and lower contribution of baseflow to total flow). Consistently with the climatic characteristics of the catchments investigated, the TEMP catchments having a lower but more evenly distributed rainfall during the year, no extreme rainfall events ($> 50\,\mathrm{mm\,day^{-1}}$) and lower temperature (and therefore low evapotranspiration), and the SUBTR catchments exhibiting an opposite profile. The results of the present work provide insight into the hydrological future for Danish streams given the predicted changes to a more extreme, warmer and wetter climate, and probably flashier streams (Hanssen-Bauer et al., 2005).

The established point source and diffuse source relationships between TP concentrations and discharge clearly showed that climate and hydrology control TP concentrations in streams (Fig. 4), as expected. Several authors have found similar relationships and used them to characterise P dynamics (e.g. Meyer and Likens, 1979), calculate P sources (e.g. Bowes et al., 2008) or simply to calculate P transport (e.g. Kronvang and Bruhn, 1996).

According to C–Q relationships, the P dynamics of the streams and catchments studied differed in several ways. Firstly, only the SUBTR catchments showed strong impacts from point sources on stream TP concentrations, an effect that was much more pronounced in the intensive agricultural than in the extensive agricultural catchment. This pattern is consistent with the well-documented reduced influence of P from larger point sources in Europe due to improved wastewater treatment (European Environment Agency, 2005; Kronvang et al., 2005b). Secondly, as to diffuse source-generated TP in streams, the intensive catchments exhibited a more pronounced TP response at low flow in both climates, while the extensive catchments showed a more gradual but sustained increase in TP with increasing flow. When focusing on diffuse source inputs, the resultant P dynamics were similar for the two TEMP and the SUBTR-EXT catchments, while the SUBTR-INT catchment exhibited the highest TP concentrations at comparable flows (Fig. 4). The results agree with Jarvie et al. (2010) as catchments with intensive livestock farming had much higher stream water P loadings (derived from highly consistent diffuse source TP yields) than catchments with arable farming only.

4.2 Comparison of different phosphorus monitoring schemes

The performance of different monitoring frequencies and load estimation methods seems to reflect the hydrologic character or flashiness of the investigated streams. Low frequency sampling and interpolation methods are prone to very high uncertainties due to under-representation of high discharge, short-duration events (Defew et al., 2013; Jones et al., 2012; Jordan and Cassidy, 2011; Stelzer and Likens, 2006). However, we did not find a notorious poorer performance of LFS-LI in estimating P exports in flashy SUBTR compared to TEMP streams. On the other hand, the results suggest that climate and hydrological conditions generate a bias in load estimations towards underestimation in TEMP (hydrologically stable streams) and overestimation in SUBTR (flashy streams). This underlines the inadequacy of the method to depict stream dynamics, which is consistent with previous findings (e.g. Jones et al., 2012). Furthermore, we detected considerable interaction between sampling frequency and concentration–discharge relationships, and similar to Richards and Holloway (1987), we conclude that loads of substances whose concentration increase during runoff periods (as the TEMP catchments with only diffuse P sources) will be underestimated, while loads of substances whose concentration decrease during runoff periods (as the SUBTR catchments with high contribution from point sources) will be overestimated.

Additionally, we found signs of interaction between climatic/hydrological and land use factors, such as lower deviation of LFS-LI estimates for TEMP-INT compared to TEMP-EXT catchments. Therefore, land use intensity seems also to be an control factor that has to be considered when planning a sampling strategy to capture P dynamics in streams.

The concentration-discharge (C–Q) relationships established for the streams appeared as relatively poor in all cases. However, the estimated annual TP export based on the C–Q method produced similar results to those of the LFS-LI method, except for the SUBTR-EXT stream where the C–Q method yielded strongly disproportionate overestimations of P export. The C–Q method also produced close-fitting results like the Comp method for the intensive catchments, irrespective of climate zone.

4.3 Importance of agricultural intensification on P forms, P dynamics and P sources

The impact of intensification of agriculture on stream P concentrations and P exports differed between the two contrasting climate zones. Intensification had a significant impact on P concentrations and P export in the SUBTR catchments, with much higher TP, PP, TDP and SRP concentrations and higher P export considering all sampling and load estimation methods considered. Estimated P losses from the SUBTR-INT catchment exceeded the maximum range of 35 comparable Nordic/Baltic micro-catchments studied by Kronvang et al. (2007).

The difference found between the TEMP-INT and TEMP-EXT catchments, with the extensive catchment showing higher concentrations of TP and PP, can possibly be explained by different processes, including higher bank erosion related to the year-round higher discharge (higher stream power; Laubel et al., 2003), discharge of anaerobic groundwater with high natural SRP concentrations (Kronvang et al., 2007) and deeper soil aeration promoted by tile draining and resultant higher binding capacity for surplus P from agricultural production in the intensive catchment (Leinweber et al., 2002).

Even if the TEMP-EXT stream had similar TP concentrations to the TEMP-INT and SUBTR-EXT streams, the former had a higher TP export as a consequence of higher flow. However, all the calculated annual TP export values were within the range of estimations reported for comparable micro-catchments with grassland-agriculture production ($5\,\mathrm{km}^2$; 0.89 to $3.98\,\mathrm{kg\,P\,ha^{-1}\,yr^{-1}}$; Campbell et al., 2015), arable (9 and $11\,\mathrm{km}^2$; 0.12 to $0.83\,\mathrm{kg\,P\,ha^{-1}\,yr^{-1}}$; Melland et al., 2012) in Ireland, and for Norwegian arable catchments (4.5 and $6.8\,\mathrm{km}^2$; 0.5 to $5.8\,\mathrm{kg\,P\,ha^{-1}\,yr^{-1}}$; Kronvang et al., 2005a).

The contribution of TP from point sources was negligible in both TEMP catchments, but never contributed with less than 83 % in the two SUBTR catchments irrespective of land use. These results may be due to an interaction between climate and differences in land use management between the investigated catchments. A higher contribution of dissolved P forms to TP is probably a result of the lack of local treatment of sewage from dairy facilities and is exacerbated by direct cattle access to the stream channel. The joint effect of the two factors can explain that the highest levels of TP, TDP, SRP and SNRP were found in the SUBTR-INT catchment, together with the highest relative importance of dissolved P forms. The direct contribution of phosphorus from local inhabitants was relatively low in SUBTR catchments (4 to 8 % of exported P), and slightly higher in TEMP catchments (10 to 18 %) but too low to be detectable in our established C–Q relationships as point sources. In the SUBTR-EXT catchment, increased rates of bank erosion, deterioration of buffer strips, direct deposition in water and mobilisation from sediments, likely promoted, among other factors, by cattle activity, could lead to the high proportion of dissolved P in the water (Laubel et al., 2003; Sheffield et al., 1997; Jarvie et al., 2010; Kronvang et al., 2012).

Despite the level of consistency in the results on the relative magnitude of point sources in the SUBTR catchments, the contribution of diffuse sources to exported P seems to be underestimated by the C–Q model. This is probably a consequence of the underrepresentation of the grab sampling programme during high discharge events (due to inaccessibility to the sites), aspect that would become more relevant as the flashier character increases. Higher frequency data on P concentrations should therefore be derived, perhaps using sequential samplers instead of composite samples; stratifying sample collection in function of the hydrologic status of the system (e.g. baseflow condition, stormflow condition), and changing sampling frequency following a strategy of adaptive assessment (i.e. time paced monitoring programs complemented with storm sampling, thereby increasing the number of potentially diffuse-dominated data points at high flows). Whenever possible, flow-weighted sampling has to be implemented, through automatic samplers triggered by increases of flow (Rodríguez-Blanco et al., 2013), water level or rain events, or by means of (expensive) automatized bank-side analysers (Campbell et al., 2015). Other strategies, such as passive sampling using flow-proportional samplers (Audet et al., 2014; Jordan et al., 2013) still remain to be evaluated for flashy-warm streams.

Assumptions of the C–Q model applied for source apportionment of P, such as that all point source inputs are continuous and all diffuse inputs are flow dependent, are probably not fulfilled for the analysed SUBTR catchments due to processes such as sediment mobilisation by cattle trampling and storm flow water running from cattle milking yards.

Both SUBTR catchments showed a contribution of P from point sources that was not detected in the two TEMP catchments (Fig. 4 and Table 4). This result is possibly linked to the high efficiency of effluent treatment facilities and productive regulations in TEMP catchments which are so far absent in the SUBTR catchments. Moreover, all the cattle have direct access to the stream channel in the SUBTR catchments, which is not the case in the TEMP catchments where fencing off the stream channels is mandatory. The impact on P by cattle accessing the stream channel can be noticeable, arising from trampling (Trimble and Mendel, 1995), bank erosion (Laubel et al., 2003) and direct pollution via excretion (James et al., 2007). Such impact is included in both the point source and diffuse source signal from established C–Q relationships.

One of the strongest differences between the TEMP and SUBTR catchments was that dissolved P forms dominated over particulate forms in SUBTR streams, irrespective of methods used. The high stream flashiness combined with intensification of agriculture was expected to increase the contribution of particulate P to the TP export. However, this was not the case as TDP dominated the TP export in both SUBTR streams (52–86 %). The reason is probably related to farming practices in the SUBTR catchments where cattle have access to the stream channel and tertiary treatment of sewage is lacking. In agreement with previous works (Sharpley and Smith, 1994; Sharpley et al., 1996), we suggest that one of the factors potentially increasing TDP losses to streams is the dominant no-till practices associated with the application of fertilizers over the soil surface, a practice that has become absolutely dominant in Uruguay (Derpsch et al., 2010).

4.4 Implications to management

Our work confirms that intensive agricultural systems can be developed without detrimental effects on water quality in streams as long as agricultural production and its various environmental impacts are properly managed, as is the case in, for instance, Denmark (Kronvang et al., 2005a). In contrast, this study clearly proves that today's Uruguayan intensive agricultural production, associated with dairy production, has severe environmental implications for the quality of receiving surface waters where P concentration may markedly exceed biological limits values, contributing to the eutrophication process of downstream reservoirs, as seen elsewhere (Carpenter et al., 1998; Carpenter, 2008; Correll, 1998; Dodds and Welch, 2000; Jeppesen et al., 1999; Moss et al., 1996; Smith et al., 2006).

In Uruguay, a large part of the population has experienced eutrophication-induced events of bad flavour and odour of drinking water, and the Uruguayan Environment Ministry has therefore introduced an action plan for the protection of environmental quality of surface waters (DINAMA, 2013). The plan includes compulsory effluent treatment in dairy farms. Although it is not currently allowed, re-utilisation of manure as fertilizer could assist in establishing a more closed P cycle in agriculture, contributing both to reducing the extent of P inputs to the streams and to lowering the import and use of mineral fertilizers in catchments (Kronvang et al., 2005a).

Occurrence of the highest P concentrations during low-flow periods, predominance of total dissolved phosphorus (TDP) and highly reactive forms (SRP) in the SUBTR catchments exacerbate the environmental and sanitary risks associated with eutrophication, particularly when the values frequently reach and strongly exceed the allowed milligram of P per litre. According to the Uruguayan national water quality standards 25 µg P L^{-1} is the maximum allowed, and this will probably be raised to 100 µg P L^{-1} as a result of more than a decade-long negotiations (DINAMA, 2008). The comparatively high levels of P in the SUBTR-INT lead to the question whether nitrogen could become the limiting nutrient here. In this case, nitrogen-fixing primary producers might be favoured, involving environmental and health risks arising from the development of toxic cyanobacteria blooms when or where the residence time of the water becomes sufficiently high.

Even at low density, cattle activity in the SUBTR-EXT catchment might lead to predominance of dissolved P forms in the stream, reflecting strong point source influence, and dissolved P concentrations that exceeded the national standards in almost half of the grab samplings. To reduce dissolved P, some management plans include fencing off of cattle (Laubel et al., 2003; Sheffield et al., 1997) or ensuring availability of off-stream water sources, which has been shown to reduce the time spent by the cattle in the stream by 92 % in Virginia, USA (Sheffield et al., 1997).

To achieve compliance with water quality targets, long-term efforts to reduce TP/TDP losses to surface waters should probably include other measures than just soil conservation centered on reduction of erosion (Decree 405, 2008). Although they are necessary for soil conservation and contribute to reduce P losses, in the Uruguayan reality probably does not guarantee water quality themselves. Strategies that allow to generate scientific based management actions which maximize agronomic productivity while reducing environmental concerns include the development of catchment models (e.g. SWAT; Gassman et al., 2007), establishment of P budgets (e.g. McKee and Eyre,

2000) and mass balances (e.g. Bowes and House, 2001), evaluation of P surplus (e.g. Wismer et al., 1985) and/or generation a soil P index (e.g. Andersen and Kronvang, 2006). One or more of these approaches should be implemented in Uruguay to ensure best-practice management actions.

5 Conclusions

This work comparing two intensive and two extensive agricultural farmed catchments across two climate zones (Danish temperate and Uruguayan subtropical) shows that climatic and hydrological characteristics of catchments expressed as flow responsiveness, exert clear control on catchment and stream TP dynamics, having consequences that are more significant than the outcome of different TP monitoring and export estimation strategies.

Our results suggest that the lack of environmental regulations of agricultural production has more severe consequences on water quality, than climatic and hydrological differences between the analysed catchments. These consequences includes high TP concentrations (as high as 4436 μg P L^{-1}), P exports (as high as 5.20 kg P ha^{-1} y^{-1}), and extremely high proportion of dissolved P (as high as 86.4 %), as in the case of subtropical intensively farmed catchment studied.

Investigations of the P dynamics in subtropical streams are at a starting point, and further research and high frequency sampling is needed to investigate and explain the important hydrological pathways linkages between fields and streams, and to achieve an improved knowledge about the magnitude of diffuse sources utilizing new innovative monitoring methods such as automatized P bankside analysers.

Finally, we believe that calibration of hydrological and phosphorus models on data from the four catchments is needed to allow for a more detailed interpretation of the processes behind the nutrient cycling and dynamics measured.

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Table 1. Site coordinates (datum WGS84), catchment size, dominant soils and land use.

Id	Stream name	Coordinates	Catchment size	Dominant soils	Land use (area %)
TEMP-EXT	Granslev	56°17′2″ N 9°53′51″ E	740 ha	Haplic Luvisols[a]	Forest (59); arable farming (29); pasture/meadow (7); other (5)
TEMP-INT	Gelbæk	56°13′29″ N 9°48′41″ E	1180 ha	Gleyic Luvisols[a]	Arable farming (92); forest (2); urban (1); other (5)
SUBTR-EXT	Chal-Chal	33°49′31″ S 56°16′55″ W	1880 ha	Luvic Phaeozem and Eutric Vertisols[b]	Extensive pasture (∼ 70); arable farming (∼ 30)
SUBTR-INT	Pantanoso	33°54′13″ S 56°00′23″ W	840 ha	Eutric Regosols[b]	Arable farming and dairy farms (90); extensive pasture (7); urban (3)

Source: [a] World Reference Soil Database classification, European Commission and European Soil Bureau Network (2004); [b] SOTERLAC database, ISRIC Foundation, (www.isric.org).
TEMP: temperate streams; SUBTR: subtropical streams; EXT: extensive land use; INT: intensive land use.

Table 2. Yearly accumulated rainfall and runoff in mm (direct measures), runoff ratio (percentage of rainfall water exported as runoff) and R–B Index of flashiness for each monitored year. Percent contribution of base flow to total flow (BF/TF) was estimated for the complete data set.

	TEMP-EXT	TEMP-INT	SUBTR-EXT	SUBTR-INT
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
BF/TF (%)	88.2 %	63.6 %	39.2 %	29.4 %

TEMP: temperate streams; SUBTR: subtropical streams; EXT: extensive land use; INT: intensive land use.

Table 3. Correlations matrices of total (TP), particulate (PP), total dissolved (TDP), soluble reactive (SRP), soluble non-reactive (SNRP) phosphorus from grab samples. Numeric values represent Spearman rank order correlation and were included only when significant ($p \leq 0.05$).

	TP	PP	TDP	SRP	SNRP	TP	PP	TDP	SRP	SNRP
	TEMP-INT					SUBTR-INT				
TP	–	0.78	0.75	0.68	0.57	–	0.63	0.90	0.67	0.84
PP	0.81	–	ns	ns	ns	0.80	–	ns	ns	0.41
TDP	ns	−0.31	–	0.93	0.70	0.58	ns	–	0.83	0.81
SRP	ns	ns	0.86	–	0.44	ns	ns	0.56	–	0.40
SNRP	ns	−0.34	0.56	ns	–	ns	ns	0.41	−0.37	–
	TEMP-EXT					SUBTR-EXT				

ns: non-significant. TEMP: temperate streams; SUBTR: subtropical streams; EXT: extensive land use; INT: intensive land use.

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Table 4. Estimated parameters for the load apportionment model fitted for each stream.

Source	Parameter	TEMP-EXT	TEMP-INT	SUBTR-EXT	SUBTR-INT
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

RSS: residual sum of squares. NSC: Nash–Sutcliffe model efficiency coefficient. TEMP: temperate streams; SUBTR: subtropical streams; EXT: extensive land use; INT: intensive land use.

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} $year^{-1}$.

	TEMP-EXT			TEMP-INT			SUBTR-EXT			SUBTR-INT		
	COMP	LFS-LI	*C–Q*	COMP	LFS-LI	*C–Q*	COMP	LFS-LI	*C–Q*	COMP	LFS-LI	*C–Q*
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	–
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	–

Estimation strategies: "COMP": composite sampling strategy. "LFS-LI": low frequency sampling and linear interpolation strategy. "*C–Q*" concentration–discharge relationships applying the load apportionment model. % PP.: percentage TP exported in particulate form. "% hs" under COMP represents the percentage of annual exported P from human sources. "% ps" under CQ represents the percentage of the total annual exported load from point sources sensu the model. TEMP: temperate, SUBTR: subtropical. EXT: extensive or low intensity land use; INT: intensive land use.

Table 6. The percentages resumes relative fit of alternative estimation methods in relation to the annually exported load estimated by composite sampling programme (as reference). 100 % represents the same annual P exported in $\mathrm{kg\,ha^{-1}\,year^{-1}}$. Values below 100 % (italic) represents underestimation (less 90 %) relative to the estimation of composite sampling. Values over 110 % (bold) represents overestimation relative to the estimation of composite sampling.

		TEMP-EXT		TEMP-INT		SUBTR-EXT		SUBTR-INT	
		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 %**	–

TEMP: temperate streams; SUBTR: subtropical streams; EXT: extensive land use; INT: intensive land use.

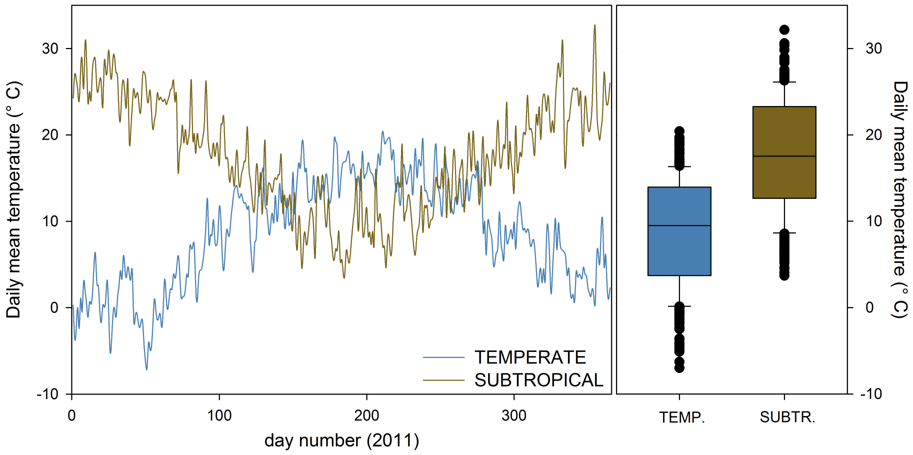

Figure 1. Left: mean daily air temperature variation for one temperate (TEMP) and one subtropical (SUBTR) catchment for 2011. Right: boxplots of the same data. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest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

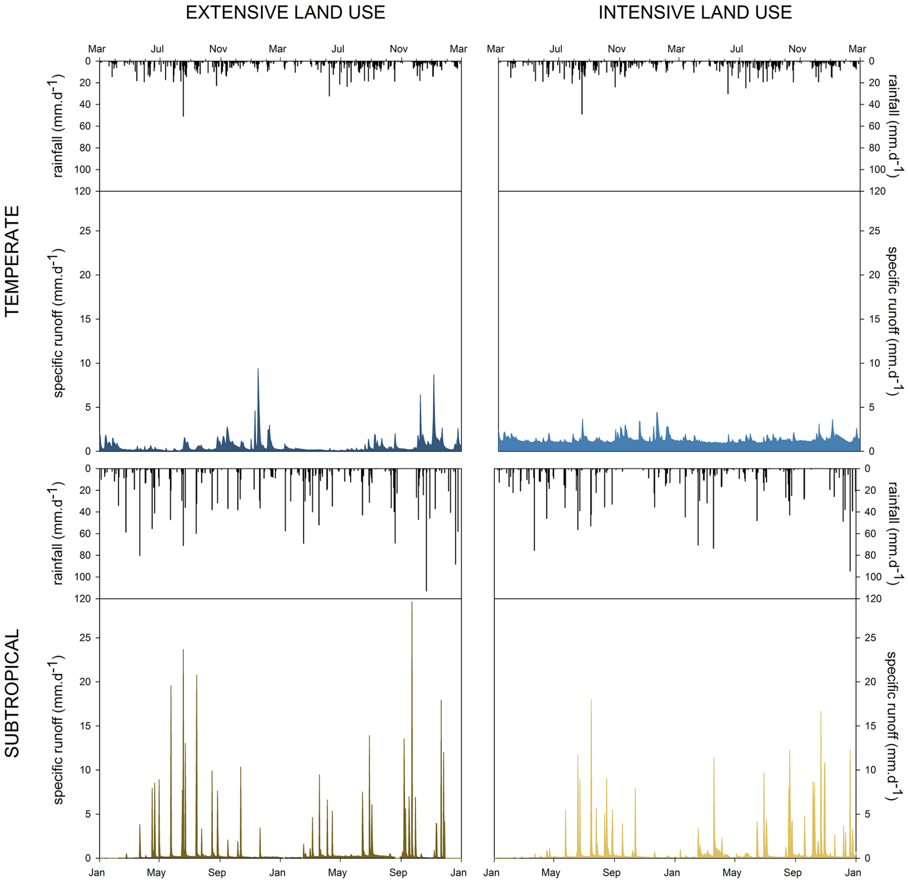

Figure 2. Accumulated daily rainfall and specific runoff hydrographs for the four monitored streams. For each variable a fixed scale was used to aid visual comparison. Flashiness of subtropical streams is clear.

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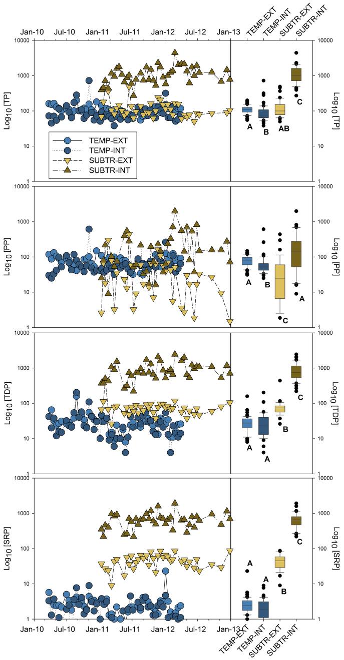

Figure 3. From top to bottom: temporal variation of total (TP), particulate (PP), total dissolved (TDP) and soluble reactive phosphorus (SRP) concentrations from gram samples for all the monitored catchments. Log_{10} scale was selected on the vertical axe to improve visualisation. The phosphorus concentration is always expressed as $\mu g\,P\,L^{-1}$. Right: boxplots are based on the same data. Letters A, B and C are used for display statistical groups following 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. TEMP: temperate streams; SUBTR: subtropical streams; EXT: extensive land use; INT: intensive land use.

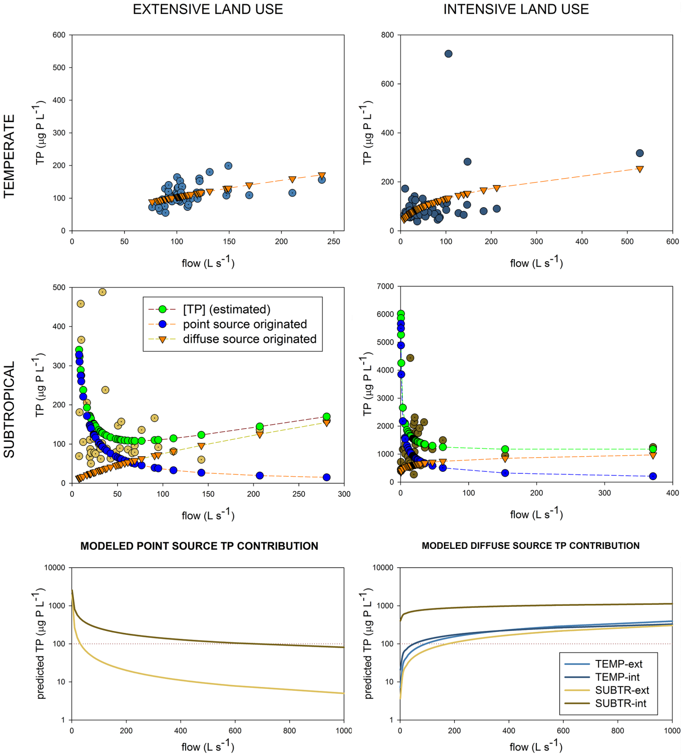

Figure 4. Scatterplots of total phosphorus (TP) concentration of grab samples relative to discharge from the four streams. The dots connected by lines represents the predicted values according to the load apportionment model (see Table 4). For temperate catchments, only the diffuse originated term of 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}. Noted the log$_{10}$ scale for TP. TEMP: temperate streams; SUBTR: subtropical streams; EXT: extensive land use; INT: intensive land use.

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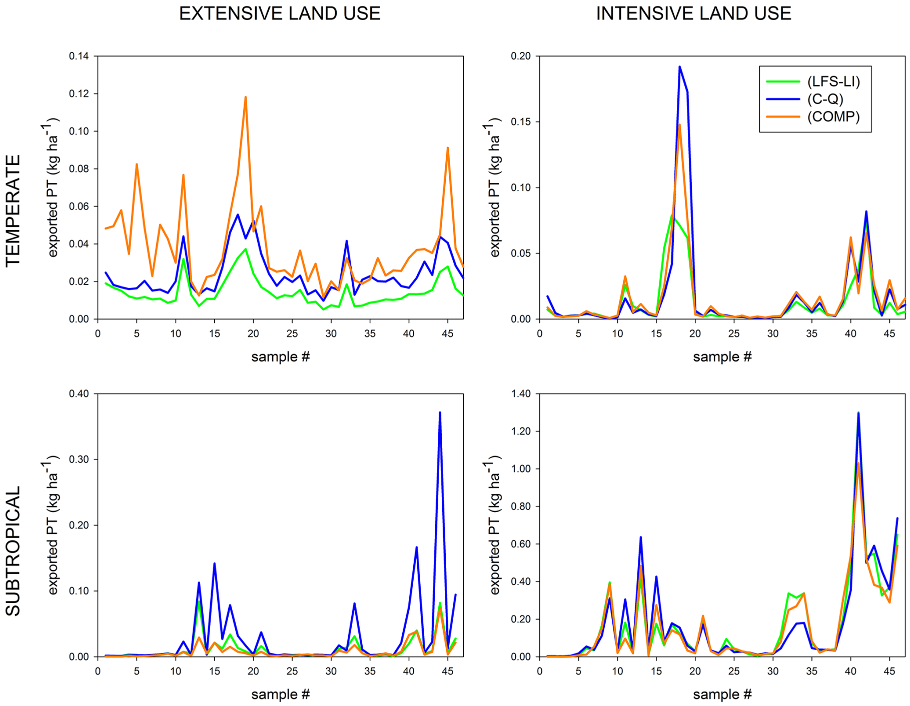

Figure 5. Accumulated fortnightly total phosphorus (TP) exported loads estimated low frequency instantaneous-grab sampling and linear interpolation (LFS-LI), concentration–discharge relationships by applying the load apportionment model (*C*–*Q*) and by high frequency-composite sampling (COMP). TEMP: temperate streams; SUBTR: subtropical streams; EXT: extensive land use; INT: intensive land use.

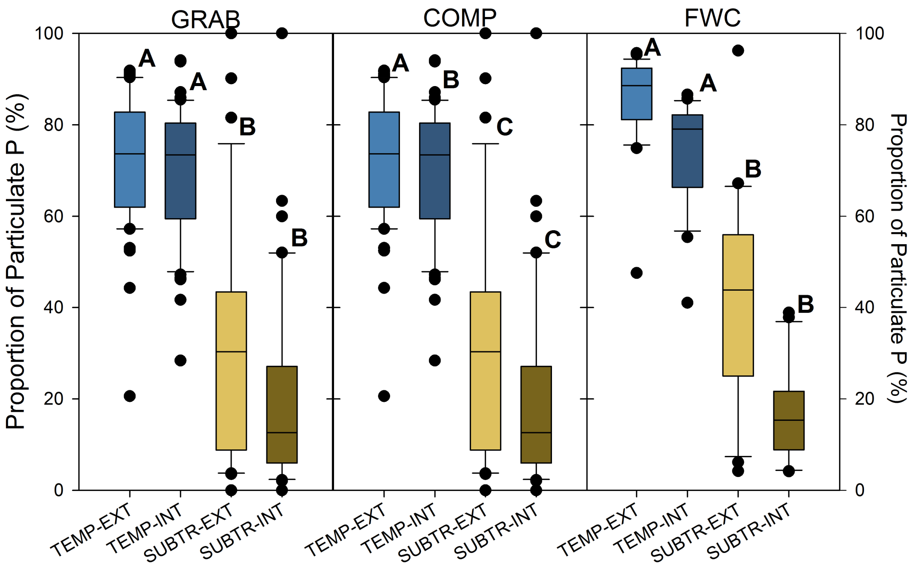

Figure 6. Contribution of particulate phosphorus (PP) to total phosphorus (TP). Left boxplots are based on grab concentrations, centre boxplots are based on composite data and right boxplot on flow-weighted concentrations. Letters A, B and C are used for display statistical groups following post hoc 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. TEMP: temperate streams; SUBTR: subtropical streams; EXT: extensive land use; INT: intensive land use.