

Impact of calculation method, sampling frequency and hysteresis on suspended solids and total phosphorus load estimations in cold climate

Pasi Valkama and Olli Ruth

ABSTRACT

Load calculations of nutrients and suspended solids (SS) transported by rivers are usually based on discrete water samples. Water quality changes in cold climate regions often occur very rapidly and therefore discrete samples are unrepresentative of the range of water quality occurring. This leads to errors of varying magnitude in load calculation. High-resolution turbidity data were used to determine the SS and total phosphorus (TP), and paired with discharge to determine loads from two small catchments in southern Finland. The effect of sampling frequency was investigated by artificially sub-sampling the high frequency concentrations. Regardless of the sampling frequency, the TP load was more likely underestimated while using discrete samples. To achieve $\pm 20\%$ accuracy compared with the reference load, daily sampling should be performed. Hysteresis was detected to have an impact on TP load. Hysteresis analysis also revealed the main source of the TP to be in the fields of the catchment. Continuous measuring proved to be a valuable method for defining loads and short-term fluctuations in water quality in small clayey watercourses in a boreal cold climate, where the climate change will increase the frequency of winter floods.

Key words | high-resolution monitoring, hysteresis, load calculation methods, sampling frequency, suspended solids, total phosphorus

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INTRODUCTION

Nutrient loading from agriculture, manifested as diffuse loading, is considered to be one of the major environmental problems on a global scale and in many European countries (Bechmann *et al.* 2008; Kronvang *et al.* 2009; Withers *et al.* 2014). Most of the diffuse loading from catchments in boreal environments occurs outside the growing season during the snowmelt period in spring and in the rainy autumn season. Dynamic hydrological events cause wide variation in runoff and in suspended solid (SS) and nutrient concentrations in rivers and streams. Consequently, most of the annual sediment and nutrient loads may be transported during relatively short-term flow periods (Langlois *et al.* 2005; Gao *et al.* 2007; Drewry *et al.* 2009). Water quality monitoring of rivers and streams is mostly based on monitoring programmes employing low sampling frequency,

traditionally one or two samples per month. Therefore, the suspended sediment and nutrient loads mobilized during high-flow periods in rivers and streams may be largely uncharacterized.

The calculation of SS and nutrient loads transported in rivers and streams is still widely based on discrete samples (Vuorenmaa *et al.* 2002; Scholefield *et al.* 2005; Bowes *et al.* 2009). This leads to errors of varying magnitude in load calculations (Skarbøvik *et al.* 2012). Monitoring techniques that can measure high SS and nutrient concentrations at high-frequency time intervals are therefore needed.

Various calculation methods have been introduced to reduce the uncertainties in load estimations (Walling & Webb 1985; Quilbe *et al.* 2006; Strobl & Robillard 2008). The relationship between discharge and concentration has

also been used when river discharge is monitored continuously, but the concentrations are measured less frequently (Phillips *et al.* 1999; Horowitz 2003). The problems encountered in using the discharge/concentration relationship to estimate loading often arises from poor correlation between these variables. Typically, concentrations in the rising stage of floods may be different from those in the falling stage during similar discharge (Gentile *et al.* 2010), but there may also be seasonal variability in the concentration/discharge relationship. Some studies have focused on refining rating curve methods to improve the feasibility and precision of the load estimations (Asselman 2000; Cheviron *et al.* 2014).

Varying discharge/concentration relationship on the rising stage and the falling stage of the hydrograph is commonly described by the term hysteresis (Bowes *et al.* 2005). Time lag between the peak values of the discharge and concentration usually leads to a non-linear relationship between discharge and concentration (Gentile *et al.* 2010). Higher concentration in the rising stage of the hydrograph than in the falling stage is described as clockwise or positive hysteresis. Anti-clockwise or negative hysteresis means higher concentration in the falling stage of the hydrograph compared to the rising stage. The size and shape of the hysteresis loops have been suggested to be the indicator of the location of the nutrient sources and the runoff processes in a catchment (Krueger *et al.* 2009; Bierozza & Heathwaite 2015; Bowes *et al.* 2015; Lloyd *et al.* 2016) and thus it has an important role in nutrient load calculation (Eder *et al.* 2010).

There are no economical, robust sensors available to directly measure SS and total phosphorus (TP) in water. To compensate for the lack of frequent concentration measurements, turbidity has been used as a surrogate measure for SS concentration (Gippel 1995; Wass & Leeks 1999; Pavanelli & Pagliarani 2002; Gao *et al.* 2007), as well as for estimating TP concentration (Grayson & Finlayson 1996; Stubblefield *et al.* 2007; Valkama *et al.* 2007; Jones *et al.* 2011; Viviano *et al.* 2014).

High frequency water quality data have also been collected using automatic water samplers (Jordan & Cassidy 2011; Halliday *et al.* 2012; Williams *et al.* 2015). In cold climate regions, the malfunction caused by freezing of a sampler could cause a problem. Also, the long chain from programming the sampler, getting samples from the site to the

laboratory and from analyses to the results is not only a slow process, but it also increases the amount of uncertainty in the results. As well, the autosampler's capacity may restrict higher sampling frequency. International standard ISO 5667-3:2003(E) stresses the importance of the preservation time and handling of water samples. Compounds of P and N may change considerably between the time of sampling and the commencement of analysis if the preservation time of the samples exceeds 24 hours.

In boreal cold climate regions, where the watercourses typically have ice cover during the winter regime, water sampling may be very challenging. Climate change scenarios predict northern areas' temperature and precipitation increase, especially in winter (Bouraoui *et al.* 2004; Graham 2004; Deelstra *et al.* 2011). This would increase the nutrient load and extend the loading time when sampling frequency, typically, is low. Therefore, high frequency *in situ* nutrient monitoring would be essential to get more accurate load estimations in cold climate rivers.

Here, we present water quality data collected by automated on-line sensors from the upper course of the Lepsämäenjoki River and the Lukupuro River located in southern Finland. The study sites differ in size, but they are both agricultural, clay-dominated areas where turbidity and SS would likely correlate. Continuous on-line turbidity and flow measurements were used to calculate the SS and TP loads transported by these watercourses. The objectives were to:

1. acquire high-frequency TP and SS data, using on-line turbidity sensors in a cold climate region;
2. compare the various SS and TP load calculation methods, based on discrete samples and continuous monitoring;
3. investigate the effect of sampling frequency on TP load estimations;
4. study the impact of hysteresis on TP load.

MATERIALS AND METHODS

Study sites

The study area of the upper course of the Lepsämäenjoki River catchment is located in southern Finland in the Vantaa River drainage basin (Figure A1, available with the online version

of this paper). It has an area of 23 km², covering approximately 10% of the total catchment area of the Lepsämäenjoki River. Of the land use, 36.5% is devoted to agriculture. The arable land is mainly used for growing grain (spring cereals 44% in 2006). Cultivated fields are typically located on the flat clayey plain with low gradients near the channel and close to the monitoring point.

The soil type in the river catchment is mostly clay (52%) and till (24%). In the northern part of the study area there are gravel and sandy soils in the region of the Salpausselkä I stage. These coarser soils cover only a small part (10%) of the total area of this catchment. The landscape ranges in elevation from 40 to 130 m above sea level (a.s.l). The maximum relative heights are several tens of metres.

The Lukupuro River has a smaller catchment area (7.6 km²), in which agricultural activities were ended in late 2006 due to land use change for a new housing development. A total of 18% of the area was devoted to agricultural use in 2006; 40% of the soil type is composed of rocky areas and 33% is clay. Fields are located in the upper reaches of the river, in the northern part of the catchment. The annual mean precipitation in southern Finland is 660 mm and the mean temperature is 5 °C. During winter months (December to February) the mean temperature is -3.5 °C and the lowest temperature may be under -30 °C.

On-line monitoring

The automatic water quality sensors used were YSI 600 OMS (YSI Inc., Yellow Springs Instruments, OH, USA) Series Sondes. Turbidity, electric conductivity and water temperature were continuously measured every hour. Here, only the turbidity data are presented. The manufacturer guarantees ±5% or 2-nephelometric turbidity unit (NTU) accuracy for the turbidity sensor. The sensitivity is 0.1 NTU and the measurement range 0–1,000 NTU. The optical turbidity sensor was equipped with a wiper blade to ensure good data quality under extremely turbid conditions. This automatic cleaning of the measuring window was performed before every individual measurement. The measurement system was maintained and cleaned manually at 2-week intervals. The sensor has a probe guard that allows water to flow in front of the sensor and protect it during *in situ* measurements. The turbidity sensor has relatively small optics, a factor that results in minimal

penetration of the light beam into the sample and thus the probe guard or ice cover above the sensor does not affect the results. The water level was also measured automatically every hour with a water level sensor (Keller AG für Druchmesstechnik, Winterthur, Switzerland).

Discharge in the Lepsämäenjoki River was measured indirectly, based on the stage/discharge relationship for this measurement location. An OTT C31 current meter (OTT Hydromet, Kempten, Germany) was used to measure individual discharges at different water levels. A measuring weir was used in the Lukupuro River to determine the discharge. The data from the sensors were collected with data loggers equipped with transmitters, using a Global System for Mobile Communications (GSM) mobile phone network to automatically send the data measured into the server. The data presented here were gathered at both sites between June 2006 and June 2007 to examine the hydrological events over an entire year. In all, 8,670 turbidity and discharge measurements were collected at both study sites during the year.

Manual samples

The water samples were collected as discrete samples under different flow circumstances. Sensor data transferred from the measurement stations were used to determine the timing needed to gather a sample. The purpose was to gather manual samples under high and low flow conditions and high and low turbidity situations. In all, 31 samples were collected from the Lepsämäenjoki River and 84 from the Lukupuro River during the study period. Samples were taken by Limnos sampler at the same time and depth as the probe measured water quality. Automatic turbidity data were compared with the turbidity analysed in the laboratory to examine the performance of the sensors.

The turbidity, SS, TP and dissolved phosphorus (DP) concentrations from the Lepsämäenjoki River were analysed according to European or Finnish standard methods in an accredited laboratory in Helsinki. Analyses from the Lukupuro River were performed in the laboratory of the Department of Geography, University of Helsinki. The SS concentrations from the water samples were measured by filtration through glass fibre filters (SFS-EN 872). Before filtration the sample was homogenized by shaking and an empty filter was weighed. A suitable volume of sample was transferred to the filtering

device with filter. After filtration, the filter was dried in the oven at 105 °C for at least 1 hour and after that it was weighed again. Turbidity was measured nephelometrically with Hach 2100 AN IS turbidometer according to SFS-EN ISO 7027. The presence of P was analysed by the ammonium molybdate spectrometric method (SFS ISO 6878), with ascorbic acid as a reducing agent. Before TP analysis, the sample was digested by acid peroxodisulfate at 120 °C. DP was determined on a filtered sample (Whatman nucleopore polycarbonate, pore size 0.4 µm) without digestion.

Load calculations

The turbidity/SS concentration and turbidity/TP concentration relationships were established for both catchments, using data collected during the study year. The TP and SS concentrations were calculated based on the sensor-recorded 1-h frequency turbidity data. Regression analysis was used to estimate TP (µg/L) and SS (mg/L) from turbidity. Hourly loads were calculated by multiplying the estimated concentration with the hourly measured discharge (L/s). The annual loads were computed as the total sum of these hourly loads (Equation (1)):

$$L_a = \int_{t1}^{t2} Q(t)C(t) dt \quad (1)$$

where L_a is the annual load between period $t1$ and $t2$, $Q(t)$ is the discharge at time t , $C(t)$ is the concentration at sampling time t and dt represents time in seconds between sampling times. Loads calculated, based on hourly concentration data (i.e., hourly loads), were assumed to be the most accurate and the results calculated by other methods were compared against these reference values.

Calculation methods used to estimate loads were: yearly averaging, ratio method, linear interpolation method and concentration/discharge relationship (rating curve). These are methods traditionally used to calculate loads from discrete water samples.

Yearly averaging method

The yearly averaging method was based on arithmetic means of concentration (\bar{C}) and discharge (\bar{Q}), and the

loads were calculated according to:

$$L_1 = \sum_{i=1}^n \bar{C}\bar{Q}[Ti] \quad (2)$$

where $[Ti]$ is time in seconds. This method has been used in sampling methodologies and load estimation techniques study, for example, by Cassidy & Jordan (2011).

Ratio method

In the ratio method described by Walling & Webb (1985), Kauppi & Koskiaho (2003) and Skarbøvik *et al.* (2012), the annual load (L_2) was calculated as the product of the annual flow-weighted mean concentration and annual flow (Q_a) according to:

$$L_2 = \left(\frac{\sum_{i=1}^n C_i Q_i}{\sum_{i=1}^n Q_i} \right) Q_a \quad (3)$$

where (C_i) is the concentration in sample and (Q_i) is the flow at the sampling time.

Linear interpolation method

In the linear interpolation method, the daily concentration (C_d) was interpolated between the sampling day concentrations (Skarbøvik *et al.* 2012; Williams *et al.* 2015). Sampling day concentrations refer to TP and SS analysed in the laboratory. The daily load was then calculated by multiplying the interpolated concentration by the mean discharge of the day (Q_d) calculated from continuous flow measuring. The annual load (L_3) was calculated as the sum of these daily loads (Equation (4)):

$$L_3 = \sum_{d=1}^{365} C_d Q_d \quad (4)$$

Rating curve method

Finally, in the rating curve method (Asselman 2000; Chevion *et al.* 2014), we used the relationship between concentration and discharge of the sampling days to calculate the daily concentrations between sampling times. Least-square regression was used, and a linear equation was fitted for both study sites.

The daily concentration values (C_d) were derived according to:

$$C_d = aQ_i + b \quad (5)$$

The daily loads for each day were then calculated by multiplying the daily discharge by the concentration. The amount of the yearly load was summed up from these daily load values similar to Equation (4). Logarithmic transformation was considered, but not performed, because it could have led to transformation bias (Asselman 2000).

Testing of different sampling frequency

We tested the effect of the sampling frequency on TP loading, using systematic sub-sampling from hourly modelled, high frequency TP data described by Jones *et al.* (2012). Concomitant concentration and discharge values were selected randomly for each sampling intervals. Sub-sampling was repeated 100 times at each sampling interval to get a distribution of load estimations. Sampling intervals of 6, 12, 24, 52, 100, 200 and 365 samples per year were selected. Equations (2) and (3) were used to calculate the yearly TP loads from each sampling frequency. The results were compared against the reference data calculated from the high-frequency sensor data, and the probabilities of achieving TP loads that were $\pm 20\%$ of the reference loads were estimated.

Characteristics of single event discharge/TP concentration relationship and the impact of hysteresis on TP load

Flow events leading to a 50% increase in discharge that affected the TP concentration were identified from both the Lukupuro River (34 events) and the Lepsämäenjoki River (23 events). Hysteresis index (Hi), discharge (Q_{max}) and TP maxima (TP_{max}), duration, mid-point discharge (Q_{mid}) and TP in the rising stage (TP_r) and the falling stage (TP_f) of the discharge and TP load were determined. Hysteresis index, mid-point discharge and TP were calculated according to Lawler *et al.* (2006). The greater the hysteresis is the higher is the Hi . Negative Hi values indicate

negative hysteresis and positive Hi positive hysteresis. If no hysteresis is present, the Hi is zero. Also, the hysteresis loop size was determined according to Bowes *et al.* (2015) to describe the size and shape of the hysteresis effect.

The impact of varying time lag (h) between TP maxima ($\mu\text{g/L}$) and discharge maxima (hysteresis) on the highest TP load (kg/h) of single flow events were analysed in both catchments. A high flow event in October 2006 was selected and the actual hysteresis and actual hourly TP load maxima were determined. The hourly TP load maxima was calculated also in cases where the time lag was set at -15 to 15 h in the Lepsämäenjoki River and -10 to 10 h in the Lukupuro River. Time lags covering the actual range detected in the hysteresis analysis were selected to cover the impacts of positive and negative hysteresis on TP load.

Statistical analyses

Descriptive statistics including mean and its 95% significance, minimum and maximum, standard deviation, medians and 25% and 75% quartiles were calculated from the Lepsämäenjoki River and the Lukupuro River to study the characteristics and the variation of turbidity. Differences between turbidity from manual samples and sensor data in the Lepsämäenjoki River and the Lukupuro River were compared using non-parametric Mann-Whitney U-test for two unrelated populations because of non-normal distribution of most of the datasets (Rock 1988; Ranta *et al.* 1991). Normality and log-normality were tested using the Kolmogorov-Smirnov test and by visual evaluation of frequency distribution as suggested by Reiman & Filzmoser (2000). Pearson's correlation coefficient was used in correlation analysis between turbidity and SS and turbidity and TP. The errors of created models were studied by using root mean square error (RMSE), as suggested by Jones *et al.* (2011). Two-tailed paired *T*-test was used for comparison between laboratory analyses and sensor data measured at sampling time to test the function of the sensors and to reveal possible systematic malfunction of the turbidity sensors. Differences and correlations were considered statistically significant when $p < 0.05$. All statistical analyses were performed with IBM SPSS Statistics 22 (IBM SPSS, Armonk, NY, USA).

RESULTS

Laboratory vs. sensor turbidity and TP

The range of turbidity measured with the sensors at both study sites was wider than that calculated from the manual samples (Figure 1). The mean turbidity (99 NTU) was significantly higher ($p < 0.01$) in the manual samples than in the sensor data (43 NTU) in the Lepsämäenjoki River, but in the Lukupuro River the means were nearly equal (22 and 18 NTU). Still, the Mann–Whitney U -test revealed a significant difference in the turbidity measured by sensor and laboratory ($p = 0.012$). Standard errors of the means were 16.36 NTU (manual samples) and 0.55 NTU (sensor) in the Lepsämäenjoki River and 1.98 NTU and 0.19 NTU in the Lukupuro River, respectively. The turbidity data from the manual samples of the Lepsämäenjoki River covered 0.35% of the data provided by the sensors and from the Lukupuro River 1.0%. Thus, there was a higher probability of detecting higher maximum values with the sensors than with manual sampling. The two-tailed paired T -test values indicated no significant difference between the turbidity analysed in the laboratory and that recorded by the YSI sensors at sampling time ($p < 0.001$). On average, 79% and 81% of TP was found to be bound in particles in the Lepsämäenjoki River and the Lukupuro River, respectively.

Deriving continuous TP and SS data

Turbidity, as measured by the sensors, showed a statistically significant ($p < 0.01$) correlation with the SS concentration analysed in the laboratory (Figure 2(a)), both from the Lepsämäenjoki River ($SS = 0.59 \text{ turbidity}$, $R^2 = 0.96$, $n = 31$) and the Lukupuro River ($SS = 0.85 \text{ turbidity} + 6.84$, $R^2 = 0.81$, $n = 84$). The residuals were normally distributed and the RMSE for these regression models were 11.6 mg/L for the Lepsämäenjoki River and 7.3 mg/L for the Lukupuro River. The intercept of the equation was not statistically significant in the Lepsämäenjoki River, so the equation was forced to its origin, indicating the concentration to be 0 mg/L at a turbidity of 0 NTU (Wass & Leeks 1999). In the Lukupuro River equation, the intercept (6.84) was statistically significant ($p < 0.01$) and thus not rejected. This may be due to very fine-grained SS that flows through the filter pores in laboratory analyses.

TP and turbidity measured *in situ* by the YSI sensors also showed statistically significant correlations (Figure 2(b)). The relationship was not as strong in the Lukupuro River ($TP = 1.39 \text{ turbidity} + 16.5$, $R^2 = 0.82$, $n = 79$, $p < 0.01$) as in the Lepsämäenjoki River ($TP = 1.02 \text{ turbidity} + 50.8$, $R^2 = 0.92$, $n = 31$, $p < 0.01$). The RMSE values were 26.9 $\mu\text{g/L}$ for the Lepsämäenjoki River and 14.9 $\mu\text{g/L}$ for the Lukupuro River. The constants of the equations indicate the baseline concentration of DP in both catchments.

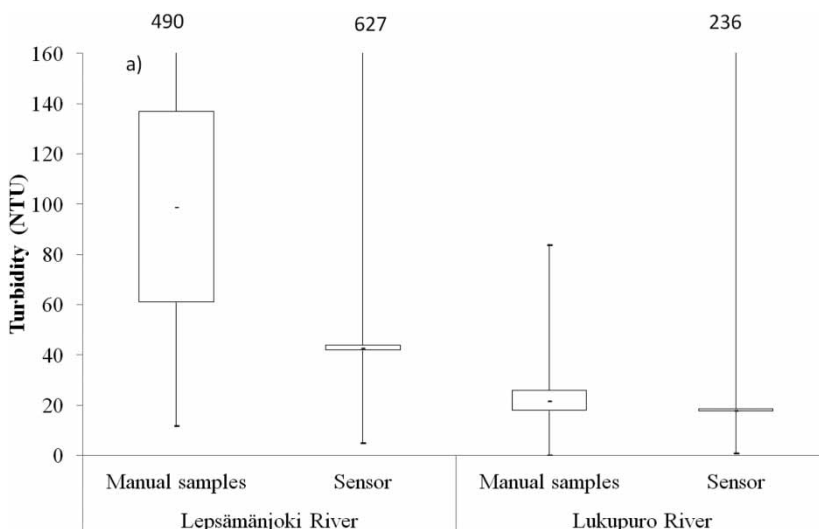


Figure 1 | Range of turbidity measured with sensors at 1-h intervals and from manual samples, the means and their 95% confidence intervals. If upper bound of the whisker is out of the range the number is used to indicate the highest value.

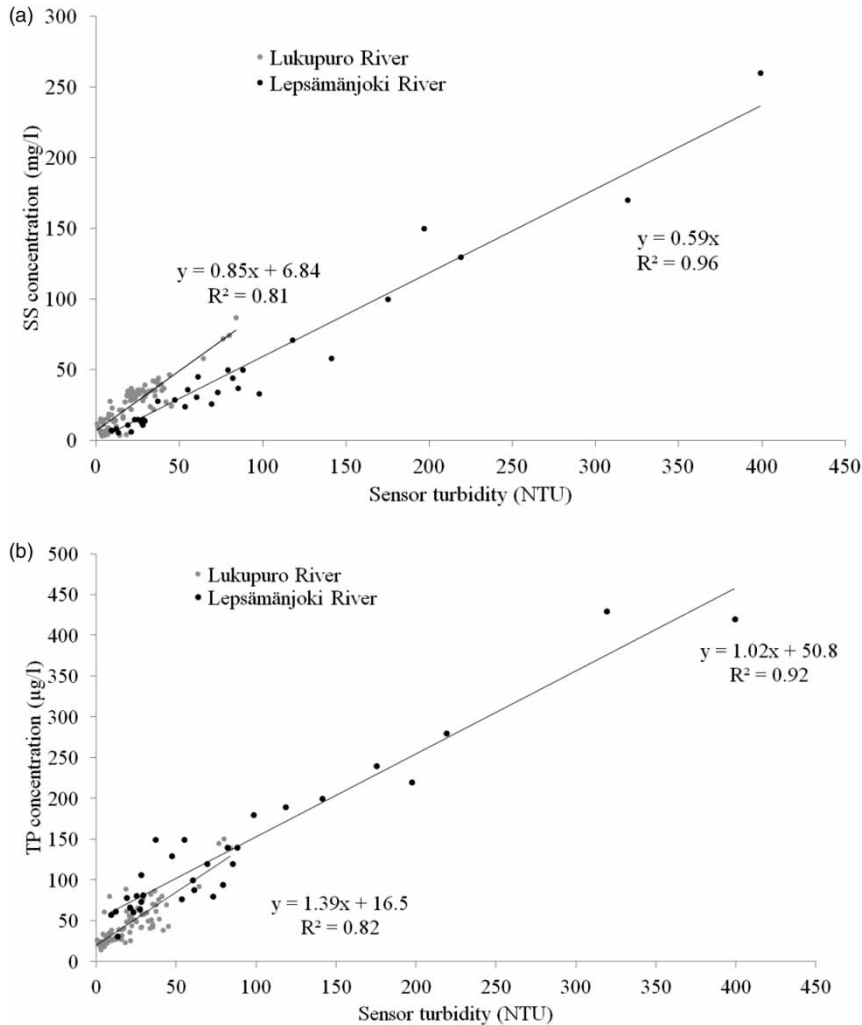


Figure 2 | (a) Relationship between turbidity measured by the water-quality sensor and SS analysed in the laboratory. (b) Relationship between turbidity measured by water-quality sensor and TP analysed in the laboratory.

Load calculations

Based on the hourly SS and TP concentrations and discharge data, the SS and TP load was calculated at 1-h intervals. With this method, the total annual SS load of the Lepsämäenjoki River during the one-year study period was 262×10^3 kg and TP load 712 kg. The maximum 1-h loads were 1,800 kg SS and 3.3 kg TP, and they occurred in late October 2006 in the rising stage of the autumn flood. The lag between the concentration and flow maxima was 13 h. The shorter the lag between these two maximum values, the larger was the load.

In the Lukupuro River, the SS load was 140×10^3 kg and the TP load 250 kg. The highest hourly SS (850 kg) and TP (1.4 kg) loads occurred in late October 2006 after a heavy rain event. During the event, the highest concentrations of TP and SS were reached 6 h before maximum discharge.

As shown in Figure 3, there were differences in the SS and TP loads calculated with the various methods at both monitoring sites. When the data were compared (ΔL) with the reference data based on high-resolution sensor data, the yearly averaging method (method 1) seemed to provide satisfactory ($\Delta L < 10\%$) results for all parameters at both sites. The most biased method, compared with the reference load, was the linear interpolation method (method 3),

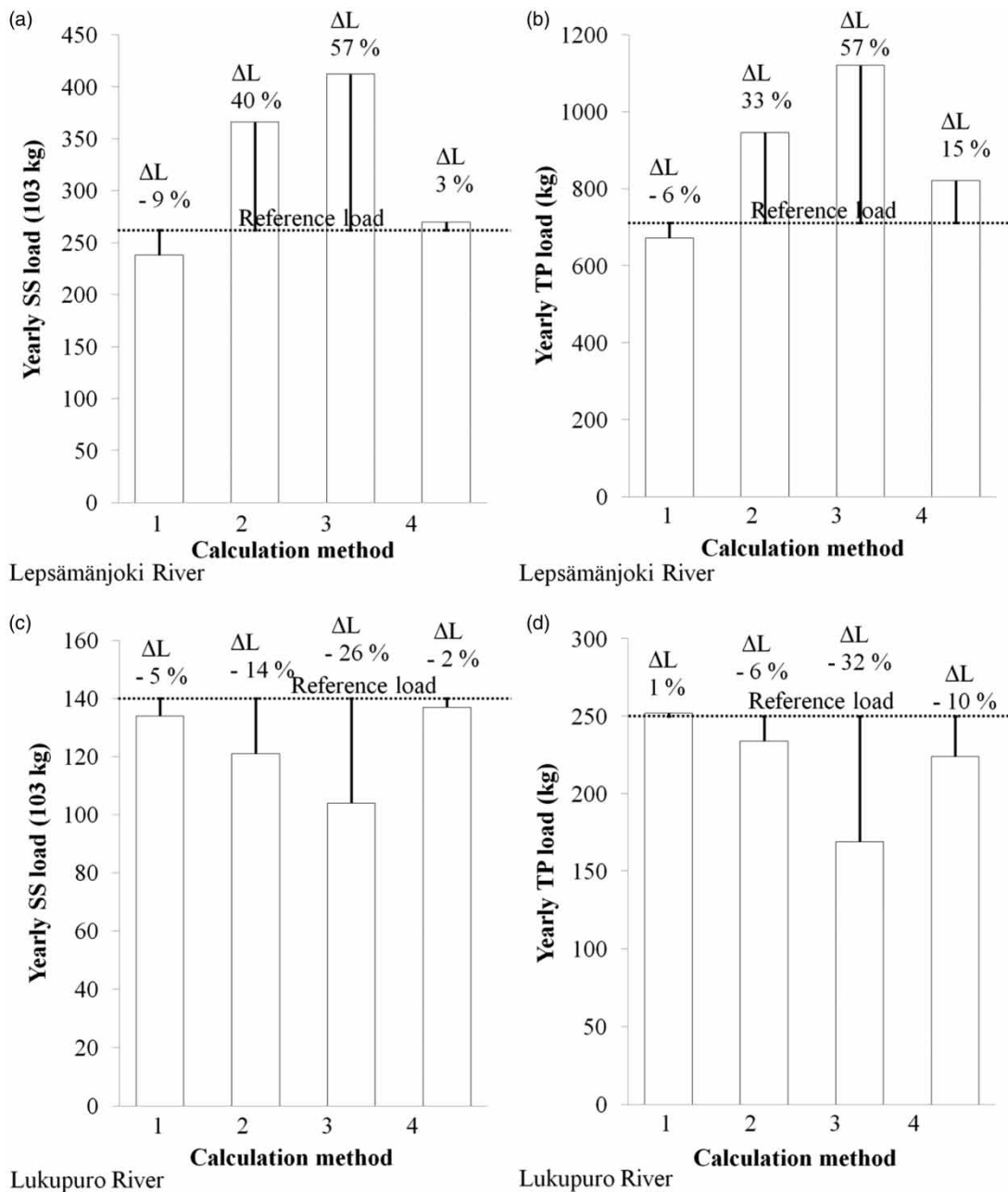


Figure 3 | SS and TP load calculations based on discrete manual samples and high frequency sensor data (reference load, dashed line). ΔL indicates the relative difference of load compared to reference (high frequency) load. 1 = yearly averaging, 2 = ratio, 3 = linear interpolation, 4 = rating curve method.

clearly resulting in values that were too large in the Lepsämäenjoki River, whereas in the Lukupuro River, the load values were under the reference. The TP load at both sites consisted of several short-term peaks that could not be detected by sparse sporadic sampling (Figure 4(a) and 4(b)). The largest error in the linear interpolation method

in the Lepsämäenjoki River was due to the sparse sampling interval in winter.

Linearly fitted rating curves based on manual samples showed fairly good coefficients of correlation at both sites (0.79 for TP in the Lepsämäenjoki River and 0.64 for the Lukupuro River). The regression equations used in the

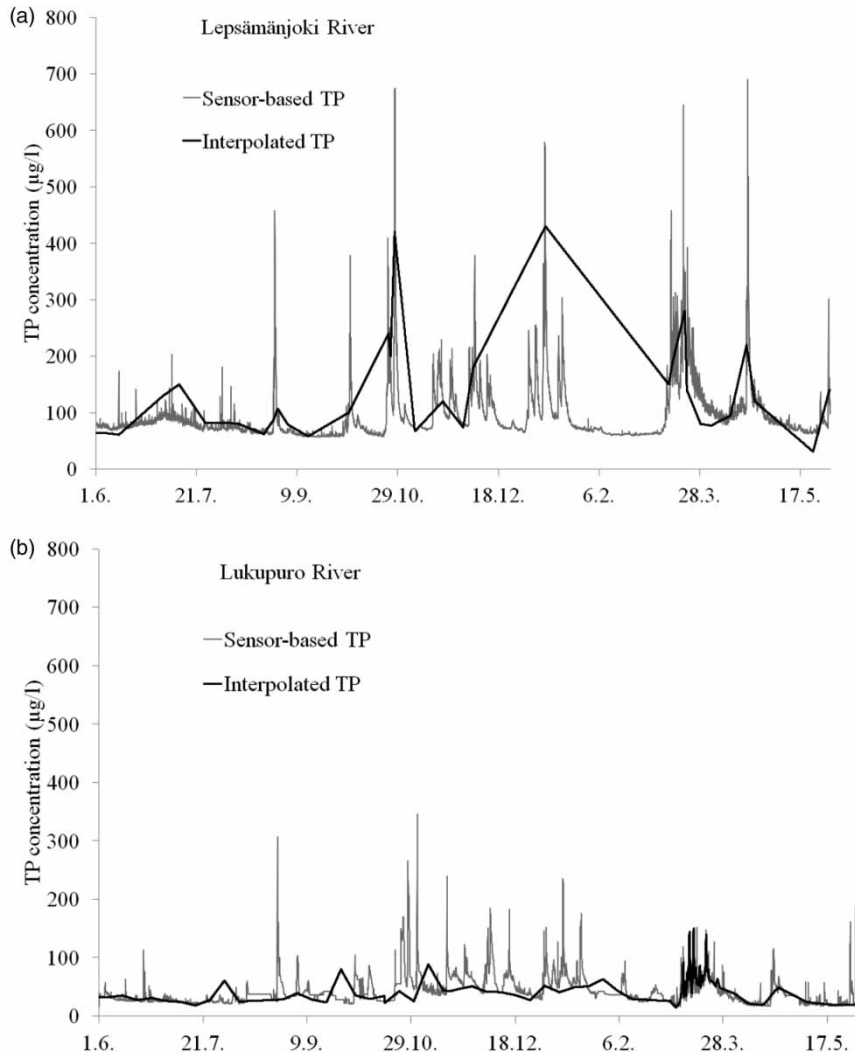


Figure 4 | Hourly TP concentrations, based on sensor turbidity, and interpolated daily TP concentrations among manual samples in the Lepsämäenjoki River (a) and the Lukupuro River (b).

Lepsämäenjoki River were:

$$TP = 0.201 Q + 74.722 \quad (6)$$

and for the Lukupuro River:

$$TP = 0.115 Q + 28.384 \quad (7)$$

There was slight overestimation or underestimation of the loads, depending on the study site. This resulted from the fact that the concentration/discharge correlation actually showed widespread scattering, leading to fairly poor correlation between the concentration and discharge in both catchments.

Effect of sampling frequency

As can be seen in Figure 5(a) and 5(b), the yearly averaging method (Equation (2)) led to systematic underestimation of the phosphorus load at both sites. When this method was used, the loads based on six- to 12-yearly samples showed wide variation in both catchments. It seemed impossible to achieve satisfactory ($\pm 20\%$ of reference data) precision with the yearly averaging method, even if there were 365 samples per year because daily sampling represented only 4.2% of all hourly data. Thus, if the mean concentration and discharge values were used, the load would likely have been roughly underestimated, because the highest load peaks would have

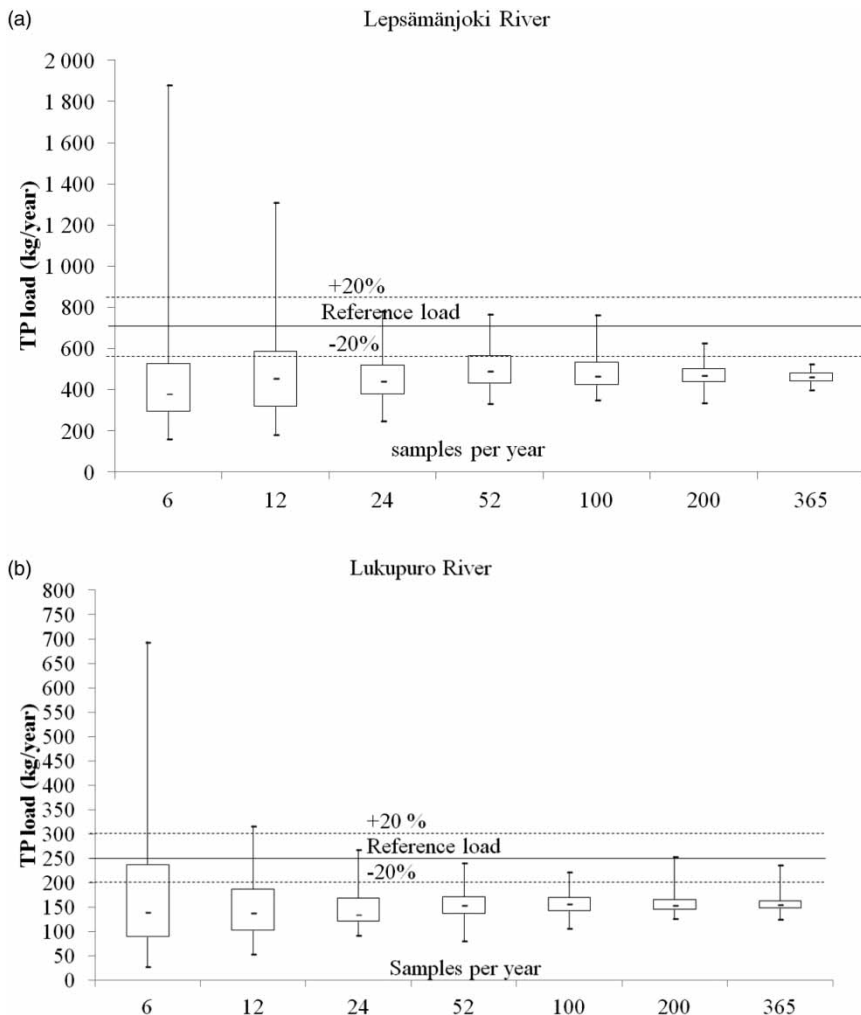


Figure 5 | Medians, upper and lower quartiles and minimum and maximum values of yearly TP load in the Lepsämäjoki River (a) and the Lukupuro River (b), based on the yearly averaging method (Equation (2)). Reference load from sensor-based calculation. Dashed lines indicate $\pm 20\%$ load of reference data.

been missed. The majority of the yearly TP loads consisted of fairly short-term peaks when high TP concentrations coincided with high discharge values.

Use of the ratio method (Equation (3)) resulted in more reliable load estimations than yearly averaging method at both study sites (Figure 6(a) and 6(b)). However, even in simulated daily sampling (365 samples), the differences compared with the reference data varied from +21% to -18% (the Lukupuro River) and $\pm 18\%$ (the Lepsämäjoki River). Commonly used sampling frequencies of 6–12 samples per year resulted in wide variation in load estimations, regardless of use of the calculation method. The probability of achieving load estimation within $\pm 20\%$ of the reference load at sampling frequencies of 12, 52 and

365 samples per year was 46%, 70% and 100%, respectively, in the Lepsämäjoki River. In the Lukupuro River, the probabilities at the same sampling frequencies were 40%, 50% and 98%. Regardless of the sampling frequency, the phosphorus loads were more likely underestimated than overestimated in both catchments.

Impact of hysteresis

The mean hysteresis index in the Lukupuro River was 0.33 ($n = 34$) and in the Lepsämäjoki River 1.65 ($n = 23$). The predominant TP hysteresis in both study sites was positive (Table 1). In five of the 34 events detected in the Lukupuro River, the hysteresis index was below 0.1 and thus the

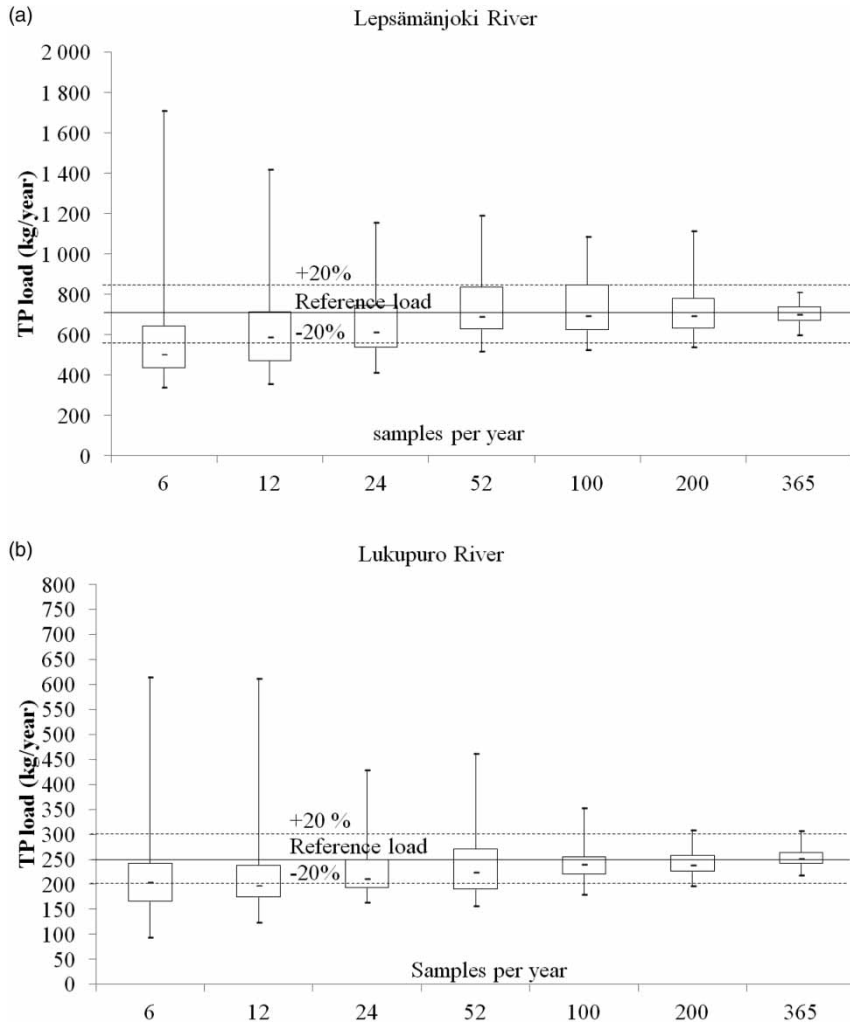


Figure 6 | Medians, upper and lower quartiles and minimum and maximum values of yearly TP load in the Lepsämäjoki River (a) and the Lukupuro River (b), based on the ratio method (Equation (3)). Reference load from sensor-based calculation. Dashed lines indicate $\pm 20\%$ load of reference data.

hysteresis effect was considered to be minor. In the Lepsämäjoki River, only one event of 23 had minor hysteresis index ($Hi - 0.02$). In both catchments the majority of the positive hysteresis loops were identified during relatively high flow events. However, in the Lukupuro River, the behaviour of the discharge/TP relationship was more complex than in the Lepsämäjoki River. There was no clear seasonal variation between negative and positive hysteresis, but from September to October 2006 there were five successive flow events with negative hysteresis detected in the Lukupuro River. In the Lepsämäjoki River, five out of the seven negative hysteresis loops occurred in winter (December–February), one in the beginning of snowmelt and one at the end of May.

Time lag between maximum discharge and maximum TP concentration (hysteresis) had an effect on TP load. The effect was stronger in the Lukupuro River than in the Lepsämäjoki River, especially in the case of positive time lag during the autumn flood period in 2006 (Figure 7).

DISCUSSION

Our findings suggest that reliable SS and TP load calculations can be achieved with continuous turbidity monitoring. However, as seen in our results, the correlation between turbidity and SS concentration and turbidity and TP concentration varied with the site. Thus, when turbidity

Table 1 | Flow event-based hysteresis index (*Hi*), loop size, maximum discharge (*Qmax*), midpoint discharge (*Qmid*), maximum TP (*TPmax*), TP in rising stage of hydrograph (*TPrs*), TP in falling stage of hydrograph (*TPfs*), TP load of the event and duration of the event in the Lukupuro River and in the Lepsämäjoki River

Peak date	<i>Hi</i>	loop size $\mu\text{g/l}$	<i>Qmax</i> l/s	<i>Qmid</i> l/s	<i>TPmax</i> $\mu\text{g/l}$	<i>TPrs</i> $\mu\text{g/l}$	<i>TPfs</i> $\mu\text{g/l}$	<i>TPload</i> kg	Duration h
Lukupuro River									
3.6.2006	-0.08	-4	98	63	57	46	50	0.29	34
27.6.2006	0.11	3	27	18	33	30	27	0.04	24
25.8.2006	1.46	179	31	18	307	302	123	0.16	20
4.9.2006	-0.44	-30	44	27	103	68	98	0.24	32
2.10.2006	-0.22	-13	137	71	104	57	70	0.86	49
8.10.2006	-0.39	-20	75	58	87	51	71	0.40	35
24.10.2006	-1.39	-77	497	263	149	56	133	3.82	11
25.10.2006	-0.01	-2	420	333	170	150	152	3.98	23
27.10.2006	0.50	57	921	545	265	170	113	15.71	57
1.11.2006	1.20	92	1,367	769	346	169	77	18.37	73
15.11.2006	2.33	145	494	290	239	207	62	6.98	57
24.11.2006	0.45	30	505	345	122	97	67	2.78	22
5.12.2006	0.20	18	423	299	151	106	88	4.06	21
6.12.2006	0.39	40	891	632	186	142	102	9.27	25
31.12.2006	0.06	4	203	149	146	75	71	1.08	22
2.1.2007	1.12	60	333	243	152	113	53	3.89	48
5.1.2007	0.31	19	377	300	96	80	61	3.90	44
9.1.2007	0.10	7	403	315	102	76	69	3.08	36
10.1.2007	1.10	89	706	518	235	170	81	7.67	30
11.1.2007	0.11	8	633	533	91	79	71	4.69	32
15.1.2007	0	0	434	341	65	58	58	2.56	33
16.1.2007	0.17	11	536	443	95	75	64	3.70	32
18.1.2007	0.58	46	1,091	715	175	125	79	12.9	39
8.2.2007	-0.50	-30	389	283	94	60	90	1.56	22
21.2.2007	-0.16	-6	466	315	49	37	43	2.09	39
8.3.2007	-0.07	-5	151	106	119	73	78	0.58	23
9.3.2007	0.41	17	169	123	61	58	41	0.49	23
11.3.2007	0.32	23	324	254	142	95	72	2.23	38
13.3.2007	-0.02	-1	323	243	135	62	63	1.80	27
19.3.2007	0.97	64	438	321	147	130	66	4.48	41
20.4.2007	0.33	13	145	97	78	53	40	0.46	22
21.4.2007	1.08	57	299	205	116	110	53	2.65	47
28.5.2007	0.65	32	136	79	161	81	49	0.42	34
30.5.2007	0.48	28	150	91	186	86	58	0.34	13
Lepsämäjoki River									
28.8.2006	0.15	19	238	135	457	150	131	7.7	138
5.10.2006	2.64	61	405	236	378	157	96	10.1	138
24.10.2006	2.06	10	792	415	409	180	170	14.4	69

(continued)

Table 1 | continued

Peak date	<i>Hi</i>	loop size $\mu\text{g/l}$	<i>Qmax</i> l/s	<i>Qmid</i> l/s	<i>TPmax</i> $\mu\text{g/l}$	<i>TPrs</i> $\mu\text{g/l}$	<i>TPfs</i> $\mu\text{g/l}$	<i>TPload</i> kg	Duration h
28.10.2006	3.43	156	1,562	1,043	672	265	109	87.4	123
15.11.2006	2.18	20	602	344	205	130	110	12.8	57
19.11.2006	2.72	72	1,363	908	213	172	100	69.0	148
24.11.2006	2.44	51	792	627	214	167	116	37.2	226
3.12.2006	-0.09	-9	387	258	216	100	109	6.4	39
6.12.2006	2.27	35	998	745	379	165	130	34.9	67
12.12.2006	-0.06	-6	405	308	203	103	109	5.8	34
14.12.2006	0.02	-2	483	397	166	112	114	16.2	155
2.1.2007	-0.18	-18	303	196	245	102	120	8.9	73
5.1.2007	2.06	10	462	308	256	170	160	13.4	83
9.1.2007	2.01	2	472	298	365	190	188	7.9	33
10.1.2007	2.30	67	892	667	579	290	223	37.4	51
16.1.2007	-0.24	-26	433	281	236	108	134	7.8	43
19.1.2007	2.23	32	1014	619	304	170	138	34.2	90
11.3.2007	-0.30	-30	443	362	171	100	130	5.5	34
13.3.2007	2.71	145	591	443	457	350	205	13.2	29
20.3.2007	2.36	61	834	546	645	230	169	44.0	72
21.4.2007	4.54	402	765	485	690	560	158	31.2	73
26.5.2007	-0.14	-10	143	92	136	70	80	1.6	43
31.5.2007	2.97	95	218	146	301	193	98	2.9	35

is used as a surrogate measure for SS or TP concentration, a site-specific relationship should always be established.

A linear relationship between turbidity and SS concentration was found in previous studies, due to the constant physical properties of SS (Gippel 1995; Pavanelli & Bigi 2005). If the size and shape of particles varied widely, a scattered relationship could be established (Zabaleta *et al.* 2007). Sediment particles suspended in the Lepsämäinjoki River and the Lukupuro River were thus probably fine-grained and relatively uniformly settled in the water mass. This fairly constant relationship may also have resulted from a single main source area of the sediment being predominant or a major contribution of land use (in this case agricultural clayey fields) to the sediment yield.

A linear relationship was also detected between turbidity and the TP concentration at both study sites. The TP/turbidity relationship was not as sensitive as turbidity/SS relationship to the differing particle-size distribution, since phosphorus tends to be particle-bound, especially in fine clay-sized suspended material (Grayson & Finlayson 1996).

Thus, the high-turbidity water contained abundant SS and phosphorus. The origin of the phosphorus may also have affected the relationship between turbidity and TP, as noted by Viviano *et al.* (2014). Thus, a single main source (agricultural clayey fields) of TP most likely also predominated at our study sites.

There was a positive correlation at both study sites between concentration and discharge indicating the dominance of diffuse SS and TP pollution (Bieroza & Heathwaite 2015) but, typically, the TP and SS concentrations peaked just before the discharge maximum, leading to positive hysteresis. Due to the hysteresis effect, there were considerable problems in calculating the loads based on discharge. If discharge and concentration peak occurs simultaneously the load would be very high.

The hysteretic behaviour of the Lukupuro River was complex throughout the year making the estimation of TP load based solely on discharge difficult. In the Lepsämäinjoki River it was likely that during positive hysteresis ($Hi > 0$) the TP load was high. In September 2006, five consequent flow

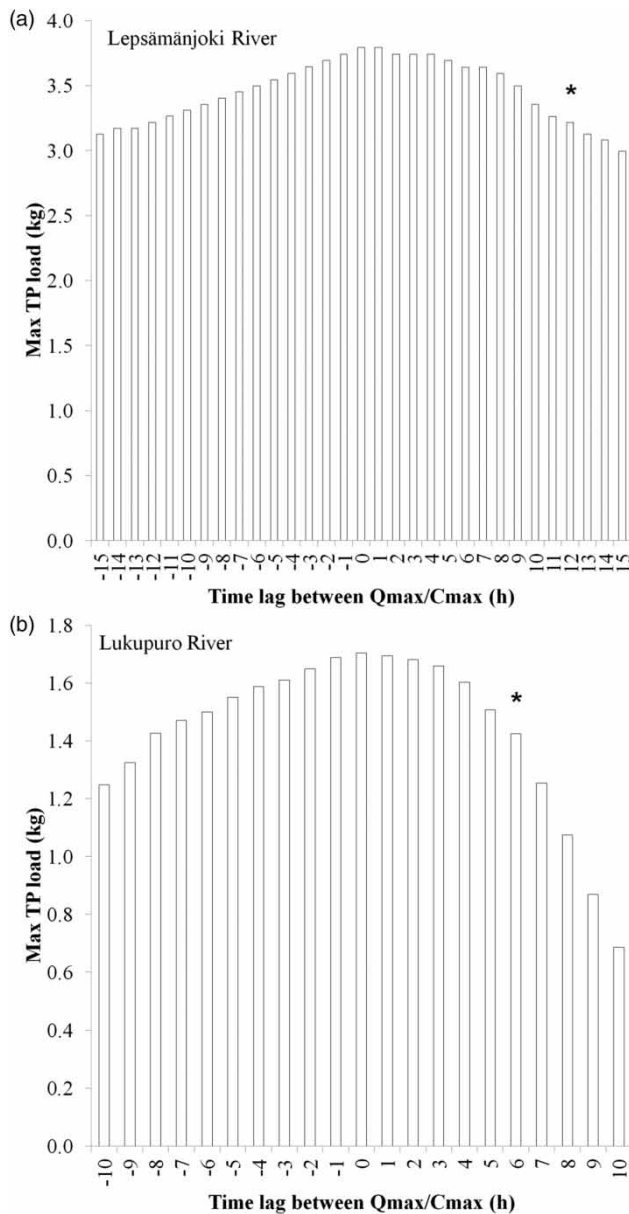


Figure 7 | The impact of time lag (hysteresis) between discharge maxima (Q_{max}) and TP concentration maxima (C_{max}) on maximum hourly TP load during an autumnal high flow event in the Lepsämäenjoki River (a) and in the Lukupuro River (b). The asterisk indicates maximum TP load in the case of actualized time lag occurring in rivers.

events with negative hysteresis loops ($Hi < 0$) were detected in the Lukupuro River. This was probably due to the main source of TP being the ploughed fields at the upper reaches of the catchment. The opposite was true in the Lepsämäenjoki River, where hysteresis was positive during the autumn rains. This appeared to indicate the source of TP

to be on the fields close to the monitoring point. Thus, the main reason for the contrasting hysteretic behaviour between the study sites was the different location of the main source of TP and SS in respect to the monitoring stations. Lloyd *et al.* (2016) also suggest that high negative Hi values are a sign of a longer transit time for the TP to reach the monitoring station. In their study site, an arable land-dominated catchment, the average Hi value for TP was -0.24 . Lawler *et al.* (2006) calculated the average Hi to be -1.64 in an urban headwater river, where the lack of sediment exhaustion led to negative values.

The positive hysteretic behaviour ($Hi > 0$) predominating in our analysis may also be related to a rapid response contribution from sediment stored in the bed of the channels, as proposed by Lenzi & Marchi (2000) and Jansson (2002). But as suggested by Lloyd *et al.* (2016), there may be certain P sources connected to the river system during high flow events leading to high SS and TP fluxes. Outside the growing season when arable fields are left without protective vegetation cover there may be a continuous supply of fine-grained sediment containing phosphorus to be mobilized. Thus, erosion would be the main driving factor controlling the TP supply in catchments similar to our study sites.

Negative hysteresis in the beginning of March 2007 in the Lepsämäenjoki River was related to the period of snow melting and the fact that the surface of the fields were still frozen which limited TP supply to the river. During the next event, hysteresis was positive when snow had melted from the fields allowing the overland flow-induced erosion to flush phosphorus-rich sediment from the fields' surface. Negative hysteresis in winter in the Lepsämäenjoki River may be due to the frozen surface of the fields and thus the TP fluxes would be supply-limited in below $0\text{ }^{\circ}\text{C}$ circumstances.

The erosion of agricultural fields in Finland is usually prevented in winter by the snow cover and ground frost, leading to minor fluxes in sediment and phosphorus load and flow. Due to the relatively constant conditions in winter, a single sample might be representative of the conditions for the entire season. The early winter of 2006–2007 was mild and rainy in southern Finland, and the Lepsämäenjoki River manual sample in January was taken under very turbid conditions. The interval between the

previous and subsequent samples was also long. This single high-concentration sample led to major overestimation of the yearly TP load regardless of the calculation procedure. Underestimation of the yearly TP load in the Lukupuro River during use of the linear interpolation method was a result of manual sampling that missed the highest concentrations. We agree with Lopez *et al.* (2000) that more samples should be taken whenever discharge rises or falls by a certain amount, especially in small watercourses where variation in discharge and concentration is high. We also agree with Cassidy & Jordan (2011) and Skarbøvik *et al.* (2012) that there are high levels of uncertainty in load calculations when infrequent and sparse datasets of concentrations are used. Our studies revealed that the wide range of variation in water quantity and quality, regardless of the calculation method used, would likely be missed if the sampling methodology were based on discrete grab samples. For example, when investigating the impacts of changes in land use or water management practices conducted in the catchment, it would be important to get reliable information concerning the nutrient load. Even if the load estimations are within the commonly used $\pm 20\%$ threshold value, the impact may still be missed due to biased estimation. High frequency monitoring allows detection of even minor changes in nutrient load and, therefore, the impacts of management practices can be evaluated more reliably compared to the biased discrete sampling.

As seen in the rating curve method, continuous measurement of only discharge with sparse manual sampling may result in load estimations close to the reference values on a yearly basis, but due to hysteresis and other factors, the flow/concentration relationship would more likely be scattered. To increase the reliability of the rating curve method, the data could be divided on a seasonal or flow variation basis, as Eder *et al.* (2010) did in their study. Cheviron *et al.* (2014) also concluded that when the improved rating curve approach is used, 200 samples would guarantee that the SS loads would lie within a $\pm 20\%$ interval. They found that load estimates are usually more vulnerable to the lack of concentration data than the lack of discharge data. Our study shows that continuous turbidity monitoring would be sufficient to compensate for this weakness.

Climate change increases wintertime temperature and precipitation in cold climate areas (Graham 2004; Deelstra *et al.*

2011) and that will also increase nutrient loads. High frequency nutrient monitoring is essential to get more accurate load estimations in cold climate rivers, especially during winter months. Frequent sampling is often expensive and difficult during winter months when ice covers the river. Our measurements show that on-line sensors are a reliable and cost-effective way to monitor SS and TP loads in cold climate areas.

CONCLUSIONS

Continuous *in situ* turbidity monitoring proved to be a valuable method for estimating the erosion and phosphorus loads from catchments with clayey waters. Turbidity could provide a viable surrogate for SS and TP concentrations. Reasonable utilization of this method is dependent on the correlation between the turbidity measured continuously and the SS or TP concentrations analysed in the laboratory. Turbidity should not be used as a surrogate measure for SS or TP without careful calibration procedures.

Our findings suggest that calculation methods based on discrete grab samples may result in an overwhelming probability of obtaining inaccurate load values if used on a yearly basis. Large fluctuations in the discharge/concentration relationship illustrate the importance of high-resolution water quality data, especially in estimating the erosion or phosphorus loads of watercourses. Varying hysteresis effect makes it difficult to estimate load based solely on discharge. Therefore, hysteresis patterns detected by the high-frequency monitoring provide valuable information for detecting also the catchment's possible nutrient sources in different hydrologic conditions. Load calculations based on continuously measured data would be more accurate than those based on discrete water samples. This is the case especially during winter months, when traditional monitoring is difficult and expensive. Thus high-frequency monitoring could also be a reasonable method to detect the impact of catchments' nutrient management practices on the water quality of rivers.

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