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Title: Evaluating the effects of BMPs on agricultural contaminants using a novel method accounting for uncertainty in water flow and contaminant loads

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Abstract

Field-scale studies have shown that beneficial management practices (BMPs), such as nutrient management plans and grass buffers, can reduce the downstream transport of non-point source contaminants. This study presents a novel method for evaluating the effectiveness of BMPs using *in situ* data. From 2005 to 2012, hydrometric monitoring and water quality monitoring were carried out at the outlet and along two main branches of a micro-watershed (236 ha) with a high proportion of cultivated land. The method was based on evaluating the uncertainty associated with the determination of water flow and agricultural contaminant loads, with the latter being based on statistical distributions of nutrient or sediment concentrations. Distribution of loads (i.e. April – November) was estimated in order to assess the cumulative effectiveness of all implemented BMPs with an emphasis in riparian buffers established on the micro-watershed under study at different spatio-temporal scales. Results showed the concentrations and loads of total nitrogen (TN), total phosphorus (TP), nitrate-nitrogen ($NO_3^- - N$) and particulate phosphorus (PP) were significantly lower following riparian buffer implementation. A significant decrease in nitrite-nitrogen ($NO_2^- - N$) and ammonium nitrogen ($NH_4^+ - N$) in the loads also occurred after riparian buffers were established. Spatially, a ratio approach based on comparing an export fraction [loads (kg) to nutrient balances (kg)] downstream from riparian buffers with that at the outlet of the same stream, showed a significant reduction in the ratio downstream from the riparian buffer for TN and TP in 2009, with no significant reduction in 2010, 2011 and 2012. Ratios calculated on a seasonal basis showed the riparian buffers were less effective in the spring, as well as during seasons marked by one or more intense rainfall events.

Keywords: nitrogen; phosphorus; riparian buffer; nutrient balance

Abbreviations: BMP: beneficial management practice; AAFC: Agriculture and Agri-Food Canada; WEBs: Watershed Evaluation of Beneficial Management Practices; TN: total nitrogen; TP: total phosphorus; DP: dissolved phosphorus; PP: particulate phosphorus; TSS: total suspended sediments; AET: Actual evapotranspiration; PET: Potential evapotranspiration; FWMC: Flow weighted mean concentration

Introduction

Eutrophication caused by phosphorus (P) and nitrogen (N) enrichment is a widespread problem in lakes, rivers, estuaries and coastal areas of oceans (Carpenter et al. 1998). In Quebec, Canada, concentrations of total phosphorus (TP) in some rivers are two to six times higher than the Quebec government's water quality guideline (0.030 mg/L of P) for preventing eutrophication (Gangbazo and Le Page 2005; Gangbazo et al. 2005). Since non-point source contaminants from agricultural activities represent the largest source of N and P pollution for surface waters (Carpenter et al. 1998; Gangbazo and Le Page 2005; Dubrovsky et al. 2010), the gradual introduction of more intensive agricultural operations in recent decades has played a major role in the degradation of water quality. Quebec has adopted a series of regulations and laws with the aim of controlling agricultural pollution, including regulations designed to control the use of P as a limiting nutrient during the application of mineral and organic fertilizers (Gouvernement du Québec 2002). Although the goal of these agri-environmental standards is to halt water quality deterioration, management of nutrient inputs at the farm level must be combined with efforts to minimize nutrient transport associated with soil erosion or leaching in order to maximize the reduction in agricultural contaminant loadings to streams.

Several studies have shown water quality improvements resulting from the implementation of BMPs (Schilling and Spooner 2006; Sharpley et al. 2009; Lemke et al. 2011; Sharpley et al. 2012; Collins et al. 2013; Chen et al. 2014; Chen et al. 2015; Feld et al. 2018). Riparian buffers have been shown to significantly reduce non-point source nutrient fluxes from surface runoff (Young et al. 1980; Peterjohn and Correll 1984; Jacobs and Gilliam 1985; Dillaha et al. 1989; James et al. 1990; Lee et al. 2003; Hefting et al. 2006).

Effectiveness of riparian buffers in mitigating nutrient fluxes depends on buffer slope and width as well as runoff conditions (Dosskey et al. 2002; Blanco-Canqui et al. 2006) and vegetation type and density (Osborne and Kovacic 1993; Lee et al. 2003). All these characteristics should be taken into account in studies on the effectiveness of riparian buffers, since the combined effect of these factors influences and explains the variability in the effectiveness of riparian buffers in reducing fluxes of contaminants (Gumiere et al. 2011). Spatial distribution of riparian buffers along a stream also plays a major role in determining how effective riparian buffers are in reducing nutrient and sediment loads. Since estimating the effect of the spatial distributions of buffers can be expensive and difficult to achieve, joint development of erosion models and vegetative filter dimensioning models can be a useful approach (Gumiere et al. 2013; 2014; 2015). Indeed, Hould-Gosselin et al. (2016) coupled VFDM with MYDHAS-Erosion. Their results illustrated that implementation of 5-m wide vegetated filters and 20-m placed at the edge of the most problematic fields (4% of the total fields) throughout a 236-ha agricultural watershed in Quebec, Canada, could reduce soil loss by 52% and 31%, respectively. Similar conclusions were achieved by Zhang et al. (2017) who interfaced a riparian management model (REMM) with a hydrological model (SWAT) to evaluate the effectiveness of variable-width riparian buffers at a segment level along the stream network of a small agricultural watershed (1315 ha) in New Brunswick, Canada.

A soil surface nutrient balance (*B)* can be used to quantify nutrient loads that may potentially accumulate in the soil and become potentially available and subsequently be exported to the river by runoff or subsurface flows. It was assumed there are positive relationships between annual N and P balances and N and P losses in surface waters

(Withers et al. 2014; Rowe et al. 2016; Kusmer et al. 2018). Indeed, this approach, rooted in the Driving forces – Pressure – State – Impact – Response [DPSIR, Smeets and Weterings (1999)] framework behind the development of the Indicators of Risk Of Water Contamination (IROWC) for agricultural land of Canada (Clearwater et al. 2016), acknowledges that soil N and P can be transported in soluble and particulate forms via subsurface flows, subsurface drain flows, overland flows and soil erosion (De Jong et al. 2009; van Bochove et al. 2011; Hong et al. 2012; Swaney et al. 2012; St-Hilaire et al. 2016).

This study was part of the Watershed Evaluation of Beneficial Management Practices (WEBs), a project initiated by Agriculture and Agri-Food Canada (AAFC) in 2004 (Yang et al. 2007). The project aimed at assessing economic and environmental performance of BMPs at small watershed sites, using a comparative approach involving paired watersheds (a treatment watershed where BMPs were implemented, and a reference watershed). This type of approach has been widely used to assess the effect of BMPs on water quality (Clausen and Spooner 1993; Grabow et al. 1999; Jaynes et al. 2004; Schilling and Spooner 2006; Tremblay et al. 2009; Lemke et al. 2011; Li et al. 2011). However, in this study, marked spatio-temporal differences in agronomic practices and pedological characteristics (Lamontagne et al. 2010) between the two selected micro-watersheds preclude their standard comparison. Accordingly, the goal of the present study was to develop a novel method for assessing the effect of BMPs on fluxes of agricultural contaminants in a context where the paired watersheds approach cannot be used. The method first involved evaluating the uncertainties associated with water flow calculations. Annual hydrological and weather characterizations were used to validate rating curves. Uncertainty associated with flow estimated by rating curves was analyzed using Monte Carlo simulations of the regression residuals. Nutrient and sediment loads were then calculated using a statistical distribution of concentrations. A model of the distribution of concentrations was developed using two covariates (explanatory variables): flow (discharge) and calendar day. Uncertainty related to the estimation of the parameters for the distributions obtained was calculated using the parametric bootstrap procedure. Finally, the effectiveness of BMPs was evaluated from a temporal (lumped evaluation of all implemented BMPs) and spatial standpoint (evaluation of riparian buffers).

Materials and methods

Study site

The micro-watershed studied was located in the Bras d'Henri watershed, roughly 30 km south of Quebec City, Quebec, Canada (Figure 1). The Bras d'Henri watershed, which covers an area of 167 km^2, is in the Chaudière River watershed. The micro-watershed drains a total area of 2.36 km^2. Agriculture accounts for approximately 70% of land use. Dominant crops are grain corn [*Zea mays*] and soybeans [*Glycine max*], which account, on average, for 32% and 15% of the watershed area, respectively. From 2005 to 2011, cultivated areas were dominated by grain corn (*Zea mays*) and grassland (mostly grasses [*Gramineae*]). In 2012, soybeans (*Glycine max*) and grassland (mostly grasses [*Gramineae*]) were the most important crops in terms of area. Soils are primarily podzols and belong mainly to the sandy to loamy textural classes. They are imperfectly to poorly drained, and their dominant slope class is 3% to 8%. With regard to water quality at the micro-watershed outlet, from 92.7% to 100% of the time (from 2005 to 2012) nitrate was found in excess of the guideline of 3 mg/L for the protection of aquatic life (chronic effect) (MELCC; 2013). The concentrations of TP exceeded the guideline of 0.03 mg/L phosphorus established for the protection of aquatic life and recreational activities (MELCC; 2013) from 67.3% to 96.4% of the time (from 2005 to 2012).

From 2004 to 2011, structural water and soil conservation BMPs were introduced within the micro-watershed, and producers made changes to their traditional farming practices (Table 1). Shrub and tree riparian buffers and grassed waterways were established in areas at risk of water erosion and of sediment and nutrient transport to streams. Two grassed waterways, one 55-m long and the other 60-m long, were implemented. Since 2007, 2,122 m of riparian buffers (composed of grasses, shrubs and trees) have been maintained in the micro-watershed, generally at a width of 3-m. If the bank was less than 3-m wide (horizontal projection), 1 m was added to the flat upper part of the riparian buffer. Shrubs included eastern white cedar (*Thuja occidentalis*), high-bush cranberry (*Viburnum trilobum),* broad-leaved meadowsweet (*Spiraea latifolia)*, golden ninebark (*Physocarpus opulifolius)* and black chokecherry (*Aronia melanocarpa*). Trees consisted of bur oak (*Quercus macrocarpa*), American white ash (*Fraxinus americana)* and Norway spruce (*Picea abies*). In some areas along the stream, the steepness of the slope was reduced and grasses were planted on the embankment to reduce the risk of erosion and stabilize banks. Outlets of runnels, furrows, ditches and drains were covered with a layer of stone underlain by a geotextile membrane. Stone-lined culvert inlets and outlets help to stabilize the embankment at these locations and reduce soil loss caused by erosion. A 25-m long drainage ditch was also installed in a poorly drained area. With regard to the application of pig slurry (a major source of organic fertilizers in the watershed), an enhanced spreader was introduced in order to control N losses associated with volatilization and leaching. Finally, side-dressing applications of N were made to meet the requirements of corn and to reduce N losses through volatilization, runoff and leaching.

Water Quality Sampling and Laboratory Analysis

Water quality samples and hydrometric data were generally collected from April to November at three sampling stations: the first was located at the micro-watershed outlet from 2005 to 2012 and the other two on the two main branches of the watershed (branches 14 and 15) from 2009 to 2012 (Figure 1). The sampling station on branch 14 was installed downstream from a section of riparian buffers. In the field, multi-probe meters were used to measure pH, conductivity, temperature, turbidity and oxidation-reduction potential, while an SR50 sensor (Campbell Scientific 2013) and a 710 ultrasonic flow module (Teledyne Isco 2013) were used to measure stream stage height every 15 minutes. An auto-sampler (Teledyne Isco 2014) located at the micro-watershed outlet collected 50 mL of water per hour. Auto-samplers located on branches 14 and 15 collected 200 mL of water every 12 hours. Composite samples were collected for analysis twice weekly (every three or four days). Water samples were analyzed for TN, nitrate ($NO_3^- - N$), nitrite ($NO_2^- - N$), ammonium ($NH_4^+ - N$), TP, dissolved phosphorus (DP), PP and total suspended sediments (TSS), using standard methods of analysis (Appendix A). PP was determined as the difference between TP and DP. Samples were filtered using $0.45\ \mu m$ filters for the analysis of dissolved forms of nutrients and $1\ \mu m$ filters for TSS.

Discharge Rating Curves

Rating curves were developed to convert daily stream stage heights to daily flow values. From 8 to 32 stage-discharge measurements were made in the field each year, generally from May to November, by using the velocity-area method [water velocity was measured using a FlowTracker (Sontek 2012) velocimeter]. The power function, which is often used to relate streamflow to stage height (Rantz 1982; Pappenberger et al. 2006; Braca 2008; Herschy 2009; Lemke et al. 2011; Guerrero et al. 2012; Le Coz 2012), was used to calculate rating curves after logarithmic transformations of discharge (Q) and stage height (h) were made using the equation:

$$\ln(Q) = \beta_0 + \beta_1 \ln(h) \quad [1]$$

where β_0 and β_1 are constants to be determined. A visual inspection of the paired h and Q values revealed considerable interannual variability, which was likely due to variations in stream bathymetry from year to year as a result of freeze-thaw action, spring flooding, agricultural operations, *etc*. Given the interannual disparity in the relationship between h and Q, annual rating curves were calculated: eight at the micro-watershed outlet (2005 to 2012) and four for each of branches 14 and 15 (2009 to 2012).

In order to assess the reliability and accuracy of the rating curves, a January-to-November weather characterization and an April-to-November water balance were calculated. Annual runoff, determined from flow values generated by rating curves, was compared with reference values for the region. The same type of comparison was made for actual evapotranspiration ($AET \cong P - Q$ on annual basis with the hydrological year starting and ending around the peak of the spring freshet, assuming no variation in storage) and the discharge (Q) to precipitation (P) ratio (Muma et al. 2013; Ratté-Fortin 2014). In the study region, annual R is from 380 mm to 518 mm (Centre d'expertise hydrique du Québec 2013), annual PET (potential evapotranspiration) from 500 mm to 600 mm (Natural Resources Canada 1974) and «P – PET» between 95 mm and 158 mm (Agroclimate Atlas of Quebec 2012). It was assumed that most of the flow occurring in April was representative of the accumulation of snow from January to March; that is why the two characterization periods are of different lengths. Uncertainty associated with flow estimation was integrated using Monte Carlo simulations performed for each annual rating curve. A distribution of 10,000 flow values was generated every day using regression residuals ε treated as random elements with $\sim N(0, \sigma_\varepsilon^2)$, where N represents the normal distribution with a mean of 0 and standard deviation σ_ε. Variability of regression residuals is linked to environmental uncertainty such as hysteresis effects, variable hydrological conditions at the time of stage-discharge measurements, intra-annual variation in stream bathymetry, seasonal changes in vegetation density and type, and human factors (measurement of water height, instrument calibration and handling). The final flow value used to calculate contaminant loads was selected randomly from these 10,000 values (Figure 2). Given that a large portion of annual loads of contaminants enters runoff during rainfall events, it is essential to include uncertainties associated with the estimation of flow, which are particularly large during periods of high water. This random selection of the daily flow was done 10,000 times in order to obtain a distribution of total daily loads.

Distribution of total nutrient and sediment loads

A common problem encountered when estimating annual nutrient and sediment loads is the lack of available water quality data. In the case of the micro-watershed under study, water quality data came from composite samples collected every three or four days. Under this framework, there can be two sources of missing data: missing daily concentrations and missing composite samples. Daily concentrations were unknown because of the nature of composite samples. As well, composite samples were at times missing because of equipment failure. For this study, flows were monitored on a daily basis, for a total of 1548 days at the outlet of the watershed from 2005 to 2012. While concentrations of TN, TP, TSS, PP and DP from composite samples were potentially available throughout the study period, concentrations of $NO_3^- - N$, $NO_2^- - N$ and $NH_4^+ - N$ were available for potentially 1355 days (2005-2011). Overall, there were 3 (TN), 43 (TP), 35 (TSS), 16 ($\mathrm{NO_3^-} - \mathrm{N}$), 46 ($\mathrm{NO_2^-} - \mathrm{N}$), 360 ($\mathrm{NH_4^+} - \mathrm{N}$), 140 (PP) and 256 (DP) unknown daily concentrations at the outlet of the micro-watershed. There were slightly more unknowns at the outlets of branches 14 and 15.

To obtain April to November loads, missing composite samples were estimated or synthetically generated. Several methods can be used for this purpose. Weighting (or interpolation) and estimation using ratios or regression are methods that are widely used, despite the fact that in some cases, they can produce an inaccurate estimate of loads (Walling and Webb 1981,1988; Cooper and Watts 2002; Moatar and Meybeck 2005). The method that Mailhot et al. (2008) developed as a robust alternative was used to estimate the nutrient and sediment loads by using statistical concentration distributions. This method considers nutrient or sediment concentration x as a random variable that can be represented by a statistical distribution. Several statistical models were tested on each contaminant concentrations in order to provide the best fit on the data. Parameters defining this distribution were the covariates, namely flow (Q) and calendar day (D). For example, for a specific three days of missing TN concentration values, the covariate Q represents the average flow value for that period, and D is the mean value of calendar day for that period. The concentration value for these three days is then estimated using the chosen model and covariates. This method can be used to work with data where there is no strong correlation between concentrations and flows (Quilbé et al. 2006; Mailhot et al. 2008; Raymond et al. 2014).

Several models representing the probability distribution of concentrations were tested, including lognormal and gamma distributions. Parameters of the distributions were estimated using the maximum likelihood method. Since a major part of the fluxes of contaminants is due to rainfall events, it is essential to validate performance of the statistical models for high discharge values. This factor was considered in selecting the best model for representing nutrient or sediment concentrations. Empirical cumulative distributions were compared with theoretical cumulative distributions corresponding to the different models. The best model representing the probability distribution of concentrations was then selected for each nutrient ($TN, TP, DP, PP, NO_2^- - N, NO_3^- - N, NH_4^+ - N$) and for the total suspended sediments (TSS).

Uncertainty associated with the estimation of concentrations was taken into account by using the parametric bootstrap method to obtain model parameters (Efron and Tibshirani 1993). The method was used to generate 10,000 sets of parameters. A set was then randomly selected from the 10,000 sets in order to generate a new series of daily concentrations. The effect of the uncertainty related to the parameters was then included in estimating the total loads. Total load was calculated using daily concentrations and daily flow (selected randomly from the distribution of flows). In summary, the detailed steps for calculating total loads are: (i) selecting randomly daily *Q* from the distribution of flows; (ii) generating 10,000 random nutrient concentration series from the selected model using daily *Q* and *D* as covariates; (iii) estimating 10,000 sets of parameters for each of these synthetic series; (iv) randomly selecting a set from these 10,000 sets; (v) generating the daily concentrations *C* using the selected set of parameters and the daily covariates *Q* and *D*; and (vi) calculating total loads using daily *Q* and *C* (Figure 2). This process was performed 10,000 times in order to obtain a distribution of total loads.

Nutrient balance

Soil surface nutrient balance was used as an indicator of agronomic pressure on the landscape. Soil surface nutrient balance represents the difference between applied fertilizers (the pressure term in the DPSIR framework) and nutrient uptake by crops. The end results may be an indicator of nutrients build-up in the soil (the state term in DPSIR). More specifically, the nutrient balance is the difference between inputs of nutrients associated with organic and inorganic fertilizers (kg/ha) and crop removal (kg/ha).

$$\begin{aligned} B = {} & \text{Loads imported by organic and inorganic fertilizers} \\ & - \text{Loads exported by crops (harvestable yield} \times \text{nutrient content of exported crop)} \end{aligned} \qquad [2]$$

Field-based nutrient inputs were provided by the local fertilization organisation overseeing the watershed farms. The organisation determines nutrient inputs according to state-of-the art practices performed by professional agronomists. It was assumed that nutrient inputs accounted for atmospheric deposition, N fixation if required, and nutrient efficiency, among other factors. Loads exported by crops were calculated as the product of plant uptake and crop yield. Data on the uptake of elements by different parts of plants were obtained from the *Centre de référence en agriculture et agroalimentaire du Québec* (2010) (Agriculture and Agrifood Reference Center of Quebec) and the reference yields from *La Financière agricole du Québec* (2013) (The Agricultural Financing Entity of Quebec). The TN and TP nutrient balances were calculated for each year on the agricultural area of the watershed (forest cover excluded).

Evaluation of the BMPs

Concentrations and loads of the different forms of contaminants measured at the micro-watershed outlet during the calibration period, i.e. the period prior to riparian buffer implementation were compared to values obtained during the treatment period i.e. after buffers were implemented. Riparian buffers were implemented in the micro-watershed in July 2007. The calibration period was from 2005 to 2006 and the treatment period from 2008 to 2012. The year 2007 was not included, because the precise start and end dates of riparian buffer implementation were not known. The number of samples for water quality was about 282 during the pre-implementation period and about 390 following implementation of the riparian buffers, depending on the contaminant of concern. The non-parametric bootstrap method, a fairly recent technique for comparing asymmetrical data (Efron and Tibshirani 1993), was used to compare distributions of concentrations and loads, because this method does not constrain the assumptions of normality, homoscedasticity or distribution shape. Unlike the rank regression method, it also considers the effect of extreme values. For X and W of size *n* and *m* representing the distributions of concentrations or loads during the calibration and treatment periods (respectively), the bootstrap procedure first generates $b = 1,2,3, \dots, B$ bootstrap samples $(\mathrm{X}^*, \mathrm{W}^*)$ where X^* is sampled with replacement from X and W^* is sampled with replacement from W. For each pair $(\mathrm{X}^*, \mathrm{W}^*)$, the two-sample *t* statistic is calculated:

$$t_b^* = \frac{\bar{X}^* - \bar{W}^*}{\sqrt{\bar{\sigma}^2_{\mathrm{X}^*}/n + \bar{\sigma}^2_{\mathrm{W}^*}/m}} \qquad [3]$$

Where $\bar{\sigma}^2_{\mathrm{X}^*} = \sum_1^n (X_i - \bar{X}^*)^2/(n-1)$, $\bar{\sigma}^2_{\mathrm{W}^*} = \sum_1^m (W_i - \overline{W}^*)^2/(m-1)$. Having observed t_b^*, the approximate achieved significance level (ASL) of the test is

$$\widehat{ASL}_{boot} = \#\{\boldsymbol{t_b^*} \geq \boldsymbol{t_{obs}}\}/B \qquad [4]$$

Where t_{obs} is the observed value of the statistic and # means number of times $\boldsymbol{t_b^*} \geq \boldsymbol{t_{obs}}$.

Given our previously mentioned working assumption, there exists a relationship between the total loads at the micro-watershed outlet and the fertilizer inputs; the latter being conditioned in part by the hydropedological conditions and the amount of soil P accumulated with time (Simard et al. 1995; Beauchemin et al. 1998; Beauchemin and Simard 2000; Simard et al. 2000). Thus, loads were normalized by the soil surface nutrient balances and ultimately the result interpreted as an export fraction, that is, the ratio of total loads (*L*), akin to the Impact in the DPSIR framework, at a given sampling station to the *B* of the agricultural land area drained to this sampling station (Figure 3). For a given year *i*, the export fraction EF_i (i.e. the ratio of Impact to Pressure) is:

$$EF_i = L_i/B_i \qquad [5]$$

In addition, an upstream-downstream analysis was used to evaluate the effect of a riparian buffer on water quality. This involves using two sampling stations: one upstream of the study area and the other downstream. It is possible to compare the export fractions obtained downstream from riparian buffers with those obtained on the stream where there is no riparian buffer. To this end, total loads at the outlet of branch 14 (Br. 14) were estimated by taking the difference between loads obtained at the watershed outlet and those obtained at the outlet of branch 15 (Br. 15) (Figure 3). No riparian buffer was established on the stream between the sampling station on Br. 14 and its confluence. If the effect of the riparian buffers is obvious, export fractions obtained immediately downstream from riparian buffers should be lower than those obtained at the outlet of Br. 14 given similar nutrient balances.

Since export fractions are calculated from distributions of total loads, a distribution of export fractions was obtained for each year. To determine whether, for each year from 2009 to 2012, the downstream riparian-buffer (RB) export fraction shows a significant decline (95% confidence interval) compared with the Br.14 export fraction, the non-parametric bootstrap method was used to compare the two samples. If the ratio of the downstream RB export fraction and the Br. 14 export fraction is lower than 1, then the effect of riparian buffers is evident.

$$Ratio = EF_{Downstr\ RB}/EF_{Br.14} \qquad [6]$$

As with the calculation of $EF_{Downstr\ RB}$ and $EF_{Br.14}$, export fractions obtained on the small section of the stream between the sampling station downstream from the riparian buffer and the outlet of Br. 14 were calculated (refer to Figure 3):

$$EF_{section} = (L_{Outlet\ Br.14} - L_{Downstr\ RB})/(B_{Section}) \qquad [7]$$

Where $L_{Outlet\ Br.14}$ (kg) is the median value of the estimated total load at the outlet of Br.14, $L_{Downstr\ RB}$ (kg) is the median value of the total load at the sampling station downstream from the section of the riparian buffer on Br.14, and $B_{Section}$ (kg) is the nutrient balance of the section between the outlet of Br.14 and the sampling point downstream from the riparian buffer section on Br.14.

A ratio between the export fraction downstream of the riparian buffer and the export fraction obtained for the section between the two sampling stations (Equation 6) was also calculated. If this ratio is less than 1, then the riparian buffer contributes to abatement of contaminant fluxes to the stream. Following this concept, it becomes useful to define riparian buffer effectiveness (%) as follows:

$$\text{Effectiveness}\ (\%) = \left[1 - \left(\frac{L_{Down\ RB}}{B_{Down\ RB}} \middle/ \frac{L_{Outlet\ Br14} - L_{Down\ RB}}{B_{Section}}\right)\right] \times 100 \qquad [8]$$

Results

Rating curves

At the outlet of the intervention micro-watershed, annual rating curves (regression between daily flows and daily stream heights) gave coefficients of determination (R^2) generally ranging from 82 to 97%, except for the year 2012, when the coefficient was 63% (Table 2). For rating curves obtained on Br.14 and 15, R^2 values varied from 67% to 88%, except for 2009 and 2012, which have lower values (37 and 47%, respectively).

Water balance results (Table 3) showed total runoff (*R*) and actual *AET* values were similar to reference values for the region, validating the robustness of the rating curves. Finally, uncertainty related to the estimation of discharge using rating curves was calculated based on the variance of regression residuals. Figure 4 presents the 10,000 simulations of parameters obtained from the model as point data showing the natural logarithm of discharge as a function of the natural logarithm of water height at the outlet of the micro-watershed.

Distribution of nutrient and sediment loads

Results indicated the concentrations of TN, $\mathrm{NO_3^-} - \mathrm{N}$ and $\mathrm{NH_4^+} - \mathrm{N}$ follow a gamma distribution; whereas, the concentrations of TP, PP, DP, $\mathrm{NO_2^-} - \mathrm{N}$ and TSS follow a log-normal distribution (Appendix 6). Improvements to log-likelihood values for linear CV models compared to constant CV models were verified using the likelihood ratio test. The coefficient of variation followed a linear function for the concentrations of TN, $\mathrm{NO_2^-} - \mathrm{N}$, $\mathrm{NO_3^-} - \mathrm{N}$ and $\mathrm{NH_4^+} - \mathrm{N}$; whereas, for the concentrations of TP, PP, DP and TSS, the coefficient of variation remained constant. With the remaining streamflow-dependent models presenting very similar log-likelihood values, we compared the observed cumulative distributions to the theoretical cumulative distributions to assess how the different models perform for large discharge values (Appendix 6). Finally, the calendar day dependence was integrated to the selected streamflow dependent models. Again, the improvements to log-likelihood values for new models were verified using the likelihood ratio test. Only the models for concentrations of TN, $NO_2^- - N$, $NO_3^- - N$ and TSS showed a significant improvement when an annual cycle was included in the mean function (TN, $NO_2^- - N$, $NO_3^- - N$, TSS) and the coefficient of variation function (TN, $NO_3^- - N$) (Appendix 6).

Median TN loads measured at the outlet of the micro-watershed varied from 12 to 35 kg/ha, while the flow-weighted mean concentration (FWMC) varied from 5.0 to 6.0 mg/L annually (Appendix 3). Loads of TP ranged from 0.2 to 0.7 kg/ha, and the FWMC ranged from 0.10 to 0.12 mg/L. Figure 5 presents median values along with the 10th and 90th percentiles of the daily discharge, daily concentrations and daily loads of TN in 2006 (2006 TP, Appendix 3).

Evaluation of BMPs

Temporal comparison

Concentrations and loads of TN and $NO_3^- - N$ were lower after the implementation of riparian buffers (Table 4). With regard to $NO_2^- - N$ and $NH_4^+ - N$, there was a decrease in loadings only. TP and PP showed a decline in median concentration and load following buffer implementation. In the case of DP, only results comparing the means of the before/after concentrations showed a decrease. The same was true for TSS, with only the median load value showing a decline. Although results show riparian buffers had a positive effect on reducing nutrient concentration and load, a number of components may have affected the variability of nutrient and sediment concentrations and loads during the study period. In general, the decline in loads is not due solely to the riparian buffers, but it is also due to other structural and non-structural BMPs introduced in the watershed such as crop rotation and crop residue management. To single out the effect of riparian buffers, a spatial comparison was performed.

Ratios (spatial comparison)

There was a significant reduction in the export fraction downstream from the riparian buffer ($EF_{Downstr\ RB}$) compared with the export fraction at the outlet of Br.14 ($EF_{Br.14}$) for TN and TP in 2009 (Table 5). Among other contaminants, $\mathrm{NO_2^-} - \mathrm{N}$ and PP showed a significant reduction in 2009, 2010 and 2011, and $\mathrm{NO_3^-} - \mathrm{N}$ decreased in 2009 and 2010. It is important to remember, however, that results for ratios of contaminants other than TN and TP are estimates obtained using nutrient balances of TN and TP.

For 2009, the year showing a significant reduction in TP and TN, $EF_{section}$ values were calculated. Export fractions were obtained are 0.407 and 0.0336 for TN and TP, respectively, which are higher than those obtained at the sampling station downstream from the riparian buffers (export fractions of 0.3033 for TN and 0.0300 for TP). This increase in export fraction for the section with no riparian buffers is not due to a difference in the contribution from nutrient balances, since loads imported to fields were similar for all three sections: 102.8 kg /ha TN for the entire drained section of Br.14, 102.4 kg /ha TN for the section upstream from the riparian buffers and 103.7 kg /ha TN in the section downstream from the riparian buffer. Loads imported to fields were also similar for TP (refer to Appendix 2).

The effectiveness calculated for 2009, the year with significant reductions in the ratio downstream from the riparian buffer, is as follows: 25.4% abatement in the flux of TN and 10.7% abatement in the flux of TP.

Discussion

Temporal comparisons of concentrations and loads before and after riparian buffer implementation show a significant decline in both for TN, TP, PP and $NO_3^- - N$ as well as in loads of $NH_4^+ - N$, $NO_2^- - N$ and TSS. To integrate information related to the different variables that might be correlated with annual loads, a multiple regression analysis was performed to model loads for different crop types, level of precipitation and nutrient balances for each year. Results showed that nutrient balances alone were correlated with loads, but not with precipitation or annual crop types. This is understandable, as nutrient balances represent the anthropic pressure on the environment. In addition, precipitation remained more or less stable (Table 3), while nutrient balances increased gradually during the study period (Appendix 2). This could potentially contribute to an increase in loads exported to the stream after 2007. Therefore, the load decrease during the period following buffer implementation was not attributable to low rainfall or to a decrease in nutrient loadings to fields.

The spatial comparison using the export fraction downstream from riparian buffers ($EF_{Downstr\ RB}$) compared with the export fraction at the outlet of Br.14 ($EF_{Br.14}$) showed a significant decrease of TN and TP (unilateral test, right reject area) for year 2009 only. Relative reductions in the ratios of loads/balances were 6% for TN (2009) and 2% for TP (2009) (Table 5). Other years (2010, 2011 and 2012) did not have significant reductions for TN and TP. Because of the important variability that limits the efficiency of the hypothesis tests, ratios can have values greater than 1 without being characterized as significant. Moreover, 2009 was the only year characterized by efficient riparian buffers during the spring (seasonal ratio significantly <1). This partially explains why it is the only year that riparian buffer could have been efficient (spring fluxes account for a substantial part of the annual flux), especially when it is well known that the riparian buffer vegetation was not fully established. An effect of similar magnitude was seen for other contaminants, with a significant decrease for $\mathrm{NO_3^-} - \mathrm{N}$ in 2009 (49%) and 2010 (44%) and for $\mathrm{NO_2^-} - \mathrm{N}$ and PP in 2009 (42% and 66% respectively), 2010 (28% and 26% respectively) and 2011 (13% and 31% respectively). These ratios are, however, estimates obtained using the nutrient balances for TP and TN.

Ratios obtained for each season showed riparian buffers are less effective in spring or spring freshet period, likely because of freeze-thaw action and the fact that buffers are not yet fully developed (Table 6). In addition, riparian buffers were less effective during seasons characterized by intensive rainfall events. For example, in 2010 (a year with little rainfall and no intensive rainfall events) and 2011 (a fairly rainy year but no intensive rainfall events), most of the contaminants had significantly lower ratios in the area downstream from the riparian buffer.

In 2009, the riparian buffer reduced TN load by 25.4% and TP load by 10.7%. Given that the micro-watershed has steep slopes (3 to 8%) and the riparian buffer was 3-m wide (if the bank width was less than 3 m wide, 1 m is added to the flat upper part of the buffer), the level effectiveness obtained is consistent with results reported in the literature. For example, a 5-m-wide grass riparian buffer showed 54% effectiveness in reducing the flux of TN and 61% effectiveness in reducing the flux of TP (Dillaha et al. 1989). Li et al. (2011) evaluated effects of BMPs, such as riparian buffers and grassed waterways, in a small watershed in Manitoba, Canada, and showed that, collectively, these practices reduced fluxes of total nitrogen (TN) and TP by 41% and 32%, respectively. Jaynes et al. (2004) studied the effect of split N application for corn production in terms of reducing TN losses within a watershed in Iowa, United States, and found a relative reduction of more than 30% in nitrate concentration in surface water.

Owing to variations in weather, runoff, crop types and fertilizer inputs, nutrient fluxes vary widely from day to day and from year to year. This makes it more challenging to assess the effectiveness of riparian buffers during the short term. In studies of this type, a lengthy data series is essential for the reliable assessment of BMP effectiveness. In addition, the response to BMP implementation can take a number of years, perhaps as many as 5 to 10 years (Mulla et al. 2005). A long-term study is especially appropriate for a paired watershed investigation. It should be kept in mind, however, that the beneficial effect of riparian buffers declines with time. A riparian buffer can become saturated with phosphorus over time (Wenger 1999). For this reason, riparian buffers or grassed waterways should not be the only approaches implemented in order to reduce fluxes of agricultural contaminants. In the studied micro-watershed, producers introduced other BMPs as well, such as crop rotation, residue management, new pig slurry spreading techniques and soil erosion control. Meeting crop nutrient requirements without over application and implementing practices to reduce excess nutrients are key. In short, it is essential to combine management of nutrient and sediment sources with management of the transport of these contaminants to streams in order to achieve optimal reductions in loadings of agricultural contaminants.

Summary and conclusions

This study involved developing a methodological approach for assessing the effect of BMPs in a context where the paired watersheds approach cannot be used. The method is based on establishing rating curves, estimating nutrient loads and assessing the effectiveness of riparian buffers implemented within a small watershed. The method for estimating nutrient loads begins with the calculation of flows. These rates are estimated using annual rating curves, which were validated based on weather and hydrological characteristics specific to each year. Uncertainty related to the calculation of flows was estimated by a Monte Carlo simulation method, based on the variance of the residuals of the rating curves. Models of nutrient and sediment concentrations were adjusted using probability distributions in which the parameters were functions of the flow and calendar day. Uncertainty of the adjusted parameters was taken into account by using a parametric bootstrap approach. Total loads were estimated using models of daily concentrations retained and daily flows generated by rating curves.

The main objective of this Watershed Evaluation of Beneficial Management Practices (WEBs) project was to evaluate the effectiveness of BMPs implemented on the Bras d'Henri River intervention micro-watershed with a view to reducing fluxes of agricultural contaminants. The BMPs included 3-m-wide riparian buffers established in 2007 over a distance of about 6,684 m (grass, shrub and tree buffers). A temporal comparison of the loads and concentrations before (2005 to 2006) and after (2008 to 2012) the implementation of riparian buffers and other structural and non-structural BMPs (Table 1) showed a significant decrease in the loads and concentrations of TN, TP, PP and $NO_3^- - N$ following buffer implementation and other structural and non-structural BMPs. In addition, the loads of $NH_4^+ - N$, $NO_2^- - N$ and TSS showed a significant decline after 2007. There was a significant decline of TN and TP in the ratio values downstream from the riparian buffers compared with the sampling station at the outlet of Br.14 in 2009. Buffer effectiveness associated with these declines consisted of a 25.4% reduction in the flux of TN and a 10.7% reduction in the flux of TP. Calculation of the ratios on a seasonal (spring, summer, fall) basis showed that the riparian buffers were less effective at intercepting contaminant loads in the spring, as well as during seasons marked by intensive rainfall events. Overall, the riparian buffers reduced contaminant loads significantly one year out of four.

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