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Journal:	*Canadian Water Resources Journal*
Manuscript ID	TCWR-2019-0028.R1
Manuscript Type:	Original Paper
Date Submitted by the Author:	n/a
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Keywords:	stables isotopes; nutrients; fecal coliforms; septic installations; wastewater treatment plants;

Seasonal contributions of water and pollutants to Lake St. Charles, a drinking water reservoir

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Abstract

Surface waters are widely used as sources of drinking water in Canada. The identification of the main sources of pollutants to surface waters, often associated with increasing urbanization, is needed to improve management strategies. We used stable water isotopes ($\delta^{18}O$ and δD), and nutrient and fecal coliform mass fluxes to estimate the seasonal contributions of water and pollutants of different inflows to Lake St. Charles (LSC). Our results indicate that out of six identified LSC water sources, groundwater (GW), Hurons River (HR) and small stream tributaries (SSTs) represent the major contributors (in terms of water volume). The three other water sources, including two wastewater treatment plants (WWTPs), Delage Lake (DL) and precipitation (rain and snow), represent smaller seasonal contributions. During the high-flow seasons (spring and fall), LSC receives water mainly from SSTs and HR, while during the low-flow season (summer), the lake relies mainly on GW inflows. Estimates of point source (WWTPs) versus non-point source (primarily septic installations) concentrations of nutrients and fecal coliforms show that the latter represents a seasonally variable and greater source of pollutants (5 % WWTPs vs. 95 % septic installations). HR and SSTs, draining densely occupied areas of single housing units with individual septic installations, are categorized as non-point sources, and as such are considered major nutrient and fecal coliform contributors. The higher precipitation in spring and fall caused increased fluxes of nutrients and fecal coliforms through higher stream discharge. Due to the seasonally variable and difficult to predict discharge dynamics of SSTs and HR, these two sources represent a potentially larger threat to LSC water quality. We advocate that improved management requires reducing the number of individual septic installations in the LSC watershed.

Résumé

Les eaux de surface sont largement utilisées comme sources d'eau potable au Canada. L'identification des principales sources de polluants dans les eaux de surface, souvent associées à une urbanisation croissante, est nécessaire pour élaborer des stratégies de gestion améliorée. Nous avons utilisé des isotopes stables dans l'eau ($\delta^{18}O$ et δD) et des charges en nutriments et coliformes fécaux pour estimer les contributions saisonnières de différents affluents vers le lac Saint-Charles (LSC). Nos résultats indiquent que parmi les six sources d'eau identifiées, les eaux souterraines (GW), la rivière des Hurons (HR) et les petits tributaires (SSTs) représentent les principaux contributeurs (en termes de volume d'eau). Les trois autres sources d'eau, dont deux stations d'épuration d'eaux usées (WWTPs), Lac Delage (DL) et les précipitations (pluie et neige), représentent une contribution saisonnière moins importante. Pendant les saisons de fort débit (printemps et automne), LSC reçoit de l'eau principalement des SSTs et HR, tandis que pendant la saison de faible débit (été), le lac dépend principalement de GW pour maintenir son niveau d'eau. Les estimations des sources ponctuelles (WWTPs) par rapport aux sources non ponctuelles (principalement des installations septiques) de nutriments et coliformes fécaux ont démontré que cette dernière source représente une contribution saisonnière variable, mais plus importante de polluants (5% des WWTPs contre 95% des installations septiques). HR et SSTs qui drainent les zones densément occupées par des maisons avec des installations septiques privées, sont classées comme des sources non ponctuelles et, à ce titre, sont considérées comme des contributeurs majeurs en nutriments et coliformes fécaux. Les précipitations plus abondantes au printemps et à l'automne ont entraîné une augmentation des flux de nutriments et coliformes fécaux en raison du débit plus élevé. La dynamique de débits saisonniers difficile à prévoir des SSTs et HR, représente une menace potentiellement plus grande pour la qualité de l'eau du LSC que d'autres sources. Nous préconisons que l'amélioration de la gestion nécessite de réduire le nombre d'installations septiques privées dans le bassin versant du LSC.

Keywords: **Quebec; stables isotopes; nutrients; fecal coliforms; septic installations; wastewater treatment plants;**

Introduction

In Canada, two-thirds of the population depend on surface waters from lakes, rivers and reservoirs for their drinking water supply (Statistics Canada 2011). In southern Quebec, surface waters provide more than 75 % of the drinking water (MDDEP 2008). Increasingly, people are moving out of city centers, because of lower housing prices, and developers are quickly converting forested areas and floodplains into building lots to respond to this growing demand, and as a consequence replacing land cover serving as natural filters (Ritchot et al. 1994)). The accelerated urbanization, often not connected to sewer systems, particularly in the urban-rural fringe areas, is viewed as a major threat to long-term sustainability in water quality and quantity and represents a major challenge for water managers.

Lake St. Charles (LSC) is the main drinking water reservoir of Quebec City providing drinking water to 300,000 inhabitants and is located in the urban-rural fringe area. There is increasing evidence that the lake water quality is undergoing accelerated degradation associated with increased urbanization (Tremblay et al. 2002; Tremblay and Pienitz 2015; APEL 2014b and 2019). Based on APEL reports (Association pour la protection de l'environnement du lac Saint-Charles et des Marais du Nord; 2012, 2014a, 2014b), a non-profit lake steward organization, urban development is increasing faster than the infrastructure capacity (e.g., the capacity of the two wastewater treatment plants upstream from Lake St. Charles in addition to the increasing number of housing on septic installations), and regulations are needed to control diffuse (non-point) and point sources of pollution from domestic waste water sources. Residential development and increased discharge of domestic wastewaters into the lake have substantially increased during the past 50 years (APEL 2019). These land cover changes have accelerated the lake eutrophication process and ensuing degradation rate, which is already perceptible by occurrences of cyanobacterial blooms occurrence, aquatic plant proliferation and increased water salinity (Légaré 1997, 1998; APEL 2012, 2014a). Indeed, the lake was classified as mesotrophic when considering both nutrient and algal biomass (APEL 2014b). Within the lake watershed, there are two wastewater treatment plants (WWTPs) serving close to 5 000 people. WWTPs are permanent point sources of nutrients and pollutants. In addition, approximately 3 000, single housing units with on-site septic installations composed of a sedimentation tank and purification field, viewed as non-point sources of pollution, are also located within the LSC watershed.

Several studies have observed that septic installation failure contributes to water quality degradation, but even a properly working septic installation, which has a working life expectancy between 10 to 20 years, does not handle all pollutants effectively and is likely insufficient to prevent pollution of downstream waterbodies and groundwaters (Aravena et al. 1992; Wilhelm et al. 1996; Ptacek 1998; Robertson et al. 1998; Wernick et al. 1998; Arnade 1999; Moore et al. 2003). To our knowledge, there are no studies that have focused on the efficiency of septic installations and contributing pollution to LSC based on geochemical proxies, and the same can be said for the two WWTP effluents located within its drainage area. The study of Wernick et al. (1998) advocates that individual septic installations are one of the main non-point sources of nitrogen pollution in stream waters. In their comparison between lakes with houses connected to a central sewer system and those surrounded by houses with individual septic installations, Moore et al. (2003) concluded that the latter had higher levels of phosphorous and *chlorophyll*-a concentrations.

The two municipalities located within the LSC watershed, are considering the possibility of connecting individual septic installations to their local sewer systems (modernised WWTPs) and/or diverting their domestic wastewaters to WWPT located in Quebec City, that is beyond the lake watershed. Therefore, there is a need to identify the dominant pollutant sources in order to prioritize investments. To provide municipalities with this knowledge, we assessed and compared intra- and inter-annual contributions of point (WWTPs) and non-point sources (septic installations drained by small stream tributaries) of waters, nutrients and fecal coliforms located within the LSC watreshed. We used water stable isotopes ($\delta^{18}O$ and δD) to partition water sources to LSC, and limnological tracers (mass fluxes, that is loadings, of phosphorus, nitrogen and fecal coliform) to assess the transport of pollutants to LSC over a two-year period. Stable isotope analysis is often used to determine the relative contribution of different water sources, but also about the evaporation effects, precipitation patterns and groundwater recharge (Clark and Fritz 1997; Turner et al. 2010; Tondu et al. 2013; Narancic et al. 2017). Moreover, water stable isotopes are considered water management tools (Tondu et al. 2013). Here we used a linear mixing model for partitioning six lake water sources using $\delta^{18}O$ and δD. The isotopic similarity of LSC waters to individual water sources is used to estimate their relative contribution to the lake water balance.

The estimation of nutrient and fecal coliform mass fluxes to the lake is paramount in assessing the sustainability of LSC water quality. The characterization of the mass fluxes through our applied hydro-limnological approach will inform governance strategies to improve or avoid further degradation of lake water quality. The results can also serve to improve the hydrological modelling through a more complete description of seasonal changes in limnological conditions, and to make projections linked to climate change, which is especially critical for this municipal source of drinking water.

Materials and Methods

Study site

LSC (46°55' N, 71°22' W), located 20 km northwest of Quebec City (Canada), is a medium-size lake reservoir (3.6 km^2) with a deeper northern (up the lake) basin (maximum depth = 17.5 m) and shallower southern basin (towards the lake outlet; maximum depth = 4.5 m; Figure 1). The drainage area of the watershed is 198 km^2, transgressing the administrative boundaries of five neighbouring municipalities: Stoneham-and-Tewkesbury, City of Lac Delage, Quebec City, Saint-Gabriel-de-Valcartier and Lac Beauport (Figure 1). Based on previous studies, the main sources of water to LSC come from the Hurons River, Delage Lake, and 34 small streams, respectively draining 82 %, 4 % and 11 % of the watershed. Diffuse runoff from lake hillslopes were estimated to drain the remaining 3 % of the watershed (APEL 2014b). LSC discharges into the St. Charles River via a dam that separates the lake and the river. The dam was built in 1934 to create the drinking water reservoir for Quebec City (APEL 2014a; APEL 2019), and is now a run-of-the-river type dam since 2012. The short water residence time, ca. 23 days for the northern basin and ca. 8 days for the southern basin, characterises LSC as a fluvial lake system (Légaré 1998; Tremblay et al. 2002). [Figure 1 near here]

LSC is located on the Canadian Shield in an ancient glacial valley surrounded by steep hills with altitudes varying between 150-450 m (the highest peak is at 750 m; Tremblay et al. 2002). Surface deposits are thin with outcrops (APEL 1981). Upstream surface water has naturally low ionic charge, and thus, low conductivity and pH (78.6 µS/cm and 6.7 pH). Approximately, 70 % of the lake watershed is covered by dense forests, dominated by deciduous and mixed wood stands. Significant macrophyte growth occurs in shallow areas along the lake shores. Since 2012, macrophyte growth has been extensive and tends to cover 55 % of the southern basin area and 36 % of the northern basin area (APEL 2014b).

Today, approximately 13 000 people live in the lake watershed, with more than 4 000 housing units located close to the shores (i.e. at less than 500 m; APEL 2014b). More than half of these housing units have on-site individual septic installations. Given the 1960 population growth in the lake watershed, some of these septic installations are more than 50 years old (APEL 2019 and references therein). In 1990, two WWTPs were built for the towns of Stoneham-and-Tewkesbury and City of Lac Delage. Both WWTPs have aerated lagoons. Since 2017, the Stoneham-and-Tewkesbury WWTP uses tertiary treatment of sewage discharge and treated waters are directly flushed out through an underground pipe system into Hurons River, ca. 4 km upstream of LSC. City of Lac Delage WWTP provides alum-based coagulation to treat the wastewaters, and treated waters are discharged into marshes (Northern Marshes) upstream of LSC (Figure 1).

According to the 1981–2010 climate normal from the closest Environment and Climate Change Canada meteorological station (Jean-Lesage airport, Station ID 7016294), the average annual temperature and precipitation are 4.2 °C and 1 190 mm, respectively (Environment Canada 2017). Most of the precipitation (ca. 75%) falls as rain. The lake is covered by ice from December to April. Annual precipitation for 2016 (1 337 mm) and 2017 (1 231 mm) were slightly above the 1981-2010 climate normal. Both years had exceptionally wet conditions during the spring and fall (710 mm = 2016; 753 mm = 2017; compared to 595 mm = 30-year climate average) and drier than normal conditions during the summer (297 mm = 2016; 222 = 2017; compared to 358 mm = 30-year climate average; Figure 2). The temperature for both years were generally similar to the 30-year climate average, with slightly warmer winter temperatures for the months of January (-8.6°C = 2016; -8.9°C = 2017; compared to -12.8°C = 30-year climate average) and February (-8.9°C = 2016; -8.6°C = 2017; compared to -10.6°C = 30-year climate average) and colder summer temperatures for the month of July (18.9°C = 2016; 17.9°C = 2017; compared to 19.5°C = 30-year climate average; Figure 2). [Figure 2 near here]

Field sampling and analysis

Waters from LSC were sampled at five different locations (stations C03, C04 and C05 in the pelagic zone; stations SCE and SCA in the littoral zone; Table 1). Hurons River (HR), Delage Lake (DL), WWTP effluents of Stoneham-and-Tewkesbury (WWTP-ST), City of Lac Delage (WWTP-LD), and 28 small stream tributaries (SSTs; DD, CC, BB, AA, FF, W, Z, GG, U, T, HH, S, R, Q, P, CPLSC18, M, KK, L, K, J, E, OO, H, C, F, G and PP) were sampled at only one location. All sites were sampled every other week from June to October 2016 and an additional six SSTs (IID, IIB, LL, NN, N and A) were sampled from April to October 2017. The HR, DL, WWTP-ST, WWTP-LD and four SSTs (AA, S, K and OO) were sampled once a month from January to March 2017. Groundwater

(GW) in private drinking water wells was sampled at five different locations near the shoreline of LSC (GW1, 2, 3, 4 and 5), once in fall 2016 and four times during the period of January-October 2017. At least one precipitation sample per month from June 2016 to October 2017, except for the months of December and January 2017, was taken at the lake outlet; that is at the aforementioned dam location (Figure 1).

Six environmental variables were used to estimate the seasonal contributions of the main water sources (SSTs, HR, DL and WWTPs) to LSC: in-situ measured discharge, water oxygen ($\delta^{18}O$) and hydrogen (δD) stable isotope composition, total nitrogen (TN), total phosphorus (TP) and fecal coliforms (Fc). Water stable isotopes were also used to estimate the seasonal contribution of GW and precipitation to LSC.

Discharge

The discharge (n = 50) was measured once a month by different methods logistically constrained by flow strength, water depth, stream bed types or pipe configuration. For most stations, it was not possible to use a single method because the flow was too variable from one visit to another. The *velocity–area method* for the determination of the stream flow of HR and discharge of DL consisted of measuring depth, distance and stream velocity between different cross-sections of the river. The velocity was measured using a current meter (Swoffer model 2100) and the average was obtained for each cross-section. The discharge rate was then derived from the sum of the product of mean velocity, depth and width between cross-sections. When the water level and flow velocity were too low to use a current meter, we used the *speed–area method* with floats. The velocity was first calculated by measuring the time the float took to travel a fixed distance, and after the area of that river section was measured. The discharge was then calculated by multiplying the section area by the velocity. When water flow was extremely low, we used the *volumetric method*. This method consisted of calculating the discharge from the time needed to fill a container of known volume. These latter two methods were used to measure discharge from the SSTs.

Water stable isotope composition

Water samples were collected in 30-ml, high-density polyethylene bottles at each sampling site (Figure 1). In total, 105 (2016) and 339 (2017) surface water samples, and 4 (2016) and 17 (2017) GW samples were collected. Samples of rain and snow were obtained when precipitation events occurred. Rainwater was collected in a plastic pan until enough water was gathered to fill the 30-ml bottles. This took 2 hours or less. Snow samples were collected in Ziploc® bags and once completely melted, the meltwater was transferred into the 30-ml bottles. Samples were stored at 4°C prior to analysis at the University of Waterloo Environmental Isotope Laboratory by Off-Axis Integrated Cavity Output Spectroscopy (Berman et al., 2013).

Isotope compositions are expressed as δ-values relative to the Vienna Standard Mean Ocean Water (VSMOW) in per mil (‰), such that $\delta_{sample} = (R_{sample} - R_{VSMOW}) / R_{VSMOW} \times 1000$, where R_{sample} and R_{VSMOW} are the ratio $^{18}O/^{16}O$ or $D/^{1}H$ in the sample and VSMOW, respectively. Results of $\delta^{18}O$ and δD analysis are normalized to 55.5 ‰ and 428 ‰, respectively, for Standard Light Antarctic Precipitation (SLAP; Coplen 1996). Analytical uncertainties are ± 0.2 ‰ for $\delta^{18}O$, and ± 0.8 ‰ for δD.

LSC water source partitioning

LSC and its source water isotope compositions were first evaluated in $\delta^{18}O$-δD space including the Local and Global Meteoric Water Line (LMWL and GMWL) for references. The LMWL ($\delta D = 8.58 \times \delta^{18}O + 15.36$) and GMWL ($\delta D = 8 \times \delta^{18}O + 10$; Craig, 1961) respectively expresses the local and global linear relationships between the oxygen and hydrogen isotope compositions of precipitation. The $\delta^{18}O$ and δD values for precipitation typically fall along the GMWL (or LMWL), and their position reflects variability in spatial and seasonal trajectory of the atmospheric vapor contributing to local precipitation (Rozanski et al. 1993). This normally leads to isotopically-depleted winter precipitation and isotopically enriched summer precipitation (Dansgaard 1964).

As shown in Figure 3, LSC does not display substantial evidence of evaporative isotopic enrichment. Lake water isotope composition will usually plot along another linear trend called Local Evaporation Line (LEL: Yi et al. 2008; Turner et al. 2010). The LEL typically has a lower slope than the LMWL and GMWL. Lake water isotope compositions in our study plot along and above the GMWL and LMWL, as expected given the fluvial setting. With the absence of evaporation, it is assumed that the measured lake water isotope composition is a straightforward reflection of the varying combinations of water sources. Prior to proceeding with source partitioning, seasonal isotopic ratios for the lake and its water sources (HR, DL, SSTs, WWTPs) were weighted by the discharge. Each $\delta^{18}O$ (and δD) value was multiplied by the corresponding discharge, and their sum divided by the sum of the total discharge during that season. For GW and precipitation, the arithmetic mean of the isotope compositions was used.

We applied the standard linear mixing model developed by Phillips and Gregg (2003) to determine multiple combinations of multiple source proportions using the IsoSource 1.3.1 program. This model is well suited when the number of contribution sources to a mixture is too large to obtain a unique value, and thus an estimated range of individual contributions (0%-100%) is provided. These ranges depend on the similarity and position within the mixing polygons of source isotope composition in reference to a mixture. In general, small mass balance tolerance (±0.1‰) of source proportions of a mixture is considered to have feasible solutions, from which the frequency (histograms) and range (%) of potential source contributions can be determined.

As a linear relationship exists between $\delta^{18}O$ and δD (Craig 1961) in meteoric water, we assumed that the water source partitioning is the same for both isotopes. We supplied the IsoSource 1.3.1 program with the water isotope compositions of the lake and its water sources, along with the desired source increment (± 1 %) and the mass balance tolerance (± 0.1 ‰) in order to include all possible contributions. As described by Phillips and Gregg (2003), the program repeatedly calculates each possible combination of source proportions. The predicted isotope composition for the lake water was computed as each combination was generated. These predicted lake water isotope compositions were compared to observed values. If they were equal or within a predetermined mass balance tolerance (± 0.1 ‰), they were considered to represent a possible solution and, thus, included in the results. All combinations were represented by histograms with descriptive statistics of the distributions for each source. Within the drawn polygons in $\delta^{18}O$-δD space, we assumed that source waters falling closest to that of LSC provided the greatest water contribution. We used the mean value of the partitioning solution for each water source to estimate the seasonal changes in source contribution to LSC.

Nutrients and fecal coliforms

As previously mentioned, waters from LSC (n= 61), SSTs (n= 393), HR (n= 24), DL (n= 27) and WWTP effluents (n= 44) were sampled at two-week intervals during the two-year sampling period for the measurement of TN, TP and Fc (except Fc not measured in LSC in 2016). The samples were collected in 250-ml high-density polyethylene bottles, and immediately stored in a cooler before taking to the laboratory of Québec City on the same day.

Total nitrogen (TN) was obtained by the catalytic oxidation method with a Shimadzu TOC-V_{CPH} NTM-1 instrument. Nitrogenous compounds were oxidized on a platinum catalyzer at 680°C under pure oxygen atmosphere, the generated nitric oxide reacted with ozone, and the product analysed by chemiluminescence (Nollet and De Gelder. 2007). Total phosphorus (TP) analysis was conducted with a sensitive automated colorimetric method for phosphate detection using a flow segmented Astoria analyzer. Phosphorous compounds were first digested with persulfate in acidic conditions, and then reacted with molybdophosphoric acid and ascorbic acid to form the molybdenum blue color complex quantified by spectrophotometry (APHA, AWWA, WEF, 2005). The detection limits for phosphorous and nitrogen are 0.08 mg N L^{-1} and 2 µgP L^{-1}, respectively.

The water discharge was used to calculate nutrients and Fc seasonal mass fluxes to the LSC from the aforementioned sources (i.e., HR, DL, SSTs and WWTPs). The mass flux for each of water source was estimated using the averaging estimators' method explained in Quilbé et al. (2006). The mass flux was first calculated for each day where both variables were measured by multiplying the concentration with the corresponding discharge on a given day (discharge × concentration × 24h), and the mean monthly mass flux was then calculated for each water source. For SSTs, the mass fluxes of 29 small tributaries were summed over each month. When more than one mass flux was available for any specific SST, the mean was calculated, and this value was then included in the total SSTs monthly mass flux. Seasonal fluxes were obtained by weighting the mean monthly flux (F) by the total number of days in a given season. For example, to obtain the seasonal flux estimation over summer (June, July and August), the weighted summer mass flux was determined as follows: $(F_{Jun} \times 30 + F_{Jul} \times 31 + F_{Aug} \times 31) / (30 + 31 + 31)$.

Results

Water isotope composition

LSC and its water source isotope compositions were plotted in $\delta^{18}O$-$\delta^{2}H$ space to assess the varying signatures of this hydrological system (Figure 3; Table 1). The isotope composition of LSC and most of its water sources cluster along and above the GMWL/LMWL, indicating the absence of any significant seasonal evaporative isotopic enrichment. WWTP, DL, HR and GW display similar ranges in isotope composition, and are also similar to the LSC signature. However, the isotope composition of SSTs and precipitation span a greater range. Thus, both SSTs and precipitation water characteristics vary from isotopically-enriched to isotopically-depleted lake water sources. The superimposed isotope compositions of LSC and its water sources makes it difficult to assess the relative contributions of individual sources, thus, a standard linear mixing model was applied to provide mathematical solutions for partitioning these waters. This required a seasonal estimation of the mean isotope composition for LSC water sources.

[Table 1 near here] [Figure 3 near here]

Water discharges of HR, DL, SSTs, WWTPs were also used to determine amount-weighted mean isotope values, while GW and precipitation mean isotope compositions were determined arithmetically (Table 2). HR, SSTs and GW presented similar ranges, while WWTPs, DL and rain had slightly more enriched values. Snow (only sampled during winter 2017) had mean isotope values of -11.2 ‰ for $\delta^{18}O$ and -81.9 ‰ for δD.

[Table 2 near here]

Source water partitioning

For most LSC water sources, results from IsoSource 1.3.1 program modelling generated broad ranges of possible contributions (Figure 4). Figure 4 illustrates mixing polygons for $\delta^{18}O$ and δD signatures of the six LSC water sources. The histograms associated with each source show the distribution of feasible contributions from each potential source to LSC. Values shown in the boxes cover 1–99 percentile ranges for these distributions. LSC isotope composition fell within the mixing polygons bounded by all sources, indicating plausible contributions from all sources during any given season (although only four sources were characterized for summer 2016).

In a first attempt to identify the dominant water sources to LSC, only source contribution ranges exceeding 50% were considered (Figure 4). With this constraint, water sources HR, GW and SSTs potentially accounted for more than 50% of LSC waters during three of the six-time intervals. The dominant contribution by HR occurred during fall 2016 (0-72%) and winter 2017 (5-63%). The high contribution of HR in summer 2016 (43-91%) may be overestimated as only four sources were characterized during that interval. GW exceeded the 50% contribution threshold during summer 2017 (36-67%), winter 2017 (0-54%) and spring 2017 (0-52%), whereas SSTs exceeded 50% in fall 2016 (0-58%), fall 2017 (0-52%) and spring 2017 (16-59%). Overall, at least one of HR, GW or SSTs was a dominant water source during any given season. DL and WWTP exceeded 50% only in spring 2017 (0-56% and 0-55%, respectively). Precipitation never exceeded the 50% threshold as expected given the small ratio of the lake surface area to the lake watershed area (1:55). [Figure 4 near here]

Using only the mean value from the possible range of solutions predicted by IsoSource 1.3.1 program for each water source and season, we estimated seasonal variability in water source contributions (Figure 5). To simplify to the four principal seasons (out of six in this two-year study), we averaged summers 2016 and 2017, and falls 2016 and 2017. The largest seasonal contribution of all sources was estimated for GW, which ranged from 17% to 53%, with the largest contribution in summer (53%). The second most important contributor was discharge from the HR, which ranged from 12% to 35%, with the highest contribution occurring in winter (35%) and fall (26%), followed by SSTs, which ranged from 11% to 33%, with the highest contribution in spring (33%). Other contributions were smaller, including those of DL (6-16%), WWTPs (5-16%), rain (6-15%) and snow (8%), with a maximum contribution in spring for DL (16%) and WWTPs (16%), and in fall for rain (15%). Based on these results, while acknowledging only two years of study, we can rank in decreasing order the annual water source contributions to LSC as follows: GW > HR > SSTs > WWTP > DL > Precipitation. [Figure 5 near here]

Contribution of pollutants to LSC

The distributions of nutrients and Fc in LSC and its sources are presented in Table 1 and Figure 6. The largest nutrient concentrations were observed in WWTP effluents followed by SST flows during all six seasons studied. The smallest nutrient concentrations were measured in the HR followed by DL. The highest Fc concentrations were measured in SST flows during all six seasons with the exception of spring 2017. The smallest Fc concentrations were observed in DL. Despite some sources being relatively large in nutrients (i.e. WWTPs) and Fc (i.e. SSTs), LSC waters have relatively small concentrations in nutrients and Fc (on average 0.40 mg N L^{-1}, 13.20 µgP L^{-1} and 13.30 CFU/100ml). [Figure 6 near here]

The calculated seasonal nutrient and fecal coliform mass fluxes are presented in Table 3 and Figure 7. HR had the highest nutrient mass flux during all seasons (2 - 9 467 kg N d^{-1} and 46 - 662 kg P d^{-1}) followed by SSTs (90 - 3 438 kg N d^{-1} and 11 - 76 kg P d^{-1}) with maximum values in fall 2016 (TP) or fall 2017 (TN). The WWTP-ST effluent nutrient mass flux, which is discharged in the HR a few kilometers upstream, was also important, particularly TN mass flux (120 - 992 kg N d^{-1} and 2.7 - 26 kg P d^{-1}). WWTP-LD effluent and DL had the smallest nutrient flux among LSC sources (WWTP-LD: 63 - 234 kg N d^{-1} and 1 - 13 kg P d^{-1}; DL: 35 - 71 kg N d^{-1} and 1 - 3 kg P d^{-1}). Fecal coliform mass flux was the smallest for HR during three seasons (summer 2016, spring 2017 and summer 2017; reaching up to 221 432 x10^9 CFU d^{-1}) and for SSTs during two seasons (falls 2016 and 2017, up to 12 286 x10^9 CFU d^{-1}). In general, WWTP effluents had lower fecal coliform mass fluxes than HR and SSTs (WWTP-ST: 5-802 x10^9 CFU d^{-1}; WWTP-LD: 0.7-78 x10^9 CFU d^{-1}), with maximum values reached in winter 2017 (WWTP-ST) or spring 2017 (WWTP-LD). DL had the smallest fecal coliform mass flux (4-51 x10^9 CFU d^{-1}) during all seasons. [Table 3 near here]

[Figure 7 near here]

Discussion

A six-season snapshot of LSC and its water source isotope composition provides insights into the hydrological regime of this lake. LSC and its water sources span a narrow range of isotope compositions and do not display any evaporative enrichment, supporting the known fluvial nature of this lake with a relatively short residence time. Some water source isotope compositions plotted above the GMWL/LMWL, reflecting the importance of precipitation from local moisture recycling (Clark and Fritz 1997; Froehlich et al. 2008; Wenling et al. 2017).

Using the mean values from the possible solution ranges and the threshold value set at 50%, we were able to estimate that HR is not the only dominant water source as previously evaluated (APEL 2014a and b). Water sources of LSC were dominated by SSTs and HR during the spring and fall high flow season, and GW and HR during the low flow periods of summer and winter (Figure 5). Moreover, the contribution of HR might be overestimated; that is, it could even be lower considering that some sources (e.g., GW) were not included in the estimate of summer 2016, and only four SSTs were sampled in winter 2017 due to logistical constrains (Section 2). Our results also indicate that WWTPs, DL and precipitation never became dominant contributors of water to LSC. Although their volumetric contributions were relatively stable throughout the year, their relative contributions were in all likelihood largest during either spring (WWTPs and DL) or fall (Rain; Figure 5). It is important to acknowledge that for most of the water sources, only broad ranges of possible contributions to LSC could be determined. There are two reasons for this outcome. First, there was a high degree of similarity between LSC and water source isotopic signatures, making the mixing polygons very narrow (Figure 4). This overlap is likely linked to the similar moisture source among waters, and to the absence of any effects caused by variations in topography or surface water temperature within the watershed. Second, the lake isotopic signature fell near the centre of the polygons (e.g., in falls 2016 and 2017), and, thus, was apparently composed of approximately equal contributions of these potential sources (e.g., more diffuse solutions) as explained in Phillips and Gregg (2003).

Based on our results, the high GW contribution to LSC water budget in summer must have played a significant role in buffering the evaporation and the lake water level drawdown, as lake water isotope composition demonstrated negligible evaporative enrichment. While Quebec City relies on the LSC during summer, the high-water demand season, the lake relies on groundwater supply to maintain its water level. Thus, additional investigations on this source are crucial to gain a comprehensive knowledge of groundwater quantity, quality and seasonal discharge enabling a more sustainable management of this drinking water reservoir in the coming years and in response to climate change.

Our results showed that SSTs are one of the three main contributors to the LSC water budget (Figure 5) despite of their small drainage areas (Figure 1) and overall discharge (Table 1). During spring, their contributions were twofold and relatively greater when compared to other sources (Figure 5). Meanwhile, during the dry summer and winter seasons, the contribution of SSTs decreased to less than about one-third of the HR (winter 2017) and one-sixth of the GW (summer 2017). These results suggest that SSTs are dominantly rain-fed, and that their discharge is in inherently governed by fluctuations in precipitation amount, making them more variable on a seasonal basis, unlike the steady and controlled discharge of WWTP effluents. It is noteworthy that almost 200 single housing units with septic installations are drained by these small streams, which makes them an important non-point source of pollutants to LSC, and comparable to WWTPs as both are domestic wastewater sources to the lake (see below). Therefore, the cumulative impact from changes in precipitation-driven discharge and densification of the septic installations through housing development will likely influence the water quality of these small streams and ultimately that of LSC (Moore et al. 2003). To gauge the amplitude of these drivers, long-term monitoring of individual small streams to gauge the amplitude of these drivers will be critically needed to assess, for example, the impacts of deforestation, groundwater abstraction by sewage contraction or housing development.

To reduce excessive nutrient mass loadings causing lake eutrophication, the assessment of both non-point and point sources at the watershed scale is required (Moore et al. 2003). Most of the phosphorus and nitrogen loading to LSC were transiting through the HR (combined sources of WWTP-ST and septic installations) and SSTs, indicating the greater nutrient contributions from areas with higher number of individual septic installations through diffuse runoff when compared to that from WWTP effluents (Figure 7). The relatively lower nutrient fluxes estimated for spring 2017 through SST flows (approximately 4% of the seasonal budget) may be linked to the under-sampling of the small tributaries (n=9) in April, which covered less than 43% of the SST watersheds. Most of SSTs were still either frozen or were difficult to access. Most importantly, the HR drains a large number of individual septic installations, approximately 2 700, septic installations in the watershed of this large river. Therefore, our estimate of the relative importance of individual septic installations draining domestic wastewaters through SSTs is conservative.

The HR watershed is heavily impacted by human activities such as deforestation, urbanization, erosion and recreational tourism (APEL 2014b). All of these activities have the potential to contribute excessively to nutrient and fecal coliform fluxes (Smol 2008; Wetzel 2011). Even though HR has nearly 10-fold mass fluxes of nutrients and fecal coliforms than those of the WWTP-ST effluent, due to its higher discharge, the high fecal coliform mass flux from WWTP-ST in winter 2017 (Figure 7) is not negligible. These exceptionally large fecal coliform values could be linked to the recreational activities occurring at the nearby upstream large ski resort over the winter period, which is connected to the WWTP-ST, and the lower ambient temperature of the aerated lagoons could be responsible for an insufficient treatment when compared to the performance during the other seasons (Stein and Hook 2010). The seasonally-driven increase in population within a watershed represents an important factor to consider when estimating the overall source-specific nutrient and pollutant contributions.

The DL (55 individual septic installations; Table 1) and WWTP-LD (connecting 600 inhabitants) showed the smallest nutrient and fecal coliform contributions to LSC. The small community size and low discharge, with the occasional LSC inflow to DL during high-flow seasons (waters flowing from LSC to DL instead of the normally opposite flow direction), are the reasons why these two water sources make a small contribution of pollutants (APEL 2014b), as compared to the WWTP-ST (5 000 inhabitants and close to 2 700 septic installations) and SSTs (ca. 200 septic installations). Moreover, the WWTP-LD effluent runs into a marsh located in the northern basin of LSC (Figure 1) that is most likely filtering excess nutrients and Fc (VeHRoeven and Meuleman 1999; Knight et al. 2000; APEL 2014b). However, a more specific investigation would be needed to evaluate the impact of the WWTP-LD during winter and fall when filtration by senescent marsh plants is inefficient.

The largest nitrogen, phosphorous and fecal coliform mass fluxes from SST runoff were detected during high-flow periods in the fall. The precipitation during fall of both studied years were above the 1981-2010 normal (notably in October; Figure 2) and are likely to have caused particularly high inputs of pollutants and nutrients over these specific years. This seasonal increase in stream flow has been identified in other studies (Nash and Gleick 1991; Rowe et al. 1994; Zhang et al. 2001; Barnett et al. 2005). On the other hand, the higher precipitation during spring was not associated with exceptionally high nutrient and fecal coliform mass fluxes (Figures 2 and 7). Spring flow depends on water equivalent of the snowpack and on the local warming temperature rates that directly influence lake ice-free conditions (Barnette et al. 2005; Ouranos 2015). Higher winter temperatures, increasing precipitation, are inducing an earlier spring freshet and higher peak flow in recent years (Ouranos 2015). Winter temperatures were warmer during our study period compared to the climate normal (January-February; Figure 2), possibly shifting the spring SST flows earlier than anticipated for the sampling campaign. Consequently, the peak spring flow might not have been entirely captured, underestimating its importance in the overall budget. Changes in the seasonal precipitation regime and temperature trends have important implications on stream flow dynamics (IPCC 2014), and therefore on changes in the SST runoff and their mass flux potentials. The urbanization of the SST watersheds, especially in the southern basin of LSC, may have amplified the effects of increased runoff and ensuing contributions of pollutants due to the associated rise in impermeable surfaces (e.g., asphalted). The SST watersheds with higher urbanisation (HH, N, J, E, H, F, A, G and PP), indeed, had larger concentrations of nutrients and Fc (Table 1).

Conclusion

Waters of Lake St. Charles (LSC) and its main water sources were sampled for two consecutive years covering six seasons (summer 2016 - fall 2017). Oxygen and hydrogen stable isotope signatures, and seasonal mass fluxes of nutrients and fecal coliforms, using stream flow and concentration measurements, were used to estimate the seasonal contributions of water to the lake. The contribution of the different water sources to LSC varied seasonally, the most important being GW, HR and SSTs followed by WWTP, DL and Precipitation (GW > HR > SSTs > WWTP > DL > Precipitation).

The major contributors of nutrients to LSC were HR, SSTs and WWTP-ST effluents. During fall, nutrient and fecal coliform mass fluxes from SSTs were highly significant and triggered by large amounts of precipitation and increased stream flow. Nearly 200 septic installations were included in the study, focusing on the area drained by the SSTs (i.e., 34 small stream tributaries). The septic installations in the HR watershed were not included in this study. These sources could potentially represent a greater input of nutrients and fecal coliform loadings to LSC, depending on the efficiency of natural degradation (i.e., of Fc) and sedimentation (P) along the hydrological pathways and influenced by the transition time. WWTP effluents (ST and LD) remain an important vector of pollutants when assessing lake water quality and sustainability (Vandenberg et al. 2005). However, their contributions of pollutants remained less important compared to those of individual septic installations within the lake watershed. The discharge of WWTP effluents is relatively constant and controlled, unlike the naturally fluctuating seasonal discharge of small stream flows.

Our results indicate that the management of this drinking water reservoir should focus on controlling the excessive nutrients and fecal coliform loadings from the widespread diffused runoff associated with individual septic installations within the LSC hillslopes and sub-watersheds (i.e., SST watersheds). Given the fact that the LSC is experiencing signs of eutrophication, HR and SST watersheds need to be regulated and carefully managed as they have the potential to increase the current trophic state of the lake. Management should deal with problems associated with residential area development. The construction of a sewage network to connect old and new residential and commercial buildings to the main Quebec City sewer system to minimize the effect of diffuse runoff should be carefully considered. Changes in amount of seasonal precipitation amount linked to climate change and the accelerated urbanization of the urban-rural fringe have the potential to accelerate eutrophication of this already fragile lake ecosystem. Mitigation strategies to eutrophication involve complex socioeconomic issues, but a reduction at the source is clearly the best alternative for sustainable lake management. This would unequivocally involve reducing the number of septic installations within the LSC watershed by connecting these to the Quebec City sewer networks and installing sewer systems in anticipation of future residential development. This is likely to be socioeconomically beneficial in the long-term.

Acknowledgments

Many thanks to employees of APEL for water sampling, and to those of the Water Quality Division of Quebec City for their assistance in the laboratory. A special thanks to James Telford who helped with the stable isotope analyses. This work would not have been possible without the shared financial support from a Mitacs Elevation Postdoctoral Fellowship and APEL.

References

APEL (1981). *Étude descriptive du bassin versant de Lac Saint-Charles, Association du Lac Saint-Charles*, 110 p.

APEL (2012). *Rapport d'étape sur le suivi des cyanobactéries et de l'état trophique du lac Saint- Charles en 2011, Association pour la protection de l'environnement du lac Saint-Charles et des Marais du Nord*, Québec, 143 p.

APEL (2014a). *Diagnose du lac Saint-Charles, Mémoire. Association pour la protection de l'environnement du lac Saint-Charles et des Marais du Nord*, 43 p.

APEL (2014b). D*iagnose du lac Saint-Charles, rapport final. Association pour la protection de l'environnement du lac Saint-Charles et des Marais du Nord*, 519 p.

APEL (2019) Diagnose du lac Saint-Charles – 2016. Association pour la protection de l'environnement du lac Saint-Charles et des Marais du Nord, Québec, 377 pages.

APHA, AWWA & WEF (2005). *Standard Methods for Examination of Water and Wastewater*, 21st ed. Washington D.C.

• Aravena, R. Evans, M.L. & Cherry, J.A. (1992). *Stable isotopes of oxygen and nitrogen in source idetification of nitrate from septic systems.* Ground water, 31(2): 180–186. doi: 10.1111/j.1745-6584.1993.tb01809.x.

Arnade, L.J. (1999). *Seasonal correlation of well contamination and septic tank distance.* Ground water, 37(6): 920–923. doi:10.1111/j.1745-6584.1999.tb01191.x.

Barnett, T.P., Adam, J.C., & Lettenmaier, D.P. (2005). *Potential impacts of a warming climate on water availability in snow-dominated regions.* Nature Reviews, 438(7066): 303–309. doi:10.1038/nature04141.

Berman, E.S.F., Levin, N.E., Landais, A., Li, S. & Owano, T. (2013). *Measurement of* $\delta^{18}O$*,* $\delta^{17}O$*, and* ^{17}O*-excess in Water by Off-Axis Integrated Cavity Output Spectroscopy and Isotope Ratio Mass Spectrometry*. Analytical Chemistry, 85:10392-10398. doi:10.1021/ac402366t.

Clark, I. and Fritz, P. (1997). *Environmental Isotopes in Hydrogeology*. CRC Press/Lewis Publishers, Boca Raton, 328 pp.

Coplen, T.B. (1996). *New guidelines for reporting stable hydrogen, carbon, and oxygen isotope – ratio data*. Geochim. Cosmochim. Acta*.,* 60: 3359–3360. doi:10.1016/0016-7037(96)00263-3.

Craig, H. (1961). *Isotopic variations in meteoric waters*. Science 133, 1702–1703.

Dansgaard, W. (1964). *Stable isotopes in precipitation.* Tellus XVI. doi: 10.3402/tellusa.v16i4.8993. doi:10.1111/j.2153-3490.1964.tb00181.x.

Environemnt Canada (2017). National Climate Data and Information Archive. http://climat.meteo.gc.ca/historical_data/search_historic_data_f.html.

Froehlich, K., Kralik, M., Papesch, W., Rank, D., Scheifinger, H., & Stichler, W. (2008). *Deuterium excess in precipitation of Alpine regions - Moisture recycling.* Isotopes in Environmental and Health Studies, 44(1): 61–70. doi:10.1080/10256010801887208

IPCC (2014). Climate Change 2014: Synthesis Report. *Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]. IPCC, Geneva, Switzerland, 151 pp.

Knight, R.L., Payne Jr., V.W.E., Borer, R.E., Clarke Jr., R.A. & Pries, J.H. (1999). *Constructed wetlands for livestock wastewater management.* Ecological Engineering, 15(1-2): 41-55. doi: 10.1016/S0925-8574(99)00034-8.

APEL (2019). *Étude sédimentaire du lac Saint-Charles (Québec).* In *Diagnose du lac Saint-Charles – 2016. Association pour la protection de l'environnement du lac Saint-Charles et des Marais du Nord*, Québec, 377 pages.

Légaré, S. (1997). *L'eutrophisation des lacs : le cas du lac Saint-Charles.* Naturaliste Can., 121: 65-68.

Légaré, S. (1998). *Étude limnologique du lac Saint-Charles.* Rapport GREPAUL 98-238, Université Laval, Sainte-Foy (Québec). 106 p.

Ministère du Développement durable, de l'Environnement et des Parcs (MDDEP; 2008). *Guide technique, Captage d'eau souterraine pour des résidences isolées. Service de l'aménagement et des eaux souterraines de la Direction des politiques de l'eau.*

Moore, J.W., Schindler, D.E., Scheuerell, M.D., Smith, D., & Frodge, J. (2003). *Lake Eutrophication at the Urban Fringe, Seattle Region, USA*. AMBIO: A Journal of the Human Environment, 32(1): 13–18. doi:10.1579/0044-7447-32.1.13.

Narancic, B., Wolfe, B.B., Pienitz, R., Meyer, H., & Lamhonwah, D. (2017). *Landscape-gradient assessment of thermokarst lake hydrology using water isotope tracers.* Journal of Hydrology, 545: 327–338. doi:10.1016/j.jhydrol.2016.11.028.

Nash, L. & Gleick, P.H. (1991). *Sensitivity of streamflow in the Colorado basin to climatic changes.* Journal Of Hydrology, 125: 221–241. doi:10.1016/0022-1694(91)90030-L.

Nollet, L.M.L. & De Gelder, L.S.P. (2007) *Handbook of Water Analysis. 2nd Edition*, CRC Press, Boca Raton. 995 p.

Phillips, D.L., & Gregg, J.W. (2003). *Source partitioning using stable isotopes : coping with too many sources,* Oecologia, 136: 261–269. doi:10.1007/s00442-003-1218-3.

Ptacek, C.J. (1998). *Geochemistry of a septic-system plume in a coastal barrier bar, Point Pelee, Ontario, Canada*. Journal of Contaminant Hydrology, 33(3–4): 293–312. doi:10.1016/S0169-7722(98)00076-X.

Ritchot, G., Mercier, G. & Mascolo, S. (1994). *L'étalement urbain comme phénomène géographique : l'exemple de Québec*. Cahiers de géographie du Québec, 38 (105), 261–300. https://doi.org/10.7202/022451ar.

Robertson, W.D., Shiff, S.L. & Ptacek, C.J. (1998). *Review of phosphate mobility and persistence in 10 septic system plumes.* Ground water, 36(6): 1000–1010. doi :10.1111/j.1745-6584.1998.tb02107.x.

Rozanski, K., Araguas-Araguas, L. & Gonfiantini, R. (1993). *Isotope patterns in modern global precipitation.* Science 80: *258*, 981–985. doi:10.1029/GM078p0001.

Rowe, C.M., Kuivinen, K.C., & Flores-Mendoza, F. (1994). *Sensitivity of streamflow to climate change: a case study for Nebraska.* Great Plains Research, 4(1): 27–49

Ouranos (2015). Vers l'adaptation. *Synthèse des connaissances sur les changements climatiques au Québec. Partie 1 : Évolution climatique au Québec. Édition 2015. Montréal, Québec: Ouranos*, 114 p.

Smol, J.P. (2008). *Pollution of Lakes and Rivers: A Paleoenvironmental Perspective. 2nd edition*. Wiley-Blackwell Publishing, Oxford, 383 pp,

Statistics Canada, Environment Accounts and Statistics Division (2011). *Survey of drinking water plants and households and the environment survey.* https://www150.statcan.gc.ca/n1/pub/16-403-x/16-403-x2013001-eng.htm. (accessed December 2018).

Stein, O.R. & Hook, P.B. (2010). *Temperature, plant, and oxygen: How does season affect constructed wetland performance?* Journal of Environmental Science and Health, 40(6-7): 1331-1342. doi:10.1081/ESE-200055840.

Tondu, J-M.E., Turner, K.W., Wolfe, B.B., Hall, R.I., Edwards, T.W.D. & McDonald, I. (2013). *Using water isotope tracers to develop the hydrological component of a long-term aquatic ecosystem monitoring program for a northern lake-rich landscape.* Arctic, Antarctic, and Alpine Research, 45(4): 594–614. doi : 10.1657/1938-4246-45.4.594.

Tremblay, R., Légaré, S., Pienitz, R., Vincent, W.F., & Hall, R.I. (2002). *Étude* *paléolimnologique de l'histoire trophique du lac Saint-Charles, réservoir d'eau potable de la communauté urbaine de Québec.* Revue des sciences de l'eau, 4(2001): 489–510. doi:10.7202/705429ar.

Tremblay, R., & Pienitz, R. (2015). *Caractéristiques limnologiques de 56 lacs du Québec méridional en lien avec l'état trophique.* Revue des sciences de l'eau, 28(2): 139. doi:10.7202/1032295ar.

Turner, K.W., Wolfe, B.B., & Edwards, T.W.D. (2010). *Characterizing the role of hydrological processes on lake water balances in the Old Crow Flats, Yukon Territory, Canada, using water isotope tracers,* Journal of Hydrology, 386: 103–117. doi:10.1016/j.jhydrol.2010.03.012

Vandenberg, J.A., Ryan, M.C., Nuell, D.D. & Chu, A. (2005). *Field evaluation of mixing length and attenuation of nutrients and fecal coliform in awastewater effluent plume.* Environmental Monitoring and Assessment, 107: 45–57. doi:10.1007/s10661-005-2020-y.

VeHRoeven, J.T.A. & Meuleman, A.F.M. (1998). *Wetlands for wastewater treatment: Opportunities and limitations.* Ecological Engineering, 12: 5-12. doi:10.1016/S0925-8574(98)00050-0.

Wenling A., Shugui, H., Qiong, Z., Wangbin, Z., Shuangye, W., Hao, X., Hongxi, P., Yetang, W. & Yaping, L. (2017). *Enhanced Recent Local Moisture Recycling on the Northwestern Tibetan Plateau Deduced From Ice Core Deuterium Excess Records.* Journal of Geophysical Research: Atmospheres, 122(23): 541–556. doi:10.1002/2017JD027235.

Wetzel, R.G. (2001). *Limnology: Lake and river ecosystems*. San Diego: Academic Press, 1006p.

Wernick, B.G., Cook, K.E., & Schreier, H. (1998). *Land-use and streamwater nitrate-N dynamics in an urban-rural fringe watershed.* Journal of the American watrer resources association, 34(3): 639–650. doi: 10.1111/j.1752-1688.1998.tb00961.x.

Wilhelm, S.R., Schiff, S.L. & Cherry, J.A. (1996). *Biogeochemical evolution of domestic waste water in septic systems: 1. Conceptual model.* Ground water, 32(6): 905–916. doi:10.1111/j.1745-6584.1994.tb00930.x.

Zhang, X., Harvey, K.D., Hogg, W.D., & Yuzyk, T.R. (2001). *Trends in Canadian streamflow*. Water Resources Reserche, 37(4): 987–998. doi:10.1029/2000WR900357.

Table 1. Range of nutrient and fecal coliform concentrations, estimated discharges, isotopic signatures, percentages of the catchment with urbanization, and number of septic installations (SI) for wastewater treatment plant (WWTP), Hurons River (HR), Delage Lake (DL), small stream tributaries (SST) and Lake St. Charles (LSC). The dotted line represents the limit between northern (upper) and southern (lower) SSTs with respect to the lake basins. N represents the number of times the sources were sampled over the study period.

Sample		TN (mg/l)			TP (µg P/l)			Fc (CFU/100ml)				Discharge (m^3/s)		δ18O ‰ (± 0.2)			δD ‰ (± 0.8)			Area(ha) /Urb(%)	SI
	N	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	N	Mean	N	Min	Max	Mean	Min	Max	Mean		
WWTP																					
ST	20	3.00	36.40	18.24	119.00	683.00	442.00	0.00	320.00	57.90	21	0.01	17	-11.48	-9.41	-10.26	-80.15	-66.32	-71.57	-	-
LD	24	2.14	13.50	7.21	112.00	1230.00	363.00	2.00	500.00	110.04	25	0.01	17	-12.14	-8.50	-10.07	-83.38	-63.91	-71.10	-	-
HR	24	0.26	0.70	0.46	6.10	57.70	14.83	6.00	2000.00	169.09	23	7.45	17	-12.23	-10.08	-11.13	-87.32	-63.73	-74.79		50***
DL	24	0.16	0.69	0.28	5.10	70.60	13.70	0.00	180.00	97.57	16	0.17	13	-12.23	-9.12	-9.81	-85.13	-63.62	-68.83	76/2	55
SST																					
DD	16	0.17	12.90	1.13	6.20	76.70	19.26	0.00	3500.00	286.53	14	0.05	8	-12.52	-8.90	-10.54	-87.68	-57.32	-70.92	19/2	1(1)
CC	15	0.13	0.54	0.24	7.20	144.0	30.43	0.00	2300.00	183.07	8	0.01	9	-13.41	-8.99	-10.80	-89.26	-57.96	-71.74	8/5	0(0)
BB	14	0.10	0.62	0.18	5.70	107.00	24.60	0.00	6000.00	476.08	10	0.01	9	-13.13	-8.91	-11.00	-90.31	-58.31	-73.93	263/1	0(0)
AA	16	0.09	0.37	0.21	4.40	41.30	11.23	0.00	440.00	56.60	13	0.08	8	-12.81	-8.99	-10.18	-86.58	-64.51	-71.23	16/36	8(8)
FF	9	0.60	1.86	1.34	10.10	120.00	45.78	0.00	210.00	54.33	5	0.00		-12.51	-9.67	-10.95	-86.31	-63.28	-74.81	62/3	24(28)
W	17	0.12	0.55	0.24	2.10	39.40	8.78	0.00	1000.00	144.38	14	0.03	11	-13.29	-9.38	-11.11	-89.54	-62.20	-74.24	31/7	2(2)
Z	17	0.15	0.37	0.19	1.00	82.50	12.45	0.00	1300.00	93.63	15	0.01	10	-13.22	-8.96	-11.07	-89.95	-59.26	-74.57	4/30	1(1)
GG	6	0.16	0.55	0.39	16.40	57.60	33.28	91.00	1500.00	378.50	6	0.00	3	-12.17	-9.49	-10.68	-87.71	-60.67	-73.70	13/7	6(6)
U	15	0.48	9.29	2.43	18.20	245.00	74.31	0.00	6000.00	448.33	14	0.00	9	-13.66	-9.41	-10.97	-93.78	-60.84	-73.47	8/11	4(4)
T	13	0.15	3.64	0.62	5.30	145.00	21.04	0.00	2400.00	204.31	12	0.00	9	-13.85	-7.93	-10.19	-94.34	-50.39	-67.68	11.07	5(5)
HH	7	1.56	4.38	3.01	8.10	22.20	15.31	0.00	5500.00	846.43	6	0.00	6	-12.47	-9.47	-11.33	-87.39	-62.34	-77.63	4/68	11(11)
S	14	0.62	8.08	2.65	3.20	93.10	15.74	0.00	3500.00	292.64	14	0.00	15	-13.75	-8.04	-10.79	-94.09	-50.36	-72.04	6/9	1(1)
*R	5	0.22	0.60	0.40	12.00	88.90	29.44	0.00	400.00	115.80		0.00	-	-	-	-	-	-	-	3/9	2(2)
Q	15	0.16	0.68	0.37	2.50	110.00	14.85	0.00	170.00	40.64	15	0.00	9	-13.81	-9.95	-11.33	-93.51	-65.50	-76.17	3/5	1(1)
P	15	0.11	0.69	0.23	2.70	37.80	7.12	0.00	110.00	20.73	15	0.00	9	-13.47	-9.31	-11.08	-90.62	-62.95	-73.86	15/10	7(7)
IIB**	3	0.23	0.68	0.41	24.50	46.70	35.20	6.00	360.00	146.33	3	0.00	5	-12.57	-9.34	-10.48	-88.91	-60.64	-72.16	122/34	41(77)
IID**	6	0.33	1.86	0.94	14.70	36.70	28.12	5.00	280.00	87.67	-	-	7	-13.06	-7.17	-9.74	-90.40	-45.60	-67.61		
CPLSC18	12	0.38	0.97	0.63	27.40	244.00	89.70	1.00	1000.00	153.25	8	0.00	7	-12.79	-9.43	-10.51	-88.36	-63.27	-71.54	0/1	1(1)
N**	3	0.2	0.64	0.4	34.50	81.00	63.00	30.00	9400.00	3154.00	1	0.0	5	-13.67	-8.43	-10.34	-92.13	-57.76	-70.10	2/51	3(3)
M	15	0.16	0.74	0.44	13.00	1710.00	144.27	18.00	16000.00	1952.07	15	0.01	9	-13.43	-10.59	-11.47	-90.13	-71.72	-77.14	38/10	20(20)
KK	11	0.42	1.32	0.77	18.10	52.10	32.43	0.00	5000.00	869.45	9	0.01	8	-12.43	-8.50	-9.78	-89.91	-52.48	-65.22	39/40	20(22)
L	15	0.42	0.76	0.56	5.80	57.50	17.02	0.00	1300.00	162.07	14	0.01	9	-13.58	-9.94	-11.76	-91.29	-68.04	-92.72	59/16	27(70)
K	18	0.16	0.52	0.26	8.50	154.60	36.524	14.00	3140.00	393.18	16	0.15	7	-12.40	-9.17	-10.69	-83.42	-61.39	-72.34	359/3	16(55)
J	8	0.60	3.19	1.38	21.75	96.20	42.81	8.50	900.00	306.60	-	-	4	-14.00	-6.95	-10.62	-100.67	-42.38	-72.63	1/92	0(12)
LL**	6	0.40	0.80	0.55	20.70	42.10	31.00	22.00	2400.00	764.00	-	-	7	-12.04	-9.33	-10.26	-83.62	-60.78	-69.35	44/38	19(67)
NN**	4	0.62	1.11	0.86	37.40	78.90	49.15	46.00	1500.00	484.50	-	-	5	-11.45	-9.09	-9.70	-81.10	-60.52	-66.41	4/28	1(10)
E	19	0.23	0.66	0.45	20.55	177.00	75.748	4.50	3650.00	772.96	-	-	8	-10.08	-7.13	-8.63	-69.64	-49.34	-58.65	7/61	0(29)
OO	26	0.34	1.38	0.81	16.80	79.05	36.78	57.50	6050.00	1226.67	21	0.05	11	-11.93	-7.85	-10.07	-83.15	-55.03	-69.43	249/31	15(55)

H	17	0.53	5.54	3.03	7.75	142.25	36.03	0.00	2900.00	371.22	14	0.00	9	-12.83	-8.54	-10.91	-87.39	-55.05	-73.55	14/45	2(71)
C	18	0.04	4.84	1.32	13.90	369.00	60.22	11.00	6000.00	833.00	13	0.00	9	-13.97	-7.87	-10.5	-92.72	-49.86	-71.2	401/17	7(171)
A**	3	0.19	0.47	0.37	18.40	81.60	48.40	240.00	2200.00	1220.00	1	0.00	4	-12.87	-8.53	-10.16	-86.13	-57.08	-67.53	0/48	10(0)
F	3	0.16	12.50	4.49	76.90	499.00	218.70	24.00	260.00	142.00	2	0.01	1	-	-	-12.89	-	-	-88.94	4/92	0(35)
G	3	0.16	0.40	0.27	29.70	165.00	81.70	100.00	1500.00	800.00	2	0.00	1	-	-	-13.10	-	-	-90.62	3/93	0(31)
PP	9	0.46	8.55	2.36	0.00	252.00	56.74	0.00	3600.00	812.13	-	-	7	-11.79	-3.77	-9.75	-83.79	-22.61	-66.89	8/63	0(37)
Lake																					
C05 (P)	10	0.18	0.34	0.26	8.90	11.90	10.19	0.00	16.00	4.91	-	-	23	-12.86	-9.61	-10.66	-87.12	-63.00	-72.30	-	-
C03 (P)	20	0.24	0.41	0.33	7.80	17.60	11.08	0.00	31.00	7.91	-	-	23	-12.36	-9.64	-10.75	-85.96	-63.15	-72.18	-	-
C04 (P)	7	0.28	0.35	0.31	8.70	10.40	9.40	-	-	-	-	-	3	-11.51	-12.40	-11.51	-86.74	-78.65	-78.65	-	-
SCA (L)	17	0.27	5.88	0.66	6.30	119.00	22.31	0.00	180.00	28.17	-	-	21	-12.71	-9.44	-10.96	-89.64	-64.53	-74.22	-	-
SCE (L)	7	0.28	0.39	0.33	10.10	15.60	13.27	0.00	48.00	12.33	-	-	21	-12.53	-9.25	-10.79	-86.61	-62.00	-73.03	-	-

* Sampled only in 2016

** Sampled only in 2017

***This number presents houses with septic tanks situated between the WWTP-ST and the lake (ca. 3 km).

(P) - pelagic zone

(L) - littoral zone

Table 2. Amount-weighted water isotope compositions using the discharges of six lake water sources: Hurons River (HR), small stream tributaries (SST), groundwater (GW), wastewater treatment plant (WWTP), Delage Lake (DL) and precipitation (rain + snow).

Sample	Summer 2016		Fall 2016		Winter 2017		Spring 2017		Summer 2017		Fall 2017	
	$\delta^{18}O$	δD	$\delta^{18}O$	δD	$\delta^{18}O$	δD	$\delta^{18}O$	δD	$\delta^{18}O$	δD	$\delta^{18}O$	δD
WWTP	-10.14	-70.7	-9.42	-66.54	-11.06	-74.67	-11.51	-80.08	-10.36	-79.12	-9.84	-68.95
HR	-11.1	-74.82	-10.24	-68.18	-12.07	-79.51	-12.18	-86.35	-10.84	-73.01	-10.23	-64.14
DL			-9.25	-63.8	-9.83	-68.01	-11.59	-80.68	-9.45	-68.17	-9.13	-66.87
SSTs	-10.12	-68.39	-9.52	-64.72	-11.07	-75.32	-12.77	-86.29	-10.24	-70.08	-9.27	-62.12
GW*			-12.08	-81.3	-11.86	-81.33	-11.46	-78.58	-12.08	-81.51	-11.84	-80.67
Rain	-8.87	-58.92	-8.93	-56.52			-9.08	-59.32	-9.17	-62.99	-9.17	-62.49
Snow					-11.22	-81.89						

* Not weighted

Table 3. Seasonal mass flux of TN (total nitrogen), TP (total phosphorous) and Fc (fecal coliform) based on measured discharges and concentrations in wastewater treatment plant effluent of Stoneham-and-Tewkesbury (WWTP-ST), Hurons River (HR), wastewater treatment plant effluent of City of Lac Delage (WWTP-LD), Delage Lake (DL) and small stream tributary runoffs (SSTs).

Sample	Summer 2016			Fall 2016			Winter 2017			Spring 2017			Summer 2017			Fall 2017		
	TN (kg/d)	TP (kg/d)	Fc (CFU/d)	TN (kg/d)	TP (kg/d)	Fc (CFU/d)	TN (kg/d)	TP (kg/d)	Fc (CFU/d)	TN (kg/d)	TP (kg/d)	Fc (CFU/d)	TN (kg/d)	TP (kg/d)	Fc (CFU/d)	TN (kg/d)	TP (kg/d)	Fc (CFU/d)
WWTP-ST	342.3	10.02	$14x10^9$	137.95	13.91	$23x10^9$	992.47	19.03	$802x10^9$	947.01	26.45	$100x10^9$	604.19	7.51	$5x10^9$	120.47	2.70	$7x10^9$
HR	2310.31	93.74	$9765x10^9$	1825.3	46.36	$1962x10^9$				9464.09	303.30	$6524x10^9$	5981.43	661.59	$221432x10^9$	4265.03	319.96	$343x10^9$
WWTP-LD	66.16	3.13	$16x10^9$	63.4	1.19	$4x10^9$	122.42	5.27	$2x10^9$	233.98	13.38	$78x10^9$	66.58	3.58	$17x10^9$	74.81	9.68	$0.7x10^9$
DL	58.79	2.45	$18x10^9$	41.78	1.14	$51x10^9$				70.59	2.97	$4x10^9$	41.4	1.87	$17x10^9$	34.93	0.94	$10x10^9$
SSTs	90.47	10.78	$510x10^9$	240.63	76.37	$12286x10^9$				352.94	11.40	$182x10^9$	133.63	10.22	$1 579x10^9$	3438.29	28.5	$915x10^9$

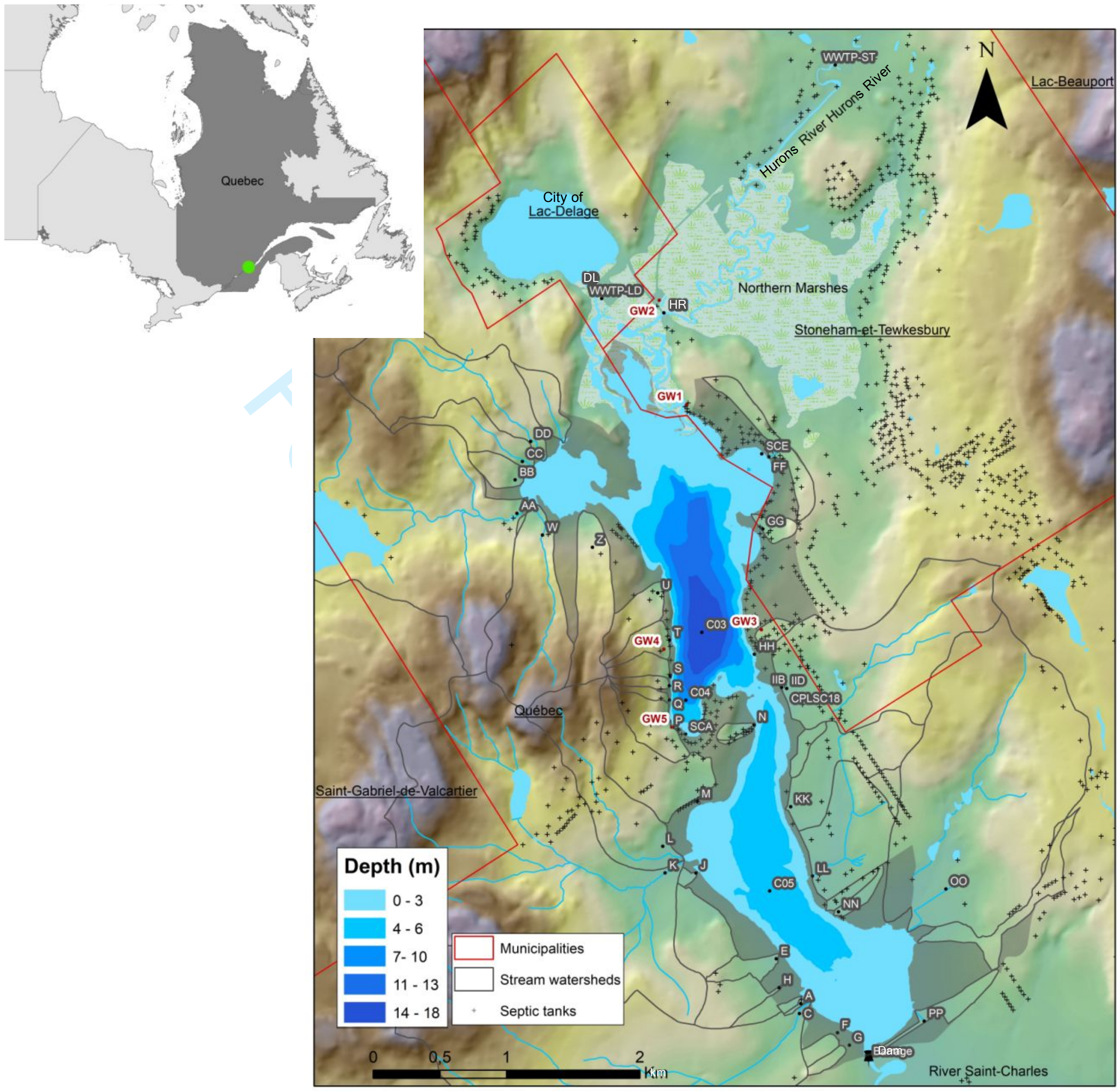

Figure 1. The Lake St. Charles along with location of municipal boundaries (red line), 38 surface water and 5 ground water (GW) sampling stations, bathymetry of Lake St. Charles and septic installation locations. The shaded area represents diffuse (i.e. hillslope) runoff to Lake St. Charles. Small stream catchments are outlined for each stream tributary (grey line). The sampling points WWTP-LD and WWTP-ST represent the wastewater treatment plan effluents of City of Lac Delage and Stoneham-and-Tewkesbury, respectively.

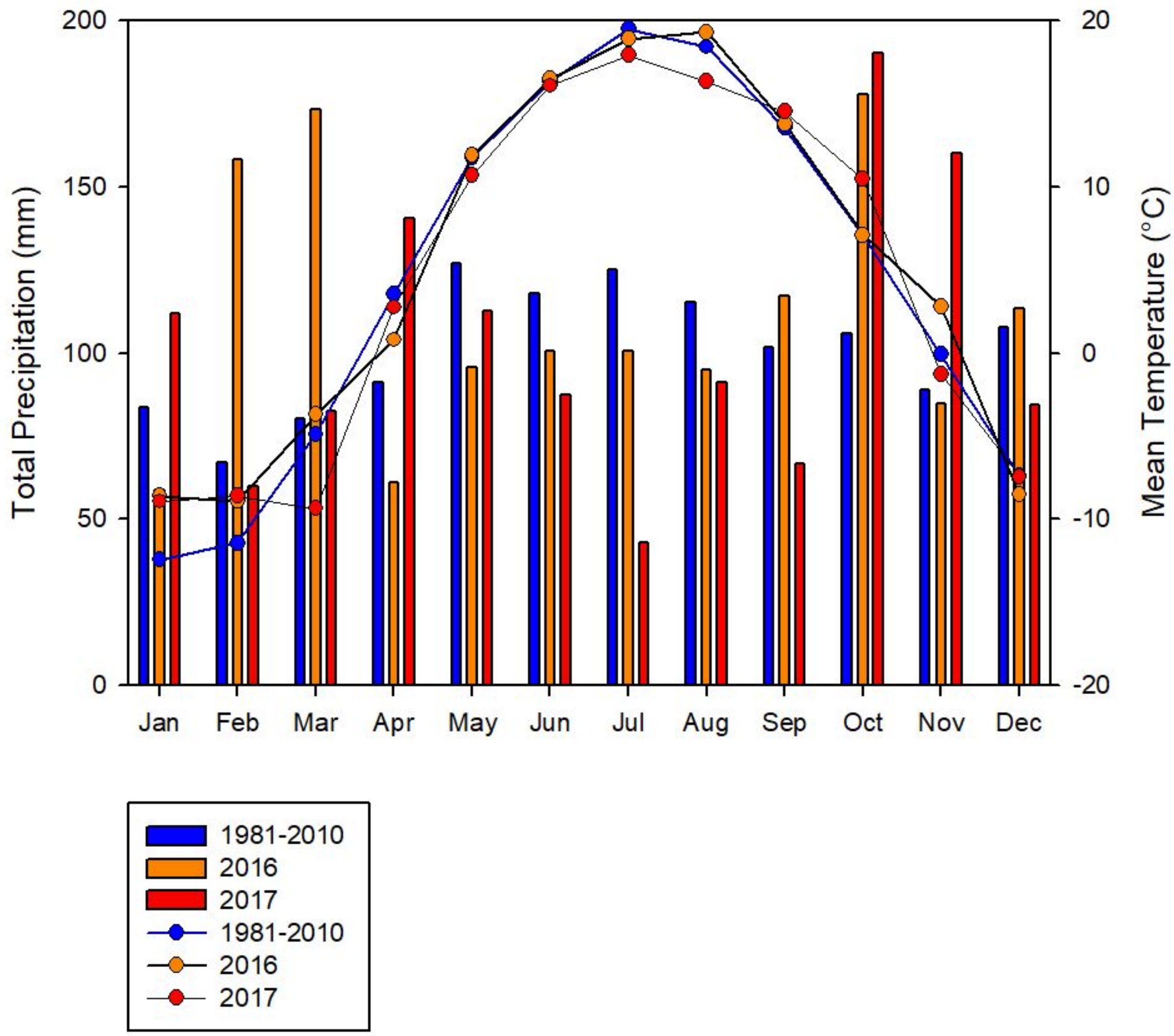

Figure 2. Mean monthly air temperature (°C; lines) and total monthly precipitation (mm; vertical bars) recorded at the Jean Lesage international airport weather station (Station ID: 701S001) for year 2016 and 2017 compared to the 1981–2010 period (Environment Canada, 2017).

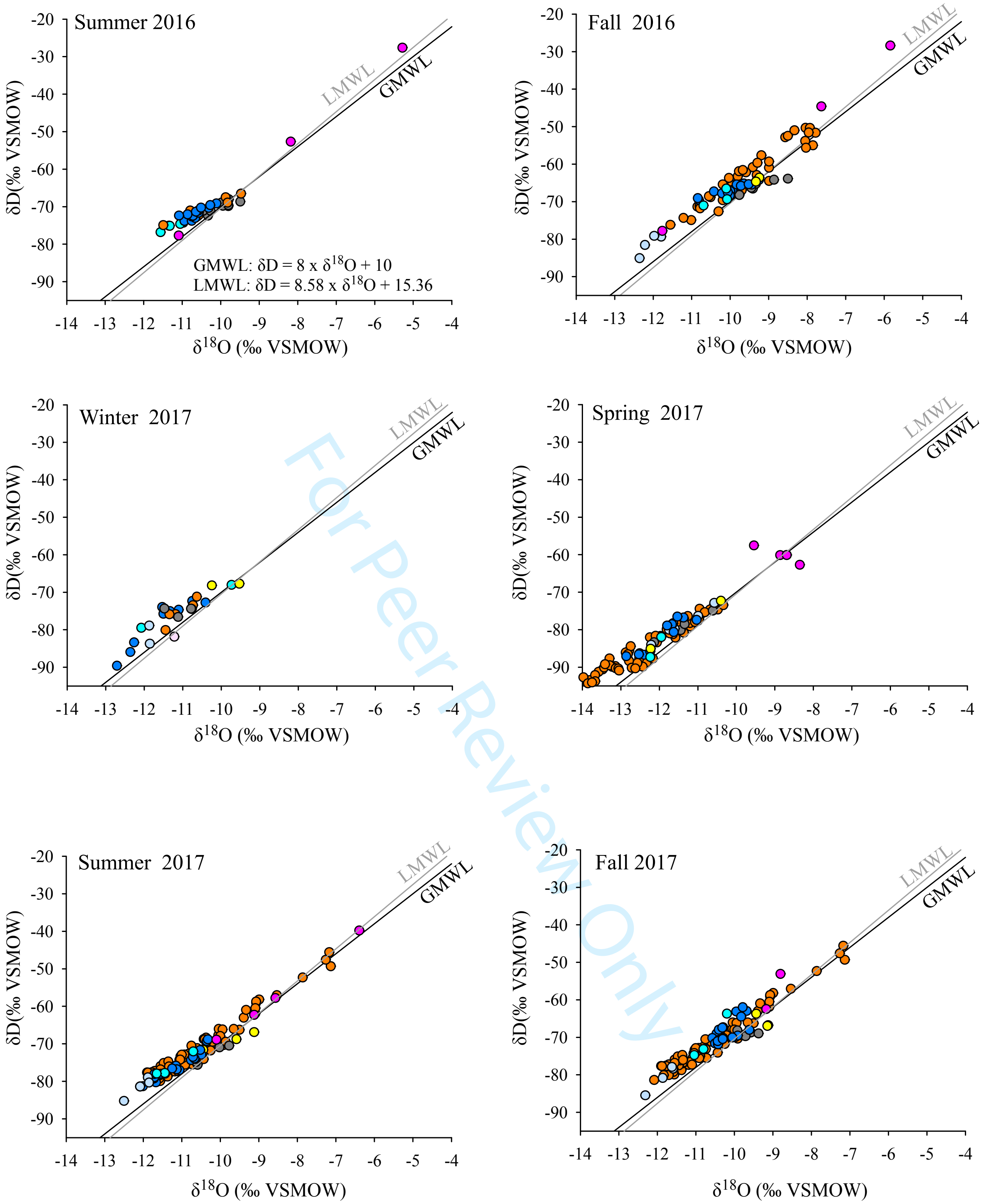

Figure 3. Isotope compositions of Lake St. Charles (LSC; dark blue) and of inflows: Hurons River (HR, light turquoise), small stream tributaries (SST, orange), wastewater treatment plant (WWTP, grey) effluents, groundwater (GW, light blue), Delage Lake (DL, yellow), and precipitation (dark pink for rain and light pink for snow) relative to the Local and Global Meteoric Water Line (LMWL and GMWL). The seasons were defined by astronomical calendar following the equinoxes and solstices.

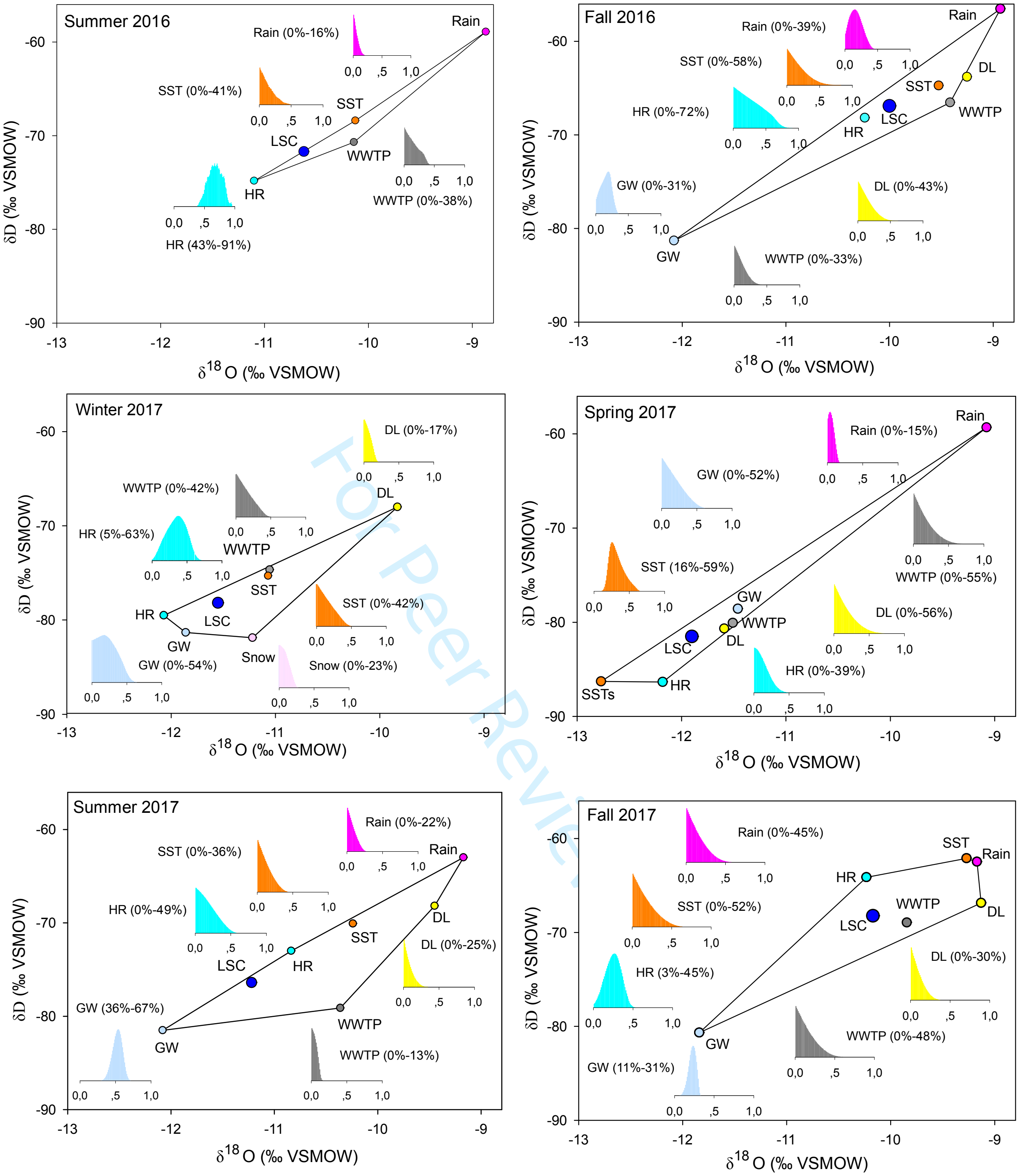

Figure 4. Mixing polygons for average values of □^{18}O and □D of six sources: Hurons River (HR turquoise), small stream tributaries (SST orange), wastewater treatment plants (WWTP grey), Delage Lake (DL yellow), groundwater (GW light blue) and precipitation (rain dark pink and snow light pink) for Lake St. Charles (LSC dark blue). The histograms show the distribution of possible contributions from each source to the lake. Values shown in the boxes depict the 1-99 percentiles for these contributions. For the summer 2016, only four sources could be characterized.

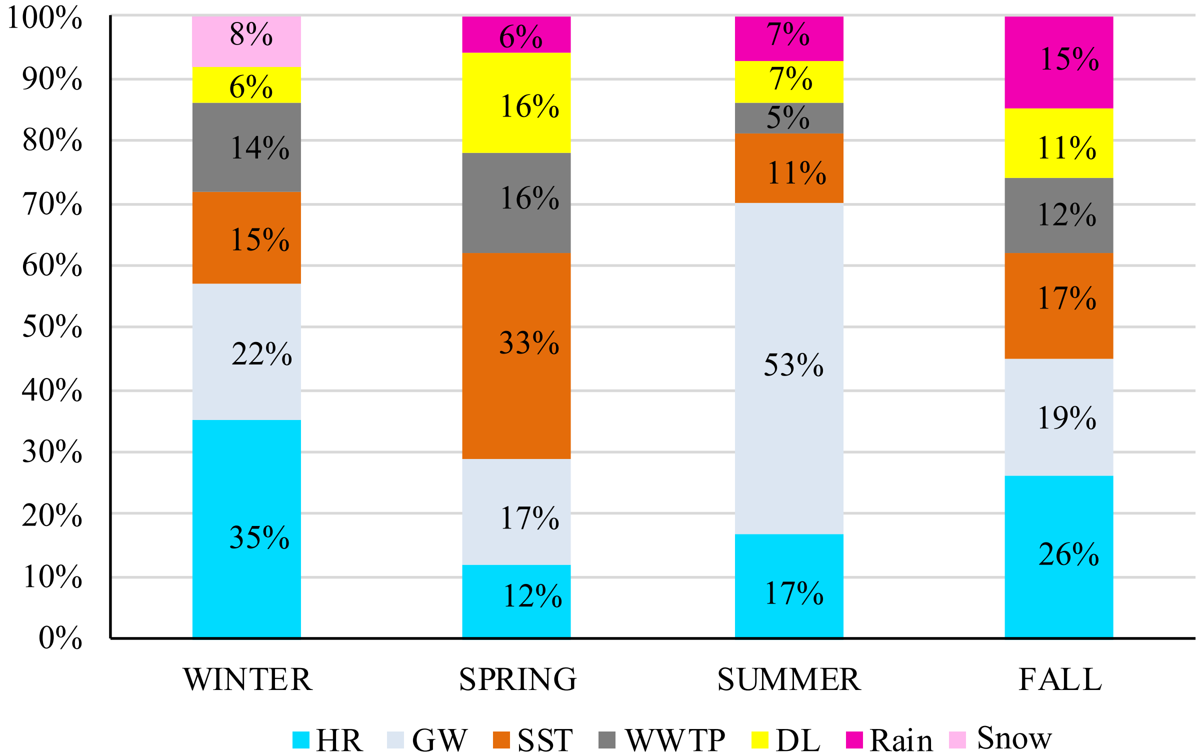

Figure 5. The mean seasonal contribution predicted in IsoSource for each water source of water: HR (Hurons River), GW (groundwater), SSTs (small stream tributaries), WWTP (wastewater treatment plants), DL (Delage Lake), rain and snow.

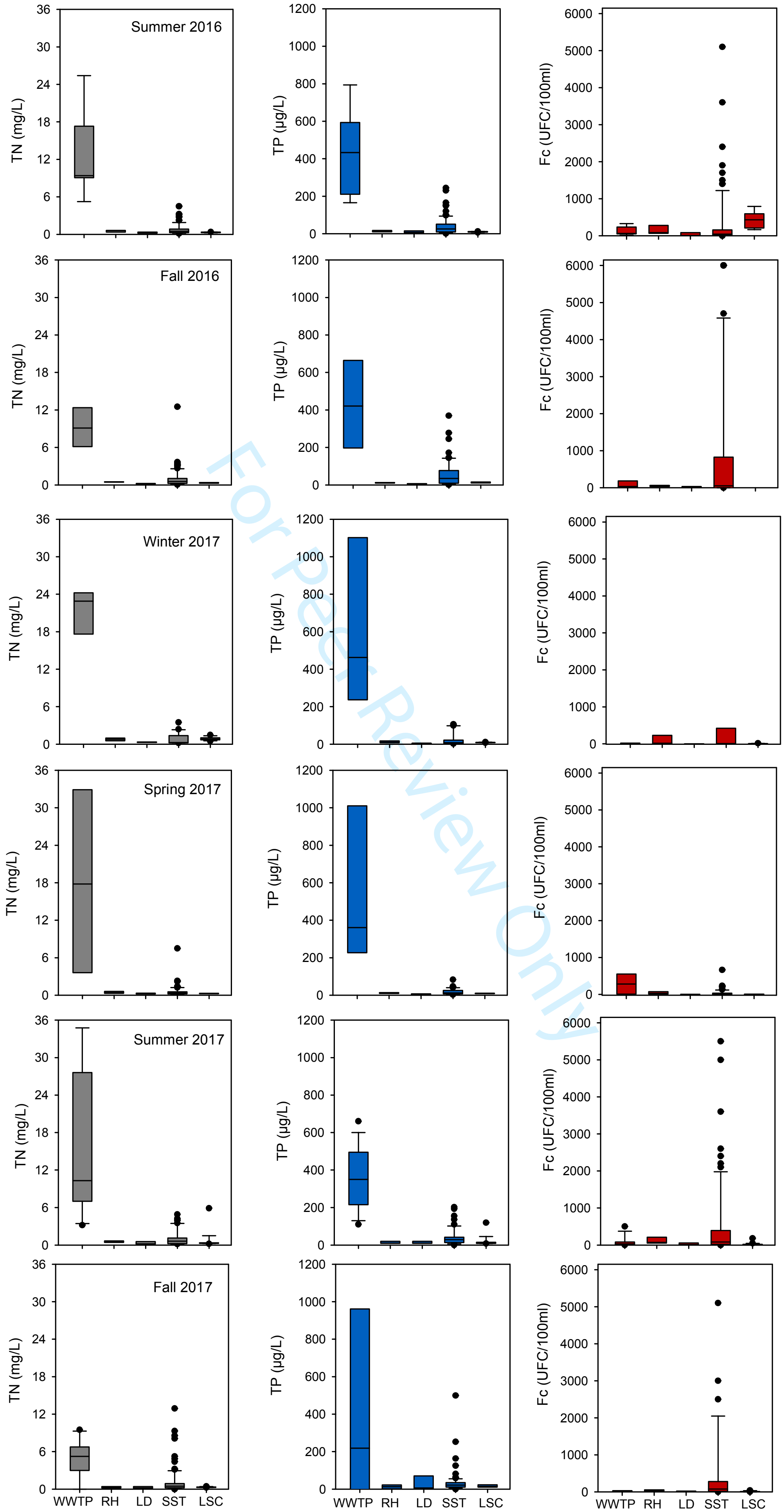
Summer 2016
Fall 2016
Winter 2017
Spring 2017
Summer 2017
Fall 2017
TN (mg/L)
TP (µg/L)
Fc (UFC/100ml)
WWTP
RH
LD
SST
LSC

Figure 6. Seasonal concentrations of total nitrogen (TN dark grey), total phosphorous (TP blue) and fecal coliforms (Fc red) from four sources of water (WWTP = wastewater treatment plants, HR = Hurons River, DL = Delage Lake, SSTs = small stream tributaries) and Lake St. Charles (LSC). Mean concentration values from both WWTP effluents are presented (WWTP-ST = Stoneham-and-Tewkesbury, WWTP-LD = City of Lac Delage). The nutrient and Fc concentrations of ground water and precipitation were not measured, and the Fc concentrations of LSC were not measured in 2016.

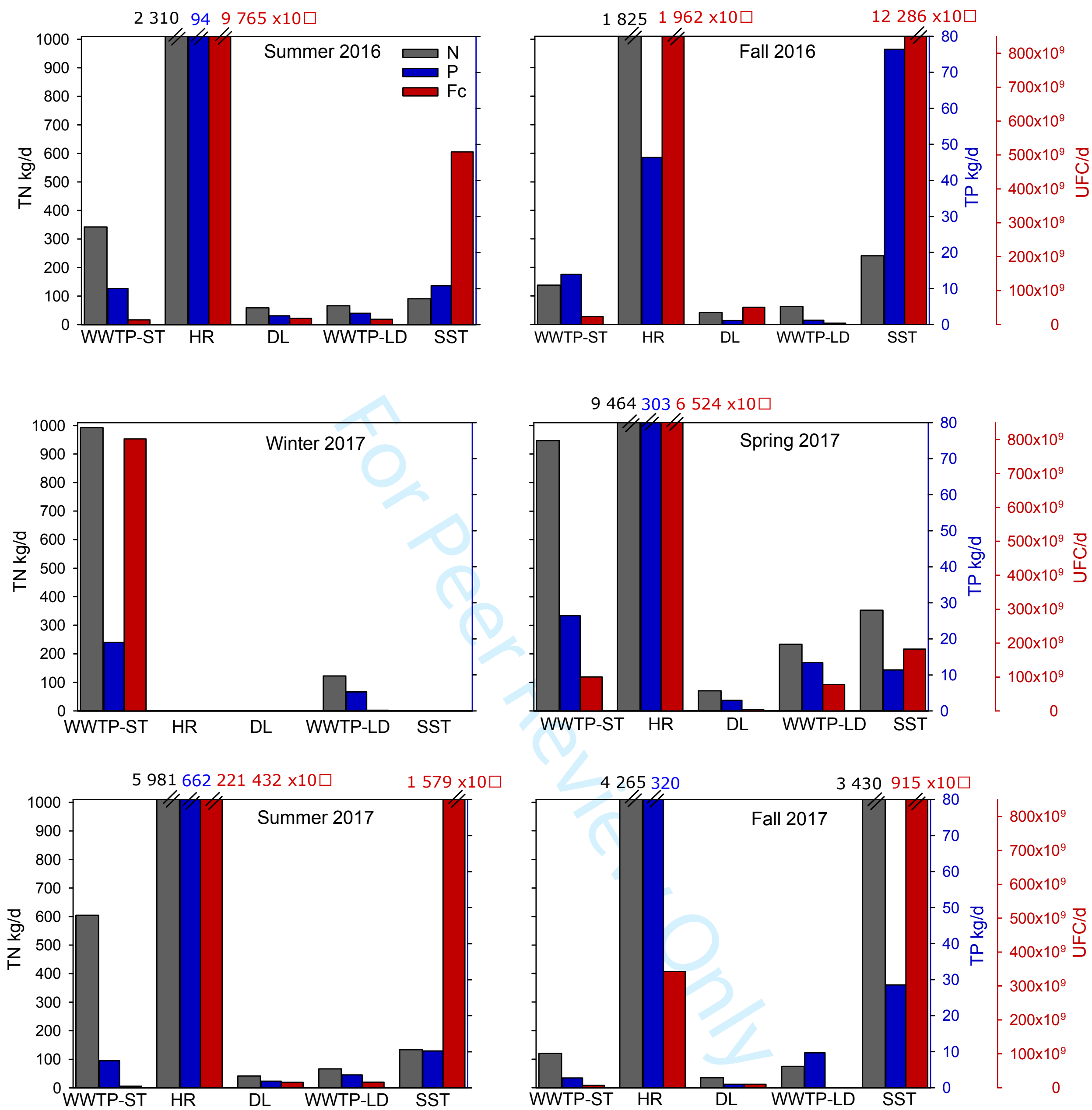

Figure 7. Seasonal mass fluxes of total nitrogen (TN dark grey), total phosphorous (TP blue) and fecal coliforms (Fc red) in wastewater treatment plant effluent of Stoneham-and-Tewkesbury (WWTP-ST), Hurons River (HR), wastewater treatment plant effluent for City of Lac Delage (WWTP-LD), Delage Lake (DL) and small stream tributaries (SSTs). Mass fluxes for HR, DL and SSTs were not calculated for Winter 2017, because discharges were not measured. HR mass fluxes include WWTP-ST mass fluxes as the latter is located upstream of the HR sampling station (Figure 1).