Journal of Great Lakes Research 44 (2018) 398–411

Contents lists available at ScienceDirect

Journal of Great Lakes Research

journal homepage: www.elsevier.com/locate/jglr

Nutrient concentrations and loadings in the St. Clair River–Detroit River Great Lakes Interconnecting Channel

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ARTICLE INFO

Article history:
Received 26 July 2017
Accepted 7 February 2018
Available online 12 March 2018

Communicated by Craig Stow

Keywords:
Phosphorus
Loadings
Nutrients
Detroit River
St. Clair River
Great Lakes

ABSTRACT

Long-term (2001–2015) water quality monitoring data for the St. Clair River are presented with data from studies in the Detroit River in 2014 and 2015 to provide the most complete information available about nutrient concentrations and loadings in the Lake Huron–Lake Erie interconnecting corridor. Concentrations of total phosphorus (TP) in the St. Clair River have reflected declines in Lake Huron. We demonstrate that St. Clair River TP concentrations are higher than offshore Lake Huron values. The recent average (2014 and 2015) incoming TP load from the upstream Great Lakes is measured here to be 980 metric tonnes per annum (MTA), which is roughly three times greater than previous estimates. Significant TP load increases are also indicated along the St. Clair River. We treat the lower Detroit River as three channels to sample water quality as part of a two year monitoring campaign that included winter sampling and SRP in the parameter suite. We found concentrations of many parameters are higher near the shorelines, with the main Mid-River channel resembling water quality upstream measured at the mouth of the St. Clair River. Comparison with past estimates indicates both concentrations and loadings of TP have dramatically declined since 2007 in the Trenton Channel, while those in the Mid-River and in the Amherstburg Channel have remained similar or have possibly increased. The data demonstrate that the TP load exiting the mouth of the Detroit River into Lake Erie is currently in the range of 3740 (in 2014) to 2610 (2015) MTA.

Introduction

The St. Clair River and Detroit River, along with Lake St. Clair, connect Lake Huron with Lake Erie, and together form part of the international boundary between Canada and the United States. The St. Clair River flows 63 km in a southerly direction from Lake Huron to Lake St. Clair and is a straight channel over much of its length. The flow of the river is controlled by the difference in water level between Lake Huron and Lake St. Clair and by the conveyance of the river. It has a mean discharge of about 5150 m^3/s and a water retention time of about 21 h (IJC, 2009; UGLCCS, 1988). Lake St. Clair has a surface area of about 1100 km^2 and is relatively shallow, with a mean water depth of only about 3 m. The average water residence time for Lake St. Clair is seven days but travel time can be as little as 2 days for water flowing through the maintained navigation channel (Great Lakes Commission, 2000).

The Detroit River is approximately 51 km long and has a mean flow of approximately 5200 m^3/s (Derecki, 1984). Nearly the entire Detroit River total outflow is contributed from Lake Huron via Lake St Clair, with only 2% contributed by tributaries (UGLCCS, 1988). The flow in the Detroit River is influenced by islands and navigation channels, particularly in the lower Detroit River near its discharge to Lake Erie. Much of the Detroit River shoreline is highly urbanized and industrialized (UGLCCS, 1988). The average flushing time for the Detroit River is 19 h (Derecki, 1984).

Ongoing monitoring of water quality in the Huron-Erie corridor is needed by Great Lakes water quality managers to assess current status and trends, and to assess the need for, and ultimately the efficacy of, nutrient management activities. Loadings from priority Canadian and US tributaries to the corridor are being monitored as part of binational efforts to set baselines and track progress toward meeting nutrient loading reduction targets set for Lake Erie (Objectives and Targets Task Team, 2015). Recently, Maccoux et al. (2016) estimated loadings by compiling all available nutrient monitoring and discharge data and determined the corridor delivers approximately one-quarter of the Lake Erie total phosphorus (TP) load. With a phosphorus loading target reduction of 40% recently set for western basin tributaries (Objectives and Targets Task Team, 2015), knowledge about the corridor's role in transmitting those loadings to Lake Erie are critical to assess and evaluate current loadings and to track future progress.

As part of its Freshwater Quality Monitoring and Surveillance Program, Environment and Climate Change Canada (ECCC) conducts

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https://doi.org/10.1016/j.jglr.2018.02.005
0380-1330/

water quality monitoring at the head (Point Edward) and mouth (Port Lambton) of the St. Clair River. The original intent of the monitoring was to track organic pollutants in the industrialized Canadian region near Sarnia, Ontario; nutrient and major ions were also included. In the Detroit River, however, there has been no ongoing, systematic water quality monitoring. Work conducted by ECCC in 2007 and prior (Burniston et al., 2009) provides the foundational knowledge upon which the current two year Detroit River study is based. Here, we report on the status and trends of nutrient concentrations and loadings from 2001 to 2015 in the St. Clair River, and augment these data with the current status of nutrient concentrations and loadings in the Detroit River in 2014 and 2015, to provide a regional-scale understanding of nutrients in the Huron-Erie Corridor.

Methods

St. Clair River stations and sampling (2001–2015)

ECCC has monitored water quality at the head and the mouth of the St. Clair River since 1987 (Fig. 1). Due to changing methodologies in the sample collection and processing, we have restricted the water quality record to the period 2001–2015.

The monitoring station at Point Edward (43.0048°N, −82.4155°W) is situated in Lake Huron upstream of its outlet, north of Sarnia. ECCC monitoring equipment is located within the (municipal) Lambton Area Water Supply System facility. A 19 mm diameter polyethylene water intake extends 50 m into the nearshore of Lake Huron, immediately upstream of the head of the St. Clair River. Information from this site is used to assess temporal trends of concentrations and nutrient loadings entering the Huron-Erie corridor.

The Port Lambton station (42.6589°N, −82.5068°W) is located 38 km downstream of Point Edward and approximately 2 km upstream of the large delta at the mouth of the St. Clair River. Monitoring equipment is housed in an abandoned water pumping station along the Canadian shore and is configured in a manner similar to the Point Edward station, with the intake located approximately 100 m from shore, at a depth of 7 m from the surface. Flow is predominantly in a stream wise direction; the horizontal component of the velocities is negligible (Derecki, 1985). As well it has been demonstrated that contaminants discharged to the river by the chemical industry located in Sarnia remain confined within 300 m of the Canadian shore, even as far downstream as Port Lambton (Chan et al., 1986). Samples from Port Lambton are therefore indicative of water quality in the Canadian portion of the river only.

Nutrient and major ion samples are collected from the intake tubes which draw water via submersible March magnetic drive pumps. Prelabelled bottles are rinsed twice, filled to the maximum level, recapped, and the bottle exterior is rinsed with raw water. Samples are immediately transported back to the Canada Centre for Inland Waters (CCIW) in Burlington, ON on ice for processing and analysis. Samples were collected every two weeks until the end of March 2012, at which point the sampling frequency was reduced to once every four weeks until present.

Detroit River stations and sampling (2014 and 2015)

Sampling in the Detroit River was conducted in the lower portion of the river, sufficiently far upstream of its discharge to Lake Erie to avoid any backwater influences. Based on the known non-mixing nature of the Detroit River in this area (Burniston et al., 2009), the river is treated as three channels. From west to east, these are: the Trenton Channel, the Mid-River (consisting in turn of the West and East portions) and the Amherstburg Channel (Fig. 2).

High frequency year-round autosampling in each of the three major channels was combined with cross-sectional surface grab samples during the ice free season to account for both the spatial and temporal variations in nutrient concentrations in the Detroit River. Burniston et al., 2009 reported diel variations in total phosphorus concentrations in the Trenton Channel that suggested within-day variability might be important, therefore, we collected daily-integrated samples as part of the present study. The study was designed to focus on capturing the spatial variability of water quality across the Detroit River (i.e., the horizontal variability) and we did not quantify the vertical variability. This approach is supported by two separate lines of evidence. Burniston et al., 2009 reported that water quality variations are primarily horizontal (lateral) and found minimal vertical variation of water quality

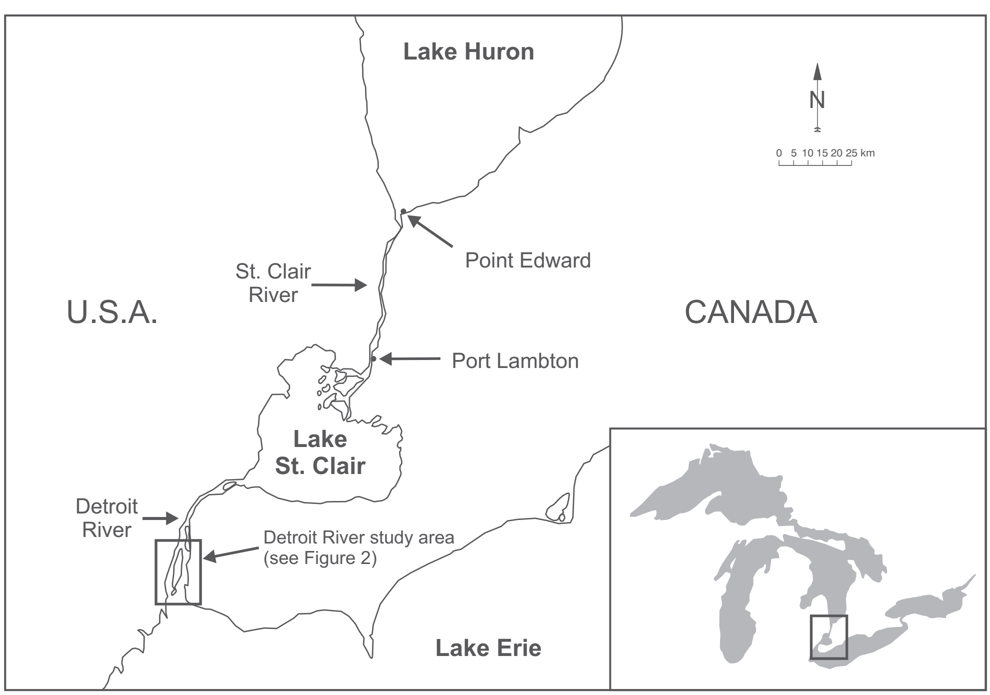

Fig. 1. St. Clair–Detroit River sampling locations. Inset shows Great Lakes context. Detroit River details are shown in Fig. 2.

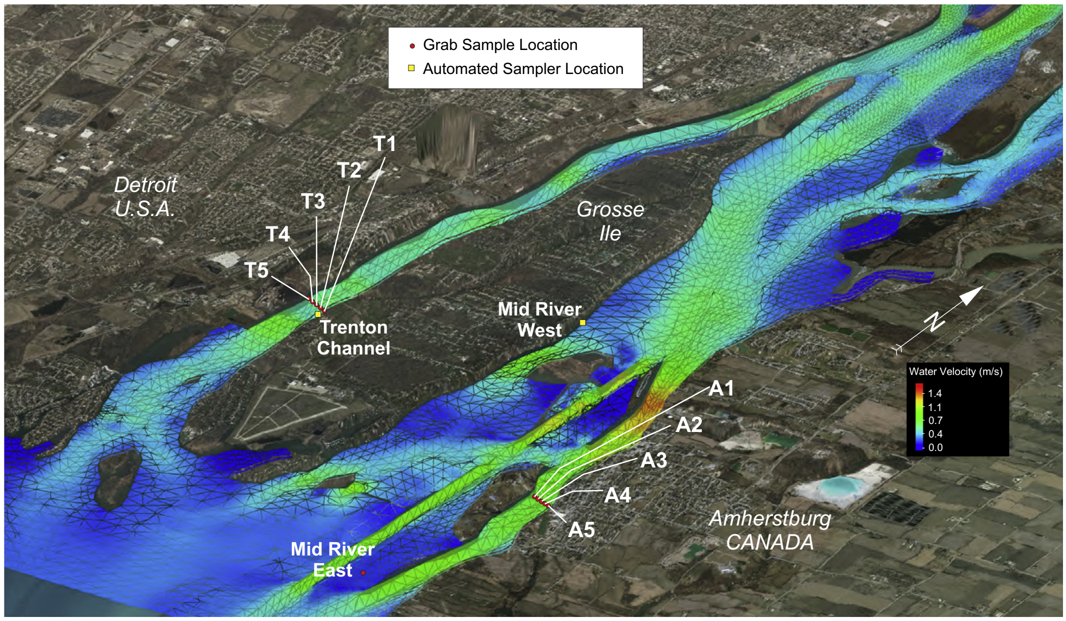

Fig. 2. Lower Detroit River water quality and hydrodynamic model. Detroit River Hydrosim 2d and Dispersim 2d hydrodynamic model nodes are co-located with sampling locations.

constituents in the Detroit River. Recently, the United States Geological Survey also determined the vertical distributions of most water quality constituents to be homogeneous (Totten and Duris, in preparation).

During the period of November 2013–October 2015, Teledyne ISCO 5800 refrigerated automated water quality samplers were operated at the Trenton Channel and at the Mid-River location. A third automated sampler was installed in July 2014 in the Amherstburg Channel, but the data demonstrated that the intake was unduly influenced by bottom sediment and the results could not be validated with surface samples taken in cross-section. The data from this sampler are not included here; the cross sectional grab sample data alone are used to indicate concentrations and compute Amherstburg Channel loadings.

The automated samplers were equipped with disposable polyethylene sampling bags and programmed to collect equal aliquots of river water every 2 h and composited daily, providing daily integrated samples. The sample lines were purged and rinsed between each subsample, and the automated samplers kept the samples at 3 °C until collection. Carousels with samples were retrieved and refreshed weekly, year round. Samples were kept on ice until return to Burlington for processing and analysis at CCIW.

In the Trenton Channel, the automated sampler was installed on a privately-owned dock extending from the west shore of Grosse Ile, with the sampling intake drawing from 0.6 m below the water surface (total depth of water 5 m). This autosampler was co-located with station T1 also sampled during the cross-sectional river surveys (see below). The Mid-River West sampler was located on the east shore of Grosse Ile with the sampling tube extending 6 m into the river from a depth of approximately 0.9 m (total depth of water 1.2 m). Heat trace was secured to all intake lines to prevent freezing and the intakes were equipped with a coarse stainless steel strainer which did not restrict the water flow. Initially, all samples were processed; this was reduced to a rate of one sample every two to three days at each site. Some samples were lost at both locations, particularly in the Mid-River West due to unusually cold conditions in the winter of 2013 which caused portions of the river to freeze to the bottom. For the water year 2014, a total of 158 samples were reported for the Trenton Channel and 132 samples for the Mid-River West location. For 2015, a total of 192 and 166 samples were collected from the Trenton Channel and Mid-River West locations, respectively.

To better determine the spatial distribution of water quality constituents across the river, grab samples collected across a transect were sampled from five stations in the Trenton Channel (T1–T5), from the Mid-River East, and from five stations across the Amherstburg Channel (A1–A5; Fig. 2) from a 22-feet boat during surveys conducted approximately biweekly during all ice-free times of the year. Transect sample locations were co-located with the nodes in the hydrodynamic mesh (see below). A total of 18 such surveys were conducted in 2014 (water year) and 16 in 2015, yielding a total of 374 grab samples. Water samples were collected manually using a pole sampler from a depth of 0.2 to 0.6 m below surface into 1 L pre-cleaned and certified amber glass bottles and were transported back to CCIW on ice for processing and analysis.

Analytical methods

The analyses of samples were performed by ECCC's National Laboratory for Analytical Testing in Burlington Ontario using Standard Operating Procedures accredited by the Canadian Association of Environmental Analytical Laboratories. Analyzed parameters, processing and analytical methods are summarized in Table 1. Samples were analyzed for a suite of water quality parameters including total phosphorus (TP), total filtered phosphorus (TFP), soluble reactive phosphorus (SRP), ammonia (NH_3), total Kjeldahl nitrogen (TKN), nitrate-plus-nitrite ($NO_3 + NO_2$) and the major ions chloride (Cl), fluoride (F) and sulphate (SO_4). For all parameters except TP, analyses represent the dissolved fraction only. For St. Clair River, samples are decanted at the laboratory prior to analysis; for the Detroit River, samples are filtered prior to submission.

River discharge — St. Clair River

St. Clair River discharge records for the 2001–2008 period were computed from daily mean water levels and the stage-fall-discharge equations developed by Fay and Kerslake (2009). Daily St. Clair River discharge data for the 2009–2015 period were obtained from the jointly operated monitoring station USGS 04159130/ECCC 02GG014 (St. Clair River at Port Huron Michigan). Discharge is computed for this station using the index–velocity method (Levesque and Oberg, 2012). Collectively, these two data sources provided the daily discharge required.

These discharge data were used for both Point Edward (upstream) and Port Lambton (downstream) stations as there is little change in discharge along the St. Clair River itself (Holtschlag and Koschik, 2002).

Table 1
Water quality parameters monitored. Note: SCR — St. Clair River, DR — Detroit River.

Parameter	Full name	2015 Detection limit (mg/L)	Method description	Sample treatment/Notes
TP	Total phosphorus	0.0005	Acidic persulfate digestion; stannous chloride-molybdate complex, photometric method	Whole water, stabilized with 1 mL 30% H_2SO_4
TFP	Total filtered phosphorus	0.0005	Acidic persulfate digestion; stannous chloride-molybdate complex, photometric method	Filtration by 0.45 μm cellulose-acetate filter and stabilized with 1 mL 30% H_2SO_4
NO_3 + NO_2	Nitrate + nitrite	0.005	Azo dye photometric method	Decanted water (SCR); 0.45 μm cellulose-acetate filtration (DR)
TKN	Total Kjeldahl nitrogen	0.014	Acid digestion; Phenate photometric method	Decanted water (SCR); 0.45 μm cellulose-acetate filtration (DR)
NH_3	Ammonia	0.005	Phenate photometric method	Decanted water (SCR); 0.45 μm cellulose-acetate filtration (DR)
Cl	Chloride	0.01	Liquid chromatography	Decanted water (SCR); 0.45 μm cellulose-acetate filtration (DR)
F	Fluoride	0.01	Liquid chromatography	Decanted water (SCR); 0.45 μm cellulose-acetate filtration (DR)
SO_4	Sulphate	0.01	Liquid chromatography	Decanted water (SCR); 0.45 μm cellulose-acetate filtration (DR)
SRP	Soluble reactive Phosphorus	0.0002	Stannous chloride-molybdate complex, photometric method	Not monitored in SCR; 0.45 μm cellulose-acetate filtration (DR)

River discharge — Detroit River

Daily total discharge for the Detroit River for 2014 and 2015 was obtained from the jointly operated station USGS 04165710/ECCC 02GH015 (Detroit River at Fort Wayne). A two-dimensional hydrodynamic model was then used to compute the distribution of the discharge between and within the three channels across the river. The model was a Hydrosim 2d and Dispersim 2d model (H2D2; Heniche et al., 2000) covering the lower Detroit River from Fort Wayne downstream to the Bar Point gauge operated by the Canadian Hydrographic Service (Gauge 12005) on Lake Erie. H2D2 is a two dimensional finite element model that calculates depth-averaged flux in two horizontal directions. The finite element mesh for the Detroit River consists of triangular elements and nodes, with node spacing ranging from 50 to 150 m. Discharge is calculated by summing the products of the depth averaged flux at the computational nodes by the distance between the nodes. Discharge computed by the model was validated against measurements of discharge collected from June 23 to 25, 2015 using a boat mounted acoustic Doppler current profiler. Water quality grab sample locations were co-located with the model nodes (see Fig. 2). Discharge was calculated for each monitoring location for the present study in cubic metres per second (m^3/s) on a daily time step using the H2D2 model.

Load calculations — St. Clair River

Loadings were calculated using the monitored chemical concentrations, the discharge data and the LOADEST program (USGS, 2013). The LOADEST software was selected as it efficiently processes large data sets, provides detailed information about its calculations, and its use permits comparison with other loading estimates in the Great Lakes basin (e.g., Wellen et al., 2012; Merriman, 2015; Indiana State Department of Agriculture and Indiana Department of Environmental Management, 2015).

As described above, the Point Edward monitoring station is located immediately upstream of the St. Clair River. These waters are considered representative of the exit concentrations from Lake Huron. Downstream, the water across the river at Port Lambton is not as well mixed, and the monitoring data reported here are considered representative only of concentrations for the Canadian side of the river. In the absence of measured concentrations on the U.S. side, it is assumed that concentrations remain unchanged from Lake Huron (measured at Point Edward). We acknowledge this assumption likely underestimates the load given some upstream-downstream concentration differences reported by the Michigan Department of Environmental Quality (MDEQ, 2013). The LOADEST program was used to estimate the Canadian load at Port Lambton by generating calibration tables using one-half of the river discharge and the measured water concentrations. The load contributed from the U.S. half of the river was estimated to be unchanged from upstream. We therefore used one-half of the total load calculated at Point Edward as the US portion of the load at Port Lambton. The sum of the loads from the Canadian and U.S. sides of the river represents the total load at the mouth of the St. Clair River.

Load calculations — Detroit River

In order to account for both spatial and temporal variability in the Detroit River, relationships were sought between sites within the three channels and between co-located grab and 24 h integrated autosamples to develop a dataset for input to LOADEST. The goal of the method was to use the high-intensity 24 h integrated data set collected from one site in the channel and extrapolate to the other sites across the channel to maximize temporal and spatial coverage. As an initial step, the daily integrated samples were compared with the co-located grab samples with common collection dates (i.e., Trenton ISCO vs T1; Mid-River West ISCO vs. Mid-River East; Amherstburg ISCO vs A1). At this stage, the suspected issue with the Amherstburg autosampler intake was verified, and these autosampler data were subsequently eliminated from further consideration. Linear models were then developed for grab samples from adjacent sites within each channel. If the data were observed to correlate with $r \geq 0.75$, the resultant regression coefficients (ranging from 1.08 to 1.13) were then applied to model 24-h-equivalent concentrations at sites T2 through T5 and at Mid-River East, using the autosampler data at Trenton Channel and Mid-River West, respectively. In the Trenton Channel, no statistically significant relationship could be described between adjacent sites for TKN; therefore, this above-noted modeling step for adjacent sites was not performed for TKN. In the Mid-River, the relationship was only significant for TP; therefore, the modeling step was only performed for this single constituent.

In the Trenton Channel, loadings were computed for each constituent at each node using 24 h integrated autosampler data (T1) or modelled 24 h equivalent data (T2–T5); total loadings were computed by summing the loads from nodes T1 through T5. In the Mid-River, loads were developed separately for the East and West sites with the exception of TP, for which the higher-frequency, daily-integrated samples at Mid-River West were used to model an equivalent dataset for Mid-River East. The total Mid-River load is the sum of loads (calculated using LOADEST, see below) from Mid-River East and Mid-River West river sections.

In the Amherstburg Channel, LOADEST was used to compute loadings for each node A1 through A5 using the grab sample data only, and these were summed to give the total Amherstburg Channel load.

Regression model development

The LOADEST program (Runkel et al., 2004) was used to compute the annual loads for this study. The Adjusted Maximum Likelihood Estimation (AMLE) was the primary method used when the regression residuals were normally distributed. The AMLE is appropriate for data sets that contain censored data (i.e., values below laboratory detection limits) and will converge with the Maximum Likelihood Estimation (MLE) when no censored data are present. The Least Absolute Deviation (LAD) method was employed when the regression residuals were not normally distributed.

As described in Runkel et al. (2004), the equation used for the AMLE calculation of instantaneous load is given by:

$$\hat{L}_{AMLE} = \exp\left(a_0 + \sum_{j=1}^{M} a_j X_j\right) H(a, b, s^2, \alpha, \mathrm{K}) \tag{1}$$

where: $L\hat{}_{AMLE}$ is the AMLE estimate of instantaneous load; a and b are functions of the explanatory variables; α and κ are parameters of the gamma distribution and s^2 is the residual variance. The model coefficients a_0 and a_j are maximum likelihood estimates corrected for first-order bias.

Calibration data (one to five years of concentration and flow data) were used to develop a regression model. LOADEST has nine (9) predefined models (see Electronic Supplementary Material (ESM) Table S1) that specify the form of the regression equation (Runkel et al., 2004). Coefficients and their standard deviations were calculated using the AMLE and the LAD by substituting each of the nine models into Eq. (1). Explanatory variables were selected to minimize the Akaike Information Criterion (AIC); the regression model which generated the lowest AIC was selected for the calibration regression. The Probability Plot Correlation Coefficient (PPCC) was then calculated for the selected model to assess the distribution of the residuals. PPCC values < 0.8 indicated that the residuals were not normally distributed, in which case the LAD coefficients were used for the model.

The performance of each regression model was evaluated using residual variance (S^2). The estimated and observed loads calculated for all of the calibration data were used to assess the efficiency of the model. Potential bias (Bp; the percentage difference between the total of the loads predicted by the model and the total of the observed), the partial load ratio (PLR; the sum of the estimated loads divided by the sum of observed loads) and the Nash-Sutcliffe efficiency index (E; Nash and Sutcliffe, 1970) were calculated to determine the extent of over- or underestimation generated by the regression. An $E < 0$ value indicated that the observed mean load was a better estimate than the model estimate; in these cases, the observed mean load is instead reported.

Estimated loads for each time period, station and parameter were generated with the calibrated model and the input data comprising constituent concentrations and discharge. A daily mean load was generated and the standard error of prediction (SEP) was calculated to describe the uncertainty associated with each estimate. The SEP is the sum of parameter uncertainty and model error.

Temporal trends (St. Clair River)

To determine the statistical significance of concentration changes observed between the two stations in the St. Clair River, a two-sided student *t*-test (Snedecor and Cochran, 1989) of independent samples was used. Long term monotonic trends for concentrations and loadings were assessed in the St. Clair River using a Lowess-based flow-adjusted Seasonal Kendall test (Hirsch et al., 1982; Kendall, 1938, 1975; Meals et al., 2011) to remove any variation in water quality explained by seasonal or daily discharge variation. The null hypothesis (no change in concentration over time) was rejected for $p < 0.05$.

Results and discussion

Corridor discharge

An overview of discharge in the corridor is provided in Fig. 3. To quantify any potential bias between the stage-fall-discharge method used for the early (2001–2008) data and the index-velocity method for the later (2009–2015) period, daily flows were computed using the Fay and Kerslake (2009) stage-fall-discharge equations for the entire time period. Flows computed using Fay and Kerslake stage-fall-discharge equations were an average of 1.7% lower than flows computed using the index-velocity method employed by the USGS. However, the graphical analysis (Fig. 3) does not show a step change when the method changed and a potential bias of −1.7% in the early data mean that the loads and the declining trends that are observed (see below) are conservatively estimated here. Because the index-velocity method is considered to be an improvement over the stage-fall-discharge method, we have opted to adopt the index-velocity-derived discharge to the greatest extent possible here.

Seasonal and annual trends in discharge for the Detroit River is given in Fig. 3. Discharge tends to be lowest in the late fall and winter and highest in the summer (July–September), following the seasonal rise and fall of Lake Michigan and Huron water levels. Discharge in the St. Clair River is also reduced in the winter by the increased resistance of the channel due to ice formation in the lower portion of the river and Lake St. Clair. Inflows from tributaries and other sources contribute relatively little to the total flow in the corridor on an annual basis. In the Detroit River, approximately 20% of the discharge in the lower Detroit River is through the Trenton Channel, with 45% through the Mid-River and 35% via the Amherstburg Channel (Table 2).

St. Clair River water quality trends

Table 3 reports the temporal trends and intersite concentration differences observed in the St. Clair River. All data are shown graphically for the phosphorus parameters, nitrogen parameters and major ions in Figs. 4 through 6, respectively. Offshore values (for sites >50 m depth in the main body of Lake Huron) from ECCC's Great Lakes Surveillance (Dove and Chapra, 2015) are shown for comparison with Point Edward values. For illustrative purposes only, linear regressions are shown in the figures to demonstrate the intersite (upstream-downstream) differences and long-term trends. These trends are consistent with the annual rates of change reported in Table 3, which are calculated using more robust, non-parametric methods. Overall, the data indicate high temporal variability, especially for TP concentrations (Fig. 4). However, the high frequency of data collection, combined with the long duration of record, permits the detection of statistically significant trends (Table 3).

Concentrations of most parameters entering the Huron-Erie corridor at Point Edward indicate unchanging concentrations since 2001 (F, TFP) or slow, statistically significant declines (i.e.,≤1.3%/year for $NO_3 + NO_2$, TKN, NH_3 and SO_4) (Table 3). In contrast, TP has declined strongly at a rate of approximately 11% per year, and Cl has increased significantly over time (0.5%/year). As demonstrated in the accompanying figures, these trends track those observed upstream in Lake Huron. Dove and Chapra (2015) demonstrated that TP in Lake Huron was relatively stable until the mid- to late-1990s, with significant declines since that time and the steepest rate of decline since 2000; the data presented here agree with a major decline in Lake Huron TP. The decline in $NO_3 + NO_2$ is in agreement with Great Lakes offshore trends (Dove and Chapra, 2015). Chapra et al. (2012) reported that chloride has been increasing in Lake Huron at a linear rate of approximately 0.041 mg/L

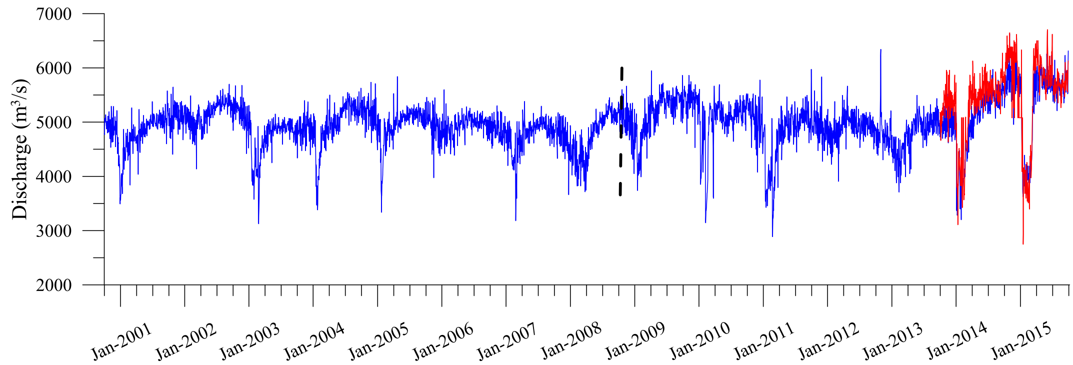

Fig. 3. St. Clair–Detroit River discharge. St. Clair River discharge is shown as the blue line; 2001–2008 values are from stage-fall-discharge equations developed by Fay and Kerslake (2009), 2009–2015 values are from USGS. The vertical dashed line indicates the timing of this method change. USGS Detroit River discharge is shown in red.

per year since 1970, which is in excellent agreement with the 0.043 mg/L per year calculated using the Point Edward dataset since 2003.

The slow but significant declines observed for $NO_3 + NO_2$ and SO_4 in Lake Huron are also observed downstream at Port Lambton. However, the steep decline of TP concentrations in water leaving Lake Huron is not reflected downstream; indeed, there has been no significant temporal change in TP concentrations at Port Lambton and concentrations are significantly greater downstream compared to upstream at Point Edward (Fig. 4; Table 3). Therefore, TP inputs along the St. Clair River are substantial and they may be increasing over time. Interestingly, concentrations of the dissolved phosphorus fraction (TFP) are significantly greater upstream at Point Edward and show no statistically-significant change over time, indicating it may be the particulate fraction causing the increase in TP inputs in the St. Clair River. An upstream-downstream comparison indicates significantly higher concentrations of TP, NH_3, $NO_3 + NO_2$ and SO_4 downstream at Port Lambton, indicating sources to the St. Clair River for these compounds (Table 3). Follow up is warranted to investigate the cause of the increasing loads within the St. Clair River watershed.

A high degree of correlation is observed between upstream St. Clair River and offshore Lake Huron values. The nitrogen species (Fig. 5) show the greatest similarity, while concentrations of the phosphorus species, ammonia, chloride and sulphate appear to be lower in the offshore environment. Higher concentrations in nearshore waters that influence water quality in the river are not observed in the Lake Huron data, which are average surface water concentrations taken during spring cruises from offshore locations (i.e., having a minimum lake depth of 50 m; Dove and Chapra, 2015). The TP data in particular indicate that offshore monitoring is not representative of conditions in the interconnecting channel (Fig. 4). Additional nearshore sources and/or entrainment of sediment likely contribute to higher concentrations as the waters exit Lake Huron and enter the St. Clair River.

LOADEST model results

A summary of all the model descriptors can be found in Table 4. A full accounting of all the load equations, model coefficients and outputs generated for the current study can be found in the ESM Tables S3, S4 and S5. Overall, the outputs demonstrate very robust results, both with respect to the goodness of fit of the calibration data to the developed model, and the post-test assessments of bias and efficiency in the chosen models. The goodness of fit and efficiency was lower for TP compared to the other parameters; however, this may be related back to the variability that is inherent in the data (for St. Clair River example, see Fig. 4 compared to other parameters in Figs. 5 and 6). The AMLE was used for most load estimations as residuals were normally distributed 97% of the time, and censored data were isolated to NH_3 at the St. Clair stations only, affecting about 15% of NH_3 values at Point Edward and 20% at Port Lambton. In the St. Clair River, residual variance (RV) was highest for TP (range of 0.397–0.79 at Point Edward and 0.248–0.629 at Port Lambton; Table 4). At both these sites, RV was consistently <0.1 for TKN, Cl and SO_4, while it was intermediate for NH_3 (mean 0.0.321 at Point Edward and 0.369 at Port Lambton). In the Detroit River, the RV for TP was lower (<0.268) compared to the St. Clair River. Here, the greatest RV was found for SRP (range 0.423–0.785), followed by TP and NH_3 (Table 4).

The partial load ratio (PLR) was calculated for all regressions to determine the difference between the estimated and observed loads for all sampled days. Very low differences were found, with many PLRs approaching 1 (no difference between estimated and observed) (Table 4). Point Edward showed 84% of the estimated loads to be within 10% of observed loads; TP loads were on average 8% less than observed (ESM Tables S3, S4, and S5). At Port Lambton, 92% of all load estimates were within 10% of the observed, with estimated TP loads on average 10% lower than observed. In the Detroit River, 90% of the estimated loads were within 10% of observed loads, and the estimated TP loads were on average 4% lower than the observed. The PLR for F and SO_4 were

Table 2
Mean daily discharge in the St. Clair and Detroit Rivers (m^3/s) in water years 2007, 2014 and 2015.

	2007	2014	2015
St. Clair River	4788	5010	5454
Trenton Channel	964	1040	1107
Amherstburg Channel	1766	1814	1896
Mid-River	2071	2432	2578
Total Detroit River	4788	5264	5581

Table 3
Seasonal Kendall test for St. Clair River water quality trends, 2001–2015 and intersite concentration differences. Statistically significant trends ($p < 0.05$) are indicated in bold font. Final column indicates intersite differences, computed as Student-*t*-test on matched pairs. PE — Point Edward (upstream); PL — Port Lambton (downstream). * — based on 2008–2015 only.

	Point Edward		Port Lambton		Difference
	% annual change	*p* value	% annual change	*p* value	
TP	**−10.90**	**0.0000**	−1.67	0.2060	PL > PE
TFP	−0.62	0.6500	−0.71	0.6300	PL < PE*
TKN	**−1.19**	**0.0002**	0.42	0.1792	PL = PE
NH_3	**−1.28**	**0.0029**	−0.82	0.2230	PL > PE
NO_3NO_2	**−0.79**	**0.0000**	**−1.36**	**0.0000**	PL > PE
Cl	**0.50**	**0.0000**	**0.99**	**0.0000**	PL = PE
F	0.58	0.6251	−1.63	0.6251	PL = PE
SO_4	**−0.15**	**0.0015**	**−0.23**	**0.0000**	PL > PE

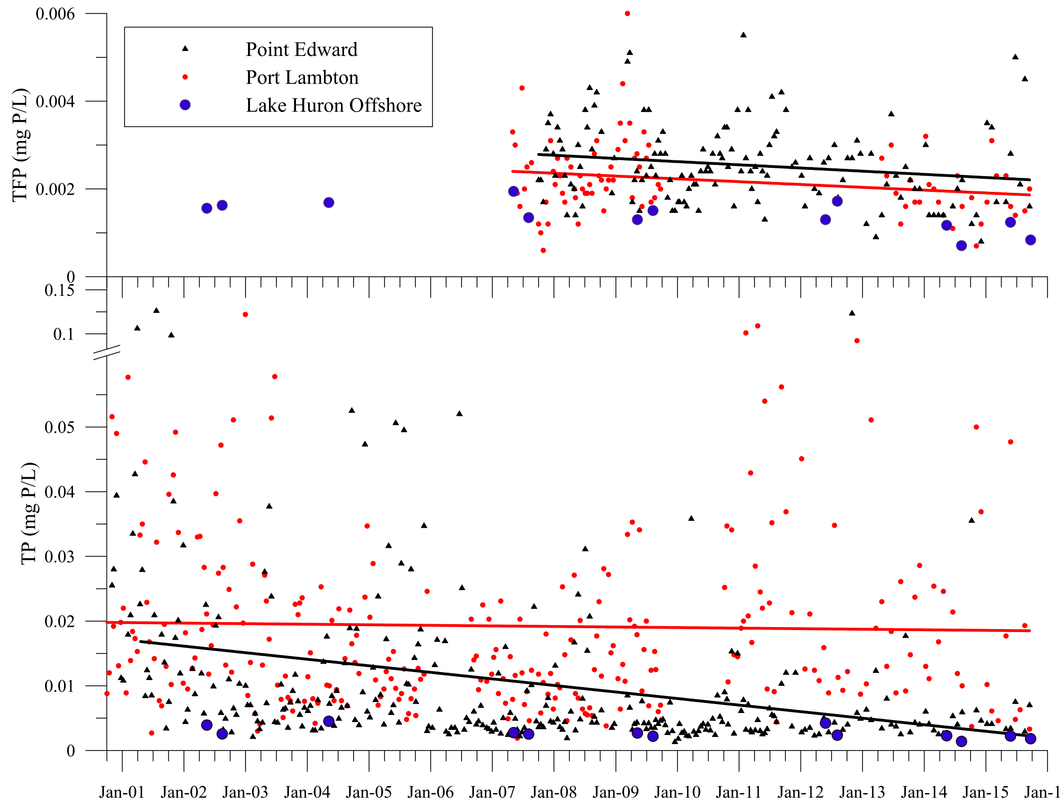

Fig. 4. Concentrations of phosphorus constituents in the St. Clair River, 2001–2015. Upstream (Point Edward) values are black triangles; downstream (Port Lambton) values are red circles. Linear trends are shown to illustrate the intersite differences and long term trends; see Table 3 for statistical test results. Mean values from Lake Huron (Dove and Chapra, 2015) are shown as reference; these represent the mean of surface values from offshore (lake depth ≥ 50 m) stations only.

equal to 1 for all regressions in the study (Table 4 and ESM Tables S3, S4 and S5).

The difference between total estimated and total observed loads is also measured as the potential bias (Bp). Positive values for Bp indicate loads are overestimated compared to observed loads. Overall, the potential bias was very low, with 73% of all estimations having a positive or negative bias of <1%. TP was underestimated consistently at Point Edward and in the Detroit River, while at Port Lambton the Bp increased over time, with the underestimations reaching 15% in 2014 and 2015 (ESM Tables S3, S4 and S5).

The Nash Sutcliffe efficiency index (E) also compares predicted loads with observed loads and is similar to the regression model coefficient of determination (R^2) except that E is based on the load prediction after its back transformation from the logarithmic scale to the data scale (Stenbeck et al., 2011). E ranges from negative infinity to 1.0, with 1.0 indicating a perfect fit to the observed data. Values below zero indicate the observed data are superior to the model estimates. Efficiencies were negative for only three estimates throughout this study: NH_3 at Port Lambton in 2014 and 2015 and SRP at A1 in 2015 (observed values were therefore reported for these loads). In the St. Clair River, E was lowest for TP with a mean value of 0.065 at Point Edward and 0.135 at Port Lambton. In the Detroit River, the three forms of phosphorus measured here demonstrated lower efficiencies, with Mid-River stations in particular showing some values of E < 0.1 (Table 4).

Loadings in the St. Clair River

Total loadings of all constituents are shown in Table 5. Because of the relatively stable discharge over time, temporal trends in loadings follow trends in concentrations. Loadings of major ions and most nutrients have shown little interannual variability, with the exception of TP. The incoming load of TP has ranged from a minimum of 719 MTA in 2012 to a maximum of 4800 MTA in 2001. The average TP load for the most recent five to ten years has been roughly 1000 MTA, as was the average load during the most recent two years (2014–15) (Fig. 7).

The TP load from Lake Huron, monitored at Point Edward, declined significantly ($p = 0.0012$) over the period of record, from 4800 MTA in 2001 to 1200 MTA in 2015. The decline appears to be driven by quickly decreasing loads until 2007 (slope −18% per year, $p = 0.048$), with little change observed since that time (slope = +0.1% per year; $p > 0.9$). The loading of TFP also has declined significantly over time at Point Edward (slope −10.6%; $p = 0.028$). For the period 2008–2013, TFP comprised between 36 and 57% of the TP load at Point Edward. In 2015, however, its contribution declined to 30%.

Downstream at Port Lambton, loadings of TP declined significantly ($p = 0.0013$) at a rate of −15% per year from 2001 to 2007, but have increased significantly ($p = 0.048$) at a rate of 5.8% since that time (2007–2015). TP loads were 4060 MTA in 2001, fell to 1440 MTA in 2007 and rose to 1950 MTA in 2014–2015 (Table 5). $NO_3 + NO_2$ showed a consistent linear decline (slope = −0.7% per year; $p = 0.04$). Overall, NH_3 showed no change in loadings over time, but a significant increase ($p = 0.0008$) is indicated for the most recent time period (2007–2015).

The MDEQ conducted limited water quality sampling in the St. Clair and Detroit Rivers during 1998–2008. Sampling was conducted monthly, eight times each year (from April until November) at stations located near the US shoreline at the head and mouth of each of the St. Clair and Detroit Rivers. Their results (MDEQ, 2006, 2013) agree broadly with our findings here; concentrations of TP are significantly higher downstream in the St. Clair River compared to upstream, and they are declining at a (somewhat slower) rate of 5% per year upstream and no trend is reported downstream. The MDEQ reports median concentrations of 0.005 and 0.008 mg/L for the time period 1998–2008 (n ≈ 90), which are lower than our 2001–2008 median TP concentrations of 0.007 and 0.013 mg/L (n ≈ 1000) for upstream and downstream

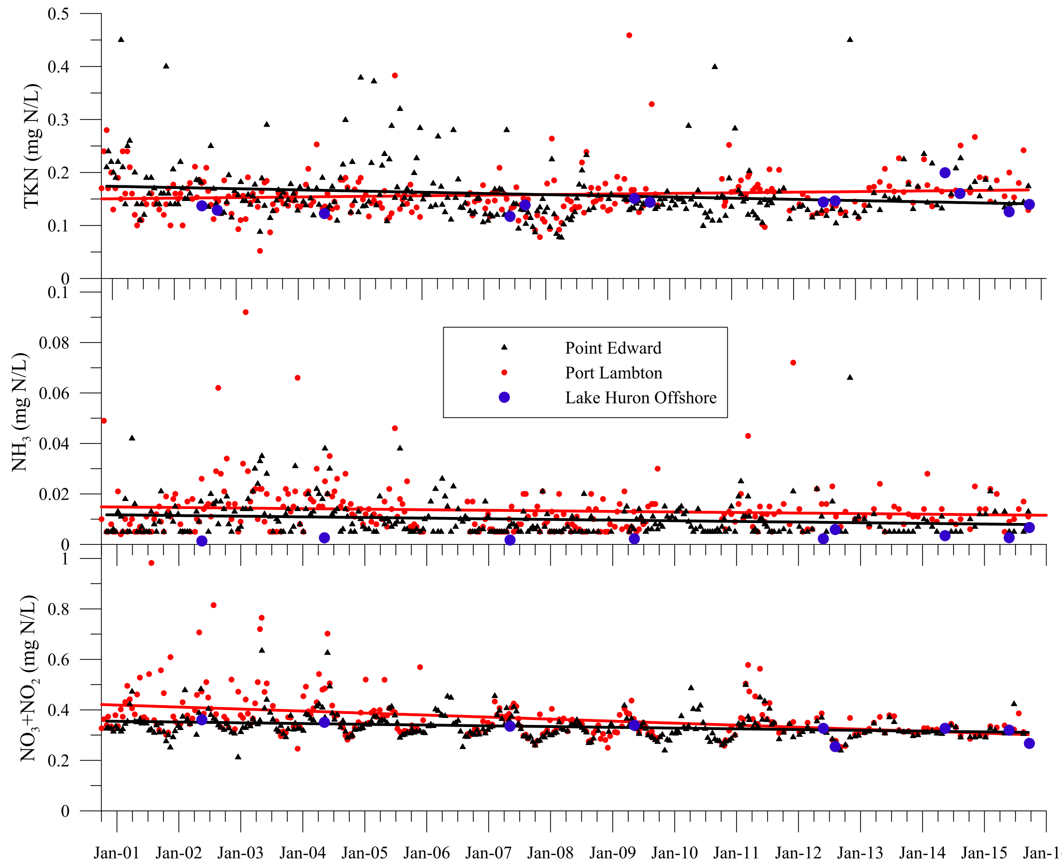

Fig. 5. Concentrations of nitrogen constituents in the St. Clair River, 2001–2015. Upstream (Point Edward) values are black triangles; downstream (Port Lambton) values are red circles. Linear trends are shown to illustrate the intersite differences and long term trends; see Table 3 for statistical test results. Mean values from Lake Huron offshore cruises (Dove and Chapra, 2015) are shown as reference; these represent the mean of surface values from offshore (lake depth ≥ 50 m) stations only.

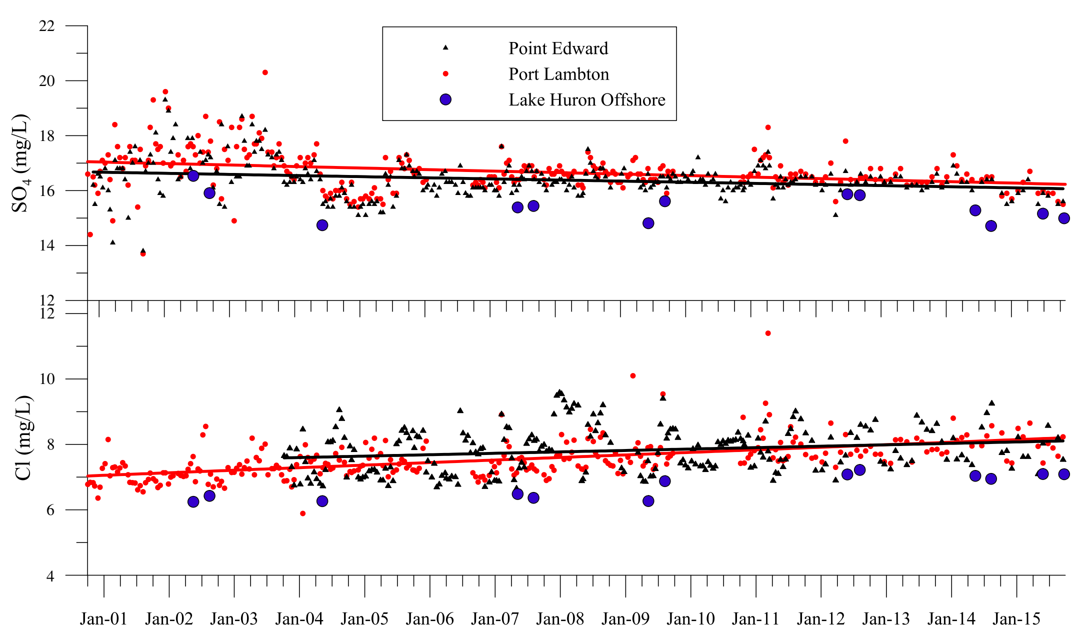

Fig. 6. Concentrations of anions in the St. Clair River, 2001–2015. Upstream (Point Edward) values are black triangles; downstream (Port Lambton) values are red circles. Linear trends are shown to illustrate the intersite differences and long term trends; see Table 3 for statistical test results. Mean values from Lake Huron offshore cruises (Dove and Chapra, 2015) are shown as reference; these represent the mean of surface values from offshore (lake depth ≥ 50 m) stations only.

Table 4
Statistical summary of LOADEST model efficiencies. A description of all variables is provided in the text. Supplemental information provides the selected load equations, model coefficients and outputs generated for the current study.

	Load bias %			Residual variance (s^2)			Partial load ratio			Nash Sutcliffe Efficiency Index (E)		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Point Edward												
TP	−15.4	−0.981	−7.45	0.397	0.790	0.597	0.846	0.990	0.925	0.002	0.138	0.065
TFP	0.023	0.327	0.160	0.058	0.111	0.084	1.00	1.00	1.00	0.045	0.631	0.281
$NO_3 + NO_2$	−0.078	−0.005	−0.039	0.005	0.014	0.010	0.999	1.00	1.00	0.448	0.658	0.559
TKN	−0.769	0.286	−0.376	0.051	0.078	0.065	0.992	0.998	0.996	0.012	0.309	0.168
NH_3	−3.74	3.54	1.06	0.228	0.398	0.321	0.963	1.04	1.01	0.032	0.309	0.123
CL	−0.011	0.018	0.001	0.002	0.008	0.005	1.00	1.00	1.00	0.490	0.919	0.738
F	0.000	3.33	1.11	0.005	0.197	0.114	1.00	1.03	1.01	0.397	0.655	0.544
SO_4	−0.039	0.072	0.014	0.000	0.016	0.005	1.00	1.00	1.00	0.347	0.976	0.700
Port Lambton												
TP	−6.48	1.62	−1.35	0.248	0.629	0.431	0.94	1.02	0.99	0.008	0.267	0.135
TFP	−0.912	0.654	−0.210	0.094	0.138	0.108	0.99	1.01	1.00	0.079	0.286	0.171
$NO_3 + NO_2$	−0.573	1.39	0.191	0.010	0.155	0.047	0.99	1.01	1.00	0.046	0.564	0.357
TKN	−0.762	0.223	−0.244	0.048	0.072	0.058	0.99	1.00	1.00	0.050	0.313	0.141
NH_3	−7.34	3.33	0.197	0.267	0.565	0.369	0.93	1.03	1.00	−0.002	0.360	0.145
CL	−0.009	0.008	−0.001	0.001	0.005	0.003	1.00	1.00	1.00	0.551	0.750	0.656
F	−0.001	0.006	0.002	0.003	0.005	0.004	1.00	1.00	1.00	0.675	0.762	0.720
SO_4	−0.001	0.018	0.005	0.000	0.005	0.002	1.00	1.00	1.00	0.368	0.963	0.801
Trenton Ch												
TP	−0.54	−0.11	−0.30	0.108	0.126	0.118	0.995	0.999	0.997	0.165	0.379	0.217
TFP	−0.39	−0.34	−0.36	0.103	0.137	0.120	0.95	0.997	0.98	0.238	0.292	0.253
$NO_3 + NO_2$	−0.90	−0.38	−0.61	0.018	0.026	0.022	0.991	0.996	0.994	0.218	0.316	0.255
TKN	−0.03	3.42	0.00	0.007	0.014	0.010	1.00	1.00	1.00	0.017	0.602	0.378
NH_3	1.34	2.98	2.15	0.094	0.153	0.122	1.01	1.03	1.02	0.435	0.505	0.467
CL	−0.38	−0.29	−0.35	0.037	0.040	0.038	0.996	0.997	0.996	0.375	0.554	0.465
F	0.00	0.02	0.01	0.003	0.009	0.006	1.00	1.00	1.00	0.163	0.680	0.429
SO_4	0.00	0.00	0.00	0.001	0.003	0.001	1.00	1.00	1.00	0.475	0.981	0.878
SRP	1.54	3.17	2.37	0.761	0.808	0.785	1.02	1.03	1.02	0.057	0.207	0.133
Mid-River West												
TP	−5.20	−5.10	−5.15	0.251	0.285	0.268	0.948	0.949	0.949	0.074	0.105	0.090
TFP	−4.97	−2.07	−3.52	0.132	0.137	0.135	0.950	0.979	0.965	0.074	0.110	0.092
$NO_3 + NO_2$	0.811	0.902	0.857	0.075	0.095	0.085	1.01	1.01	1.01	0.363	0.380	0.372
TKN	−0.198	−0.120	−0.159	0.033	0.037	0.035	0.998	0.999	0.999	0.092	0.207	0.150
NH_3	0.383	0.588	0.486	0.168	0.185	0.177	1.00	1.00	1.00	0.470	0.542	0.506
CL	−0.290	−0.085	−0.188	0.036	0.040	0.038	0.997	0.999	0.998	0.302	0.436	0.369
F	−0.020	0.013	−0.004	0.010	0.014	0.012	1.00	1.00	1.00	0.570	0.685	0.628
SO_4	−0.001	0.002	0.001	0.001	0.001	0.001	1.00	1.000	1.00	0.953	0.976	0.965
SRP	−17.00	−5.30	−11.15	0.413	0.433	0.423	0.828	0.947	0.888	0.025	0.040	0.033
Mid-River East												
TP	−4.97	−4.75	−4.86	0.240	0.253	0.247	0.950	0.952	0.951	0.072	0.085	0.079
TFP	−0.084	0.106	0.011	0.080	0.099	0.090	0.999	1.00	1.00	0.119	0.203	0.161
$NO_3 + NO_2$	−1.15	−0.839	−0.994	0.093	0.094	0.093	0.989	0.992	0.991	0.273	0.456	0.365
TKN	0.009	0.029	0.019	0.019	0.019	0.019	1.00	1.00	1.00	0.318	0.541	0.430
NH_3	0.365	0.405	0.385	0.089	0.132	0.111	1.00	1.00	1.00	0.961	0.969	0.965
CL	−0.017	−0.007	−0.012	0.010	0.012	0.011	1.00	1.00	1.00	0.670	0.772	0.721
F	−0.007	0.000	−0.004	0.006	0.007	0.006	1.00	1.00	1.00	0.486	0.605	0.546
SO_4	−0.002	0.000	−0.001	0.001	0.001	0.001	1.00	1.00	1.00	0.938	0.955	0.947
SRP	0.705	1.79	1.25	0.519	0.553	0.536	1.00	1.02	1.01	0.034	0.077	0.056
Amherstburg Ch.												
TP	−3.99	−1.34	−2.86	0.101	0.286	0.196	0.960	0.987	0.972	0.447	0.694	0.581
TFP	−1.24	0.064	−0.425	0.050	0.156	0.087	0.988	1.00	0.996	0.177	0.705	0.384
$NO_3 + NO_2$	−0.804	−0.108	−0.573	0.043	0.128	0.080	0.990	0.999	0.994	0.311	0.750	0.555
TKN	−0.048	0.062	0.002	0.012	0.029	0.019	1.00	1.00	1.00	0.230	0.703	0.453
NH_3	−1.05	0.197	−0.049	0.026	0.090	0.049	0.999	1.00	1.00	0.094	0.797	0.525
CL	−0.022	0.063	0.007	0.010	0.034	0.015	1.00	1.00	1.00	0.050	0.735	0.510
F	−0.034	0.042	0.012	0.004	0.011	0.007	1.00	1.00	1.00	0.296	0.880	0.612
SO_4	−0.003	0.010	0.003	0.001	0.002	0.001	1.00	1.00	1.00	0.748	0.964	0.903
SRP	−0.547	3.42	1.67	0.331	0.652	0.520	0.995	1.03	1.01	−0.001	0.559	0.324

stations, respectively. Omitting the December–March samples from our dataset (to better match the MDEQ methods) did not reduce this difference. Consequently, the MDEQ reported loads, calculated using a stratified Beale ratio estimator, are lower than those reported here for most years.

Lower Detroit River spatial water quality trends and interannual differences

Similar to observations made in 2007, concentrations of most parameters in 2014 and 2015 demonstrated higher values in the Trenton

Table 5
St. Clair River loadings, 2001–2015 (MTA). Values are rounded to three significant figures.

Year	TP	TFP	$NO_3 + NO_2$	TKN	NH_3	Cl	F	SO_4
Point Edward								
2001	4800		51,300	28,600	1310	1,080,000		2,530,000
2002	2760		56,900	27,900	1850	1,300,000		2,810,000
2003	1600		52,200	23,400	2280	1,180,000		2,560,000
2004	1470		56,500	25,500	2490	1,190,000		2,590,000
2005	2680		55,400	29,700	1560	1,180,000		2,550,000
2006	2050		52,600	26,400	1590	1,170,000		2,510,000
2007	1050		50,000	20,600	1060	1,150,000		2,470,000
2008	1190	430	47,200	20,200	906	1,270,000		2,460,000
2009	1110	450	51,400	24,000	1480	1,260,000		2,630,000
2010	858	394	51,300	25,000	1440	1,240,000		2,630,000
2011	934	412	51,100	21,900	1380	1,200,000		2,480,000
2012	719	410	49,100	20,200	1380	1,250,000		2,540,000
2013	934	362	49,100	22,000	1260	1,210,000	11,300	2,460,000
2014	759	274	48,500	24,500	1000	1,270,000	11,900	2,570,000
2015	1200	368	53,300	28,300	1450	1,330,000	12,800	2,730,000
Port Lambton								
2001	4060		57,500	26,600	1270	1,070,000		2,530,000
2002	3480		62,500	26,700	2320	1,230,000		2,820,000
2003	2580		57,800	22,500	2510	1,140,000		2,620,000
2004	2090		60,900	25,300	3140	1,170,000		2,580,000
2005	2580		59,900	27,200	2130	1,180,000		2,550,000
2006	1990		57,900	25,000	1560	1,170,000		2,530,000
2007	1440		51,500	21,500	1180	1,130,000		2,500,000
2008	1510	372	48,400	20,700	1160	1,200,000		2,470,000
2009	1900	424	52,200	24,500	1600	1,260,000		2,650,000
2010	1480	380	52,300	26,000	1700	1,240,000		2,650,000
2011	2350	404	53,300	24,200	1770	1,210,000		2,500,000
2012	2480	429	50,800	21,700	1850	1,250,000		2,560,000
2013	2740	370	50,300	23,700	1860	1,200,000	11,400	2,480,000
2014	1890	274	49,800	25,400	1540	1,260,000	12,100	2,590,000
2015	2020	338	53,200	28,900	1840	1,340,000	12,400	2,750,000

and Amherstburg Channels compared to the Mid-River. As an example, the distribution of TP values in cross-section is shown in Fig. 8a. The median TP concentration near the US shoreline was approximately 0.02 mg/L; along the Canadian shoreline the median value was approximately 0.015 mg/L and in the mid-River it was approximately 0.01 mg/L. This pattern of highest concentrations in the Trenton Channel, intermediate concentrations in the Amherstburg Channel and lowest concentrations in the Mid-River is observed for many other parameters (e.g., NH_3, Cl, TKN, SRP, TFP, and SO_4).

The spatial variability of water quality was especially pronounced for the nitrogen ($NO_3 + NO_2$ and NH_3) parameters. $NO_3 + NO_2$ was highest near the shoreline and most variable in the Amherstburg Channel, and NH_3 was notably higher in the Trenton Channel compared with other locations in the lower Detroit River (see Fig. 8b for NH_3; $NO_3 + NO_2$ data not shown). Because the largest wastewater treatment plant (WWTP) in North America discharges from the Detroit municipal area

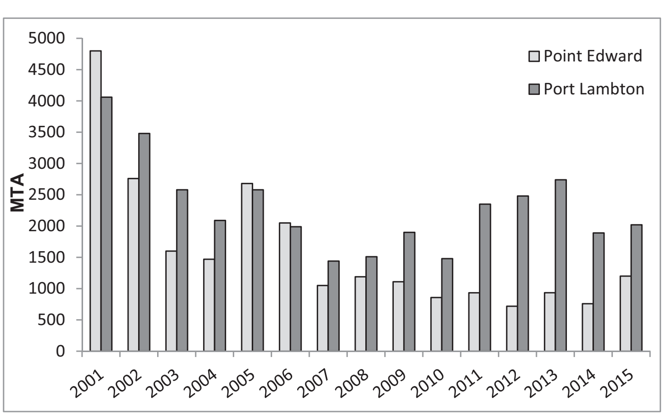

Fig. 7. Total phosphorus loads (MTA) in the St. Clair River at Point Edward (upstream) and Port Lambton (downstream), 2001–2015.

into the Trenton Channel, a wastewater source for the NH_3 pattern is suspected.

In coordination with this study, the USGS conducted monthly surveys in the Trenton Channel in 2014 and 2015 to better assess the vertical and horizontal variability of water quality constituents. They too found that the channel is not well mixed horizontally, with significant differences observed in concentrations with distance across the channel (Totten and Duris, in preparation). With the exception of suspended sediment which showed some heterogeneity in concentrations with depth, their investigations of spatial variability indicated homogenous distribution of constituents vertically in the channel, which supports our method of fixed depth sampling.

Although we have not monitored with sufficient resolution to statistically define temporal trends, the average concentration of TP in the Trenton Channel declined from 0.026 mg/L in 2007 to 0.019 mg/L in 2014 and 0.015 mg/L in 2015. TP concentrations now appear lower in the Trenton Channel compared to the Amherstburg Channel (where it was 0.023 mg/L in 2015). A decrease over time is noted for TP in the Mid-River as well (note that six mid-river stations were monitored in 2007 compared with two sites in 2014–2015). Conversely, TP concentrations in the Amherstburg Channel show a possible increase between 2007 and 2014–15, despite measurements being relocated upstream of the Amherstburg WWTP since 2007. Ongoing monitoring will be required in order to track water quality changes in the system.

Detroit River loadings

Although concentrations of most parameters are lowest in the Mid-River, almost one-half (45%) of the discharge is through the Mid-River, as reflected in the spatial distribution of the loadings (Table 6). The Mid-River accounts for between 30 and 45% of the total lower Detroit River load, for most parameters. Based on the intensive monitoring presented here, we compute the load of total phosphorus from the Detroit River to be 3740 MTA in 2014 and 2610 MTA in 2015.

Within the Trenton Channel, there was little variation in total load between the three cross sections in Table 6. For the majority of parameters, the Trenton Channel contributed approximately 20–30% to the total Detroit River load. In the Amherstburg Channel, the highest load was observed at A4, reflecting the greater river depth and higher node discharge. Loads from the Amherstburg Channel ranged from 30 to 40% of total river load, for most parameters.

Changes since 2007 indicate strong declines in the loading of TP from the Trenton Channel. Loadings of TP in the Trenton Channel have declined approximately 75% from an estimated 2250 MTA in 2007 (Burniston et al., 2009) to 705 in 2014 and 584 MTA in 2015 (Table 6). This decline reflects the reported decline in TP loadings from the Detroit Wastewater Treatment Plant (WWTP) and other point sources. Maccoux et al. (2016) report that the total point source loading of TP in the Huron-Erie corridor declined from 1800 MTA in 2007 to approximately 1100 MTA in 2013, the most recent year reported, and note dramatic improvements for the Detroit WWTP. However, this reported decline of approximately 700 MTA since 2007 comprises less than one-half of the 1550–1670 MTA reduction in Trenton Channel TP load that is measured here, indicating that the reported WWTP discharge values may underestimate the true magnitude of the declines, additional point source declines may have occurred in 2014 and 2015, or other significant loading declines may be occurring at the same time. Our data indicate that the contribution of the Trenton Channel to the TP loading in the Detroit River has declined from approximately 50% in 2007 (Burniston et al., 2009) to <25% in 2014 and 2015 (Table 6).

Loadings of SRP in the Trenton Channel also declined markedly over the same time period. In 2007, SRP made up almost half of the reported TP load in the Trenton Channel (Burniston et al., 2009); in 2014 and 2015, SRP accounted for only 8 and 18% of Trenton Channel TP loads in 2014 and 2015, respectively. Because SRP is not generally included

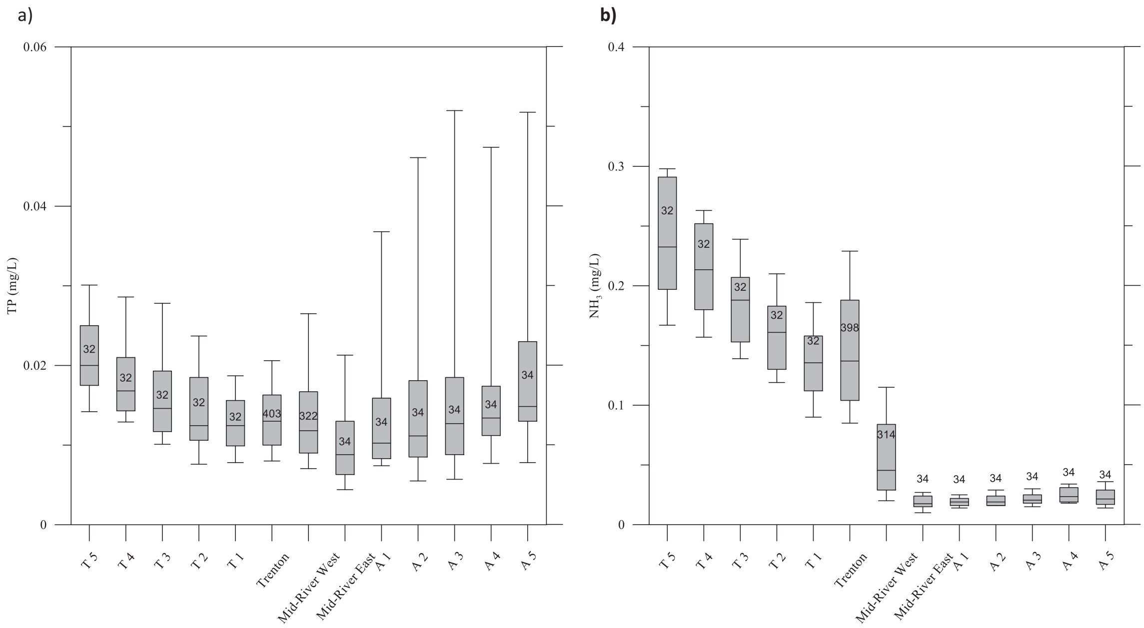

Fig. 8. Distribution of raw a) TP and b) NH_3 concentrations from west (left) to east (right) in the lower Detroit River in 2014 and 2015. Boxes represent median (horizontal line) and 25th and 75th percentiles, and whiskers represent 10th and 90th percentiles of all data. Lowest and highest 10% of data not shown. Sample sizes are indicated within or immediately above the boxes. Sampling locations are shown in Fig. 2. Note that the Trenton automated sampler is co-located with T1.

in point source reporting, Maccoux et al. (2016) estimated that SRP accounts for approximately 70% of TP in municipal point source effluent due to the high biological activity of effluents. The SRP load from point sources is not monitored and reported to the same extent as TP, but the SRP load has likely declined concurrently with the recent WWTP improvements noted with respect to TP.

In contrast, a comparison of 2007–2015 values indicates TP loadings in the Amherstburg Channel may have increased over time. In 2007, both concentrations and loadings of TP from the Trenton Channel were greater than those observed in the Amherstburg Channel, but the current study indicates somewhat higher concentrations and loads are now observed on the Canadian side. We note a concurrent (2007–2015) increase in discharge of approximately 10% throughout the Huron-Erie corridor (see Table 2), and also caution that more data are needed in order to confirm any Detroit River TP loading trends.

Few additional studies have monitored in a manner that is sufficient to report on water quality concentrations and annual nutrient loadings in the Detroit River. The MDEQ monitored phosphorus concentrations at the head (STORET #820414) and mouth (STORET #820017) of the Detroit River on a monthly basis from April–November during the years 1998–2008 (MDEQ, 2013). The upstream location, situated on the American side in the Fleming Channel at the head of the Detroit River, may not have captured all inputs from eastern Lake St. Clair. The downstream site, located mid-river as it spills into Lake Erie, may similarly have omitted the higher nearshore signatures. MDEQ (2013) reported significantly higher concentrations downstream relative to upstream, but not in all years. A full accounting of loadings is not provided, but the 2008 exit load for the corridor was reported to be 2000 MTA. This load is lower than that monitored here, indicating that spatially-explicit, cross-sectional sampling is required to more accurately capture the in-river load.

Huron-Erie corridor total phosphorus loadings

A major finding of this work is that the loading of phosphorus from Lake Huron to the Huron-Erie Corridor has been grossly underestimated in the past. In the absence of the monitoring data presented here, loadings from Lake Huron to the St. Clair River were previously estimated using the spring, surface offshore water quality concentrations measured during ECCC's Great Lakes Surveillance cruises, which are conducted approximately every two to three years, and multiplied by the annual flow in the St. Clair River. These relatively crude estimates of 419 MTA for 1994–2008 (Dolan and Chapra, 2012) and 321 MTA for 2008–2013 (Maccoux et al., 2016) are roughly three-fold lower than the monitoring data here indicate (mean 980 MTA in 2014 and 2015).

As well as demonstrating the entry and exit loads in the corridor, the current study illustrates the water quality changes that occur along the length of the corridor (Fig. 9). Despite only marginally higher discharge, TP loads are twice (2015) to 2.5 times (2014) greater exiting the corridor at the mouth of the Detroit River compared to the upstream input at Lake Huron. This indicates significant inputs of total phosphorus along the corridor. Foundational studies in 2007 (Burniston et al., 2009) determined the majority of the increase at the time was in the Detroit River compared to the St. Clair River; here, we estimate nearly equivalent contributions from each connecting channel in the corridor during 2014 and 2015.

The data for 2014–2015 indicate that TP loading from the Detroit River to Lake Erie is in the range of 2610–3740 MTA (Table 6). This is in excellent agreement with the Maccoux et al. (2016) estimate for the Huron-Erie corridor that was computed by summing all major inputs (tributaries, point sources and atmospheric deposition) for the 2003–2013 time period. Although a direct comparison is not possible due to the different time periods estimated, after adjusting the incoming load from the estimated constant of 321 MTA (since 2008) used in the Maccoux work to our measured mean 2014–2015 load of 980 MTA, the revised Maccoux et al. load of approximately 2900 MTA indicates excellent agreement with the monitoring approach conducted here. This is somewhat surprising, especially given the high uncertainty due to insufficient tributary monitoring and the underlying assumption of conservative behavior for TP as identified in the Maccoux et al. work. In contrast, the monitored SRP loads in the Detroit River (314 MTA in 2014 and 399 in 2015; Table 6) are much lower than the long-term (2009–2013) average of 1085 MTA tabulated by Maccoux et al. (2016). For SRP in particular, transformations and uptake likely complicate any mass balance approach; we submit that a direct monitoring approach is superior. Our monitoring results suggest that the Huron-Erie corridor is slightly more important to the Lake Erie phosphorus budget

Table 6
Detroit River Loadings, 2014 and 2015 (MTA). Values are rounded to three significant figures.

Panel	TP		TFP		SRP		$NO_3 + NO_2$		TKN		NH_3		Cl		F		SO_4	
	2014	2015	2014	2015	2014	2015	2014	2015	2014	2015	2014	2015	2014	2015	2014	2015	2014	2015
T5	162	134	38.8	45.6	15.5	27.0	2320	2340	2730	2860	1650	1530	140,000	130,000	599	595	116,000	122,000
T4	162	134	36.8	43.1	15.4	26.9	2440	2460	3010	2900	1650	1530	130,000	121,000	648	604	125,000	130,000
T3	153	126	33.7	39.4	13.1	22.8	2460	2410	2910	2690	1550	1370	122,000	113,000	654	650	126,000	131,000
T2	158	131	33.6	39.2	12.3	21.3	2800	2810	2850	2870	1670	1400	135,000	125,000	954	730	146,000	151,000
T1	70	59	14.5	17.4	4.85	8.61	1360	1400	1390	1330	680	593	63,000	59,200	345	352	70,800	74,800
Total Trenton Channel	705	584	157	185	61.1	107	11,400	11,400	12,900	12,700	7200	6420	590,000	548,000	3200	2930	584,000	609,000
Mid-River West	326	200	40.9	47.5	8.83	17.7	4550	4180	3710	3810	1010	1010	175,000	176,000	1130	1190	230,000	256,000
Mid-River East	1250	637	208	207	74.5	130	43,800	31,800	15,500	13,000	1470	1890	683,000	632,000	5330	5180	1,090,000	1,090,000
Total Mid-River	1580	837	249	255	83.3	148	48,300	36,000	18,200	16,800	2480	2900	858,000	808,000	6460	6370	1,320,000	1,350,000
A1	186	164	25.6	23.9	8.84	12.2	6700	3830	1640	1460	160	178	77,000	76,100	652	660	134,000	135,000
A2	334	253	58.3	47.2	45.0	19.7	9320	6850	2650	2540	276	311	130,000	126,000	1050	1040	217,000	216,000
A3	334	291	76.8	63.1	44.5	43.0	11,400	10,200	3070	3010	335	412	142,000	164,000	1180	1240	232,000	261,000
A4	353	296	80.7	76.7	50.4	41.7	14,000	10,200	3660	3310	372	443	160,000	170,000	1270	1240	266,000	265,000
A5	254	190	46.1	48.4	20.9	27.0	7420	6520	2310	2190	283	285	128,000	120,000	801	766	170,000	165,000
Total Amherstburg Ch.	1460	1190	287	259	170	144	48,400	37,600	13,300	12,500	1430	1630	637,000	656,100	4950	4950	1,020,000	1,040,000
Total Detroit River	3740	2610	693	699	314	399	108,000	85,000	44,400	41,900	11,100	10,900	2,090,000	2,010,000	14,600	14,300	2,920,000	3,000,000

than previously estimated. We now estimate that the Huron-Erie corridor delivers approximately 30% of the total TP load to Lake Erie, and about half of the total TP load to the western basin.

Conclusions and recommendations

At the head of the St. Clair River at Point Edward, the long-term trends of major ions and nutrients follow those from Lake Huron upstream, but concentrations of most parameters are higher compared to offshore, indicating that dedicated in-river monitoring is necessary to track loadings entering the Huron-Erie corridor. Loadings were previously calculated to be 321 MTA in 2008 using offshore Lake Huron concentrations (Dolan and Chapra, 2012) but are demonstrated here to have been approximately three times greater (Table 3). The difference is likely due to higher suspended solids in the interconnecting channel that contribute particulate phosphorus from nearshore Lake Huron and local sources.

Downstream in the St. Clair River at Port Lambton, concentrations of TP, $NO_3 + NO_2$, NH_3 and SO_4 monitored on the Canadian side are significantly greater than upstream, indicating local (watershed) sources to the St. Clair River. For TP and NH_3, the watershed load appears to be increasing over time and for TP, particulate sources are indicated. Monitoring data from the MDEQ for the US side indicate increased concentrations downstream compared to upstream, and US values appear to be lower compared to the Canadian side of the river, but recent data have not been assessed. Binational interagency cooperation is recommended to obtain loadings estimates that are based on data collected from locations that are representative of the spatial distribution of constituents across the river, at a frequency that is sufficient for accurate loading estimates and which includes the winter and spring months in order to track spring and annual indicators as loading reductions are implemented in the watersheds in the coming years.

In the Detroit River, previous studies by ECCC in 2004 and 2007 laid the foundation for the current investigations. At the time, concentrations of TP in the Trenton Channel were significantly greater than other locations in the lower Detroit River. However, the 2014–2015 data shown here indicate this is no longer the case; indeed, TP loadings from the Trenton Channel in 2015 were roughly only one-quarter of those measured in 2007 (Fig. 9). In the Mid-River section, concentrations and loadings have been similar over time or have declined, reflecting declining TP in the upper Great Lakes. In the Amherstburg Channel, however, no decline in loadings is observed, and a possible increasing trend is suggested.

The spatial distribution of most nutrients in the lower Detroit River indicates lowest concentrations in the Mid-River section, with values there approximately equivalent to those monitored at the mouth of the St. Clair River at Port Lambton. In the Trenton Channel, concentrations of NH_3 remain elevated and $NO_3 + NO_2$ remain low despite the reduction in TP.

The load of total phosphorus exiting the Detroit River into Lake Erie is estimated here to be 3740 MTA (2014) and 2610 MTA (2015); these loads are more than twice those observed at the input to the corridor at Lake Huron. We estimate that the Huron-Erie interconnecting channel delivers approximately 30% of the TP load to Lake Erie, and accounts for approximately 50% of the TP load to the western basin.

The upstream/downstream monitoring in the St. Clair River has provided important information about water quality trends and loadings. The data indicate significant sources of TP to the river, and increasing loads at the downstream location, despite the declining inputs from Lake Huron. Follow up to determine the potential causes for these in-river changes is warranted. We recommend that monitoring program in the St. Clair River continue, with the addition of SRP monitoring as feasible. In the Detroit River, a concerted effort is needed to establish and maintain monitoring of nutrient concentrations and loadings. This information will be increasingly sought after to track progress as Domestic Action Plans are implemented to reduce nutrient loadings, on

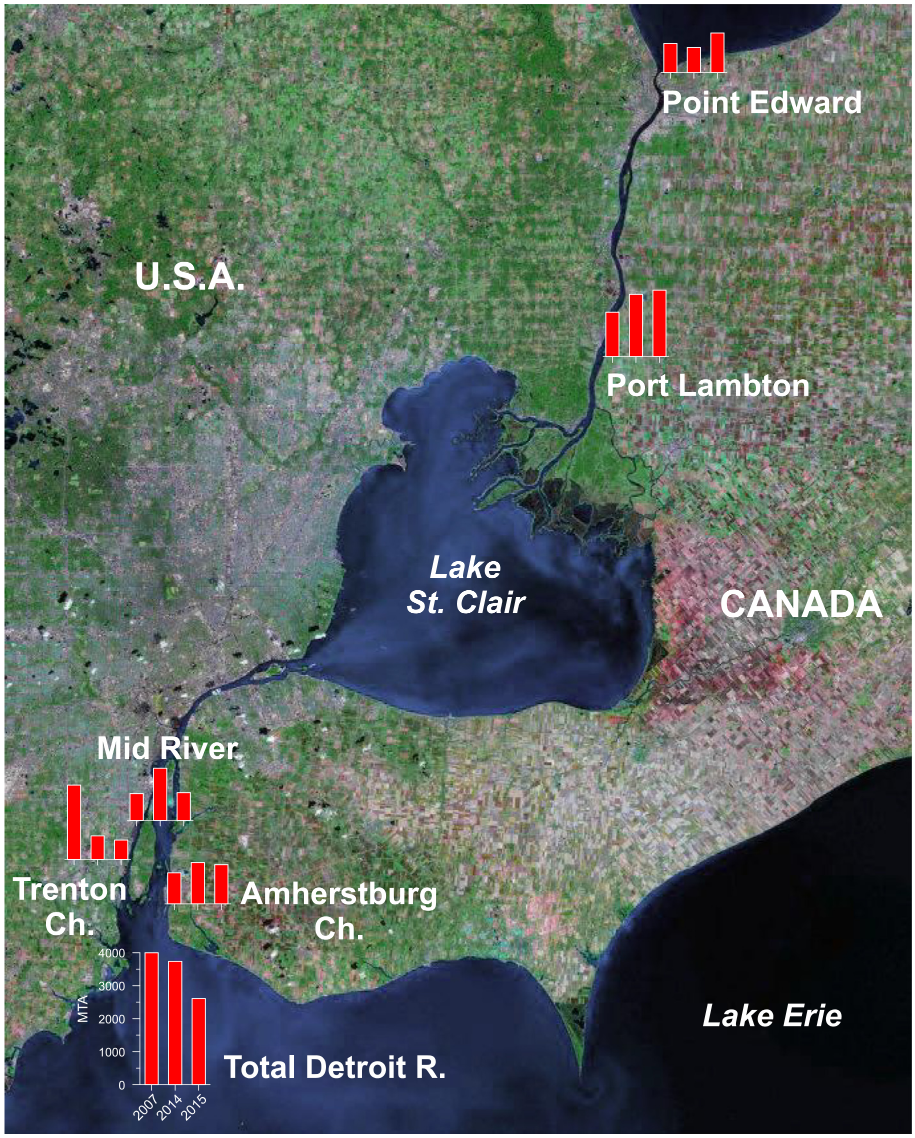

Fig. 9. Summary of TP Loads in the Huron-Erie corridor. 2007 data are from Burniston et al. (2009). All values are total load in MTA calculated at the station indicated; the total Detroit River load is the sum of three lower Detroit River channels. The x-axis legend and y-axis scale are as shown for the total Detroit River.

both sides of the international border. Dedicated efforts will be required to continue this important work.

Acknowledgments

Conducting this work in the St. Clair and Detroit Rivers has been logistically and operationally challenging due to the very high river flows, the large areas to be surveyed and the complex features of the physical environment. As the late Prof. David Dolan said, “If monitoring nutrient loadings in the Detroit River were easy, it would have been done already.” The authors wish to especially thank the Technical Operations Services of ECCC for the installation and maintenance of the intake lines and for conducting the cross-sectional surveys. We thank Amherstburg Island Developments for access and space to install samplers on the Amherstburg Channel. On Grosse Ile, USA, we thank Edge Marina on the Trenton Channel and a private partner on the eastern shores for permitting us to install and maintain the automated water quality samplers on their properties. We thank Sandrina Rodrigues and Olivier Champoux from the National Hydrologic Service for their collaboration in computing Detroit River discharge. We thank Jan Cibrowski and Jesse Gardener Costa from the University of Windsor for assisting with operating and troubleshooting the water quality samplers. A number of people contributed to the oversight and operational aspects of sample collection, transportation, processing and data tracking. We thank Vi Richardson, Jesse Baillargeon, John Kraft, Andrew Mummery, Allison Puhl and the 2014 and 2015 students at the Water Quality Monitoring and Surveillance Division of ECCC. We acknowledge Rose Ellison (USEPA) for her assistance scouting locations and facilitating water quality sampler installations on Grosse Isle. From USGS, we thank Dick Bartz, Joe Duris and Chris Hoard for their collaboration in the Trenton Channel. The authors acknowledge the technical expertise of staff at ECCC's National Laboratory for Environmental Testing. Water quality monitoring in the St. Clair River is supported by Freshwater Water Quality Monitoring at ECCC and the work in the Detroit River in 2014-2015 was supported by ECCC's Great Lakes Nutrients Initiative.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jglr.2018.02.005.

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