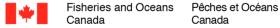
Multivariate analysis of the 40 year Project Quinte biogeochemistry dataset: water chemistry, physical characteristics, seston and climate

W.J.S. Currie and M.M. Frank

Great Lakes Laboratory for Fisheries and Aquatic Sciences, Central and Arctic Region, Fisheries and Oceans Canada, 867 Lakeshore Road, Burlington, ON, L7S 1A1

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Canadian Technical Report of Fisheries and Aquatic Sciences

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Great Lakes Laboratory for Fisheries and Aquatic Sciences, Central and Arctic Region, Fisheries and Oceans Canada, 867 Lakeshore Road, Burlington, ON, L7S 1A1

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TABLE OF CONTENTS

TABLE OF CONTENTS	iii
ABSTRACT	iv
RÉSUMÉ	iv
INTRODUCTION	1
STUDY SITE AND METHODS	1
RESULTS AND DISCUSSION	6
TIME SERIES	6
Physical Environment	6
Carbon	8
Nutrients	10
Dissolved water chemistry	12
MULTIVARIATE ANALYSIS	13
Correlations	13
Discriminant Analysis	16
SEASONALITY	16
CONCLUSION	19
ACKNOWLEDGEMENTS	21
TABLES	26
FIGURES	31

ABSTRACT

Currie, W.J.S. and Frank, M.M. 2015. Multivariate analysis of the 40 year Project Quinte biogeochemistry dataset: water chemistry, physical characteristics, seston and climate. Can. Tech. Rep. Fish. Aquat. Sci. 3125: vi: + 65p.

This report documents 40 years of biogeochemical data collected for Project Quinte. Since the 1970s, the Bay of Quinte (BoQ) has been listed as impaired due to eutrophication, though phosphorus controls and ecosystem changes have resulted in increased clarity (Secchi disc depth and light attenuation). In 1995, the Bay of Quinte shifted from a turbid to clear-phase state and currently macrophyte density remains high. Total phosphorus and nitrogen concentrations have declined, though soluble phosphorus levels remain high. Co-limitation by nitrogen in the BoQ is suggested by high correlations between TKN and seston. Summer chlorophyll values declined more than during the spring. Sodium, chloride and conductivity levels increased within the Bay of Quinte, possibly sourced from urban de-icing operations. Very cold winters of 1977-1978 and 1994 may have resulted in reduced system productivity while recent increased temperatures and precipitation variability post-1999 have changed the timing of nutrient peaks to earlier in the year.

RÉSUMÉ

Currie, W.J.S. and Frank, M. 2015. L'analyse multivariée de l'ensemble des données biogéochimiques recueillies au cours de 40 ans pour Projet Quinte: chimie de l'eau, caractéristiques physiques, seston et climat. Can. Tech. Rep. Fish. Aquat. Sci. 3125: vi: + 65p.

Dans ce manuscrit se trouve 40 ans de données biogéochimiques recueillies pour Projet Quinte. Malgré le contrôle du phosphore et les changements dans l'écosystème qui ont abouti à une augmentation de la clarté de l'eau (profondeur de Secchi et atténuation de la lumière), la Baie de Quinte, depuis les années 1970, est considéré détériorée, suite à l'eutrophication. En 1995, la baie de Quinte a passé d'un état d'eau turbide à un état d'eau clair. À ce moment, la densité de macrophytes reste élevée. Les concentrations totales du phosphore et de l'azote ont diminué, mais le niveau de phosphore soluble reste élevé. Colimitation par l'azote dans la Baie de Quinte est suggérée par des corrélations élevées entre TKN et le seston. Le niveau de chlorophylle a diminué plus au cours de l'été qu'au cours du printemps. Les niveaux de sodium, de chlorure et de conductivité ont augmenté dans la baie de Quinte, probablement comme résultat des opérations de dégivrage urbaines. Les hivers très froids de 1977-1978 et de 1994 ont peut-être abouti à la productivité réduite du système. De plus, l'augmentation récente de la température, ainsi que la variabilité augmentée des précipitations après 1999, ont modifié le calendrier de pics nutritifs à plus tôt dans l'année.

INTRODUCTION

Project Quinte is a collaborative study investigating biological and physico-chemical changes to the Bay of Quinte (BoQ) since 1972. The impetus for the study was the increased concern over the highly eutrophic conditions within the bay during the late 1960s and early 1970s. In the early years, Project Quinte was involved primarily in tracking the improvements associated with phosphorus controls and a special publication was devoted to this driver (Minns et al. 1986). In a recent special issue on the nearshore in Lake Ontario, changes in water chemistry and major ions have been analysed for coastal areas around the lake (Chapra et al. 2012, Makarewicz et al. 2012, Winter et al. 2012), but little attention has been given to the extensive physical and chemical water properties that were measured in embayments such as the BoQ beyond phosphorus, clarity (Secchi and light attenuation) or chlorophyll-a (Minns et al. 2004, Nichols 2012, Kim et al. 2013).

This report emphasizes biologically relevant geochemical measures, specifically interannual changes over the entire series, climatic forcing and regime shifts associated with invasive species and regrowth of macrophytes. Identification of the primary physical forcings and strong correlations between measures can also provide insight into which measures can be best used to characterize the biogeochemistry. To date, there has been no comprehensive publication which catalogues the extent of the biological (including under-reported seston data), physical and water chemistry data which were collected as part of the station sampling undertaken by Fisheries and Oceans Canada (DFO) in the Bay of Quinte since 1972. The objective of this report is to provide a detailed analysis and source of expanded information for the more concise publication found in the Ecology of the Bay of Quinte monograph (Currie and Koops 2015).

STUDY SITE AND METHODS

The Bay of Quinte is a long (90km) Z-shaped embayment separated from the eastern (Kingston) basin of Lake Ontario by a steep bluff barrier that forms Prince Edward County (Fig. 1). The shape of the BoQ is the result of multiple glacial scouring and outflows through shaley limestone deposits (Sly 1986). Water depth increases along the axis of the bay from very shallow conditions of 2 m near Trenton (T) to 60 m near the outlet by Amherst Island. The upper bay is characterized by mid-channel depths of 4-6 m until Napanee (N), where it transitions to the middle bay at 7-9 m in the Long Reach down to the Hay Bay arm. South of Hay Bay is a strong widening of the BoQ forming the lower part of the Z-shape encircled by embayments including Carnachan and Picton (P) Bays where the depth increases slightly to 10-12 m. The lower bay stations are to the east of Picton where the depth increases rapidly in the Adolphus Reach down to 20-21 m at Glenora (GL), 26+ m at Conway and 60 m at Lennox (LE).

The Belleville site was chosen as representative of the eutrophic conditions of the upper bay. The shallow location (5 m) is well-mixed and influenced by discharge flows and loadings of proximate rivers: the Moira (2.5 km) which flows through the City of Belleville and the much larger Trent River which flows through the City of Trenton (19 km)

upstream). The two tributaries account for 60-75% of the external phosphorous loadings to the BoQ (Kim et al. 2013). The City of Belleville had a stable population from 1971-1991 (~35 000) but increased by 30% (~46 000) by 2001 and has stabilized since, while Trenton (now Quinte West) and other settlements in the BoQ have not changed in population significantly over this time period (Statistics Canada, 2011). It is this upper bay section of the BoQ that has been most afflicted by blooms of algae including severe cyanobacterial blooms, but these can occur throughout the BoQ (see Nicholls 2002 for a historical perspective).

Hay Bay (HB) station is the middle bay transitional site located at the southern end of Long Reach and the outlet of Hay Bay. The site has complicated hydrology with water flows coming in from the upper bay, Wilton Creek which flows into Hay Bay and periodic intrusions of deep water from the lower bay (pers comm. Ram Yerabundi, Environment Canada, CCIW). Due to its greater depth (11-12 m), HB normally stratifies during the summer (Minns et al. 2011) and as a result can occasionally have higher biomass of phytoplankton and zooplankton than occurs in the eutrophic upper bay (B) location. While many measures are very similar to the Belleville location, some measures are more similar to that found in the outer bay station Conway.

Conway (C) was used as the lower bay station and reference condition for the AOC because it shows little effects of eutrophication. This station is however profoundly influenced by layered exchange flows of Lake Ontario water driven by the lake's seiche, circulation and wind-forcing (Freeman and Prinsenberg 1986). The station at Conway has historically been located off the mid-channel on a wide-shelf of 35 m depth even though the maximum depth is closer to 50 m. That location was chosen early in Project Quinte due its proximity to a benthic sampling site and sampling constraints with equipment which prevented water columns from being sampled deeper than 35 m. A decision was made to maintain the location for consistency throughout the project history. Conway was sampled continuously until 2009 when it was dropped due to time and resource constraints. The initial reasoning was that values from Station 81 (LO81). which was being sampled biweekly jointly by DFO and the Ontario Ministry of Natural Resources starting in 2007, could be used as a reference condition (outside the Area of Concern). However due to concerns that the zooplankton community is different between LO81 and Conway the sampling for this station has been reinstated for some measures on a monthly basis starting in 2013.

Two other stations have been sampled more than half of the years of Project Quinte. Napanee (N) station is the last station in the upper bay, near the transition to middle bay, located across from the town of Deseronto. The station characteristics are influenced by the Napanee River input coming from the east. Sampling here has been intermittent (Fig. 2) with a long gap in the mid-80s to 90s. Glenora (GL) is situated across from the OMNR Glenora Fisheries Station and is the first station considered to be in the lower bay and except for a gap in the mid-80s, this station was sampled until 2008. Glenora exhibits layered flows, with the hypolimnion being quite distinct from the epilimnion, amplified by the rapid change in bathymetry (Freeman and Prinsenberg 1986). It was felt that this station reflected either HB or C station conditions depending

on the nature of the flows on that day, so was deemed redundant and regular sampling of this station ceased in 2005.

The other sites were sampled for much shorter periods of time. The uppermost bay location, Trenton (T) was sampled until 1980 and again in the early 90s but was discontinued as a station because it was felt it was more reflective of the dynamics of the Trent River rather than the BoQ itself, and sampling was increasingly hampered by the increase in macrophyte growth. The other stations, Picton (P) and Lennox (LE) were only sampled until 1978. More recently the sampling of these stations in 2010 noted on Fig. 2 was completed for 3 weeks only (spring, summer and fall) as part of a spatial sampling program.

While methodological changes have occurred since sampling started in 1972, (mainly in equipment or analytical procedures), biological (e.g. phyto- and zooplankton, benthos), physical (e.g. light attenuation, mixed depth) and water chemistry (e.g. ions, pH) data are collected annually from spring to fall (May-Oct). Timing of the first sampling trip is determined by the readiness of vessels and the ice conditions of the Bay, so while a few samples occur in the month of April, the earliest samples are generally collected during the first two weeks of May. Approximately 40 biogeochemical measures result from this sampling program (Fig. 2 bottom). Only Belleville (B) and Hay Bay (HB) have been sampled every year continuously during Project Quinte while Conway (C) was sampled continuously until 2009. Samples were also collected from 2 less frequently sampled sites; Napanee (N) and Glenora (GL), and 3 occasional locations, Trenton (T), Picton (P) and Lennox (LE) (Fig. 2). From 1972 – 1981, sampling was weekly (~23 sampling trips/yr), but since 1982, sampling is biweekly (13 sampling trips/yr) due to resource constraints (Fig. 3). For most measures, biweekly sampling was generally as effective as weekly (Johansson pers. comm., and Minns 1984) and resources were required for weekly sampling associated with the Bioindex program which began in 1981 (Johannsson et al. 1998).

A detailed description of sampling methods is provided in the Project Quinte Annual Reports and other sources (see Minns et al. 1986; Millard et al. 1995; Graham et. al. 1996), but a summary of sampling methods is included here. For standard station sampling, a depth-integrated water sample is collected from the epilimnion using a glugglug sampler consisting of 4 open bottles lowered within a frame. For shallow stations (eg. B, N) which are less than 10 m, water was exclusively collected in the euphotic zone, to twice the Secchi depth up to a maximum depth of 1 m off bottom. For deeper stations such as HB and C, when unstratified, water was collected at twice the secchi disc depth to a maximum depth of 5 and 7 m, respectively. When stratified, water was collected at twice the secchi disc depth to a maximum of 1 m above the epilimnion. With the shift to increased water transparency in the Bay in the late 1990s this sampler would often not sample the entire epilimnion/euphotic zone (being limited to sampling depth of ~7 m max) but for consistency of the time-series it was decided to retain the existing methodology.

In some years, at deeper stations water is taken 1 m off the bottom and at station middepth using a Van Dorn bottle to compare against the integrated water sample, but this dataset has not been evaluated for this technical report. Water is stored in large carbuoys which are insulated and darkened with neoprene covers, kept on ice and any processing such as filtration are done at the end of the sampling day. Raw (unfiltered) water for processing at the Ontario Ministry of the Environment (OMOE) is subsampled from the carboys at the time of field sampling, and delivered or couriered to the OMOE analytical lab in a darkened state in coolers, with ice and no chemical preservation. Phytoplankton samples sent to the OMOE are also collected with this carboy water, preserved with Lugol's solution, and forwarded in the same containment as per water chemistry. In recent years, phytoplankton samples have been maintained and analyzed by DFO. Since 2000, Van Dorn casts were taken at discrete depths which are pooled to sample microbial loop and rotifers. Other measures taken at each station include Secchi disc depth, k_d light attenuation using a Licor PAR sensor (referred to as εpar in some DFO reports), a temperature profile using a hydrographic telethermometer, and later, an M-series Hydrolab sonde cast (for temperature, dissolved oxygen, conductivity and pH) and zooplankton sampling with multiple depth Schindler-Patalas traps.

In the earlier years of Project Quinte, water processing was done onboard a number of the larger research vessels (e.g. Bayfield IV or Limnos). By the 1990's sampling was done on small vessels and water samples were transported from the field to the Glenora Fisheries Station (Ontario Ministry of Natural Resources) in Picton for all water processing by DFO staff. After 2009, samples were transported back to the DFO facilities at the Great Lakes Laboratory for Fisheries and Aquatic Sciences (GLLFAS) in Burlington, Ontario for processing. As part of an interagency agreement, unfiltered station water was shipped to the OMOE lab for water chemistry testing (with a delay of approximately one day). A number of measures were also conducted at the National Laboratory for Environmental Testing (NLET) at CCIW since 1988, providing additional validation for some parameters.

The dataset contains values from a number of analytical laboratories and different agencies (OMOE, NLET, DFO-GLLFAS) with different parameters and methodologies in regards to sample storage, time to analysis and preservation and filtering of samples. For instance, the OMOE water chemistry samples are filtered at their laboratory, and the water is not preserved during transport while awaiting lab processing. The NLET water chemistry samples, when required, are filtered on the date of sampling or the following day and preserved immediately (e.g. all phosphorus samples are preserved with 1% sulphuric acid prior to sending to NLET for testing). The OMOE focus is for total parameter concentrations whereas DFO focuses on dissolved parameter concentrations. Whether a sample is filtered (dissolved) or not (total) is noted in Fig. 2. Also, some analytical procedures only take place after the late 1980s (NLET) and there are variations between stations and years for parameters analyzed for all agencies; some are no longer being measured (e.g. total nitrogen). As a result, only some parameters and stations have been sampled for the entire period whereas many have gaps where they were not measured or dropped entirely (Fig. 2).

As mentioned previously, seston samples in the past were filtered either on board ship or at the Glenora Fisheries Station; more recently filtering occurred at GLLFAS. While seston sampling for BoQ has been discontinued since 2008, filtering of BoQ chlorophyll a samples at GLLFAS continues. Seston data from the BoQ have not been published previously so methods are briefly mentioned here. Standard particulate carbon procedures were used which involved filtration of 0.2-2.0 L (depending on station and season) of integrated water through double-distilled water rinsed, ashed, pre-weighed Whatman GF/C filters, which were dried overnight at 60°C, weighed (to obtain Dry Weight), ashed again at 480°C and reweighed (for Ash Weight), from which ash-free dry weight (AFDW) was determined. GLLFAS chlorophyll-a procedures have consistently used GF/C filters which are ground prior to extraction in acetone. While the protocols for GLLFAS remain the same, as noted in Nicholls et al. (1993), after 1985 there was a change in chlorophyll-a extraction procedure for the OMOE at which time unground 0.2 µm nylon filters have been used.

While some corresponding parameter values measured by OMOE and NLET or GLLFAS were different, most were quite congruent even with differences in methodology as shown by a comparison of values from Belleville (Fig. 4). With large numbers of samples for comparison, the standard errors can be guite small so while TP values were similar between OMOE and NLET they were still significantly different using 2-tailed paired t-tests (t=-6.42, p<.0001). It is important to note that the mean difference between the series was 0.0029 mg/L, which is extremely small given the reporting values are only to 3 decimals. While OMOE SRP values (Fig. 4) were consistently about 1.3-1.8x higher than those measured at NLET (paired-t, t=2.45, p=0.015), the differences were similarly small (0.001). The largest differences in SRP occurred in September but there is no difference over time (though the NLET and OMOE can only be compared from 1988-2012, $SRP_{MOE}=1.08*SRP_{NLET}+0.001$, $r^2=0.51$). Likewise, ammonia values measured by the OMOE lab were generally higher except for some high spikes in the NLET series (paired-t, t=7.45, p<0.0001). The correlation between these series is also quite low (0.22), NH3_{MOF}=0.32*NH3_{NIFT}+0.044, r^2 =0.05. This may well be due to the time delay associated with analysis of the OMOE samples which can permit additional SRP and ammonia conversion in the containers.

Chlorophyll-a (uncorrected) values from Belleville were consistently lower in the OMOE samples than measured at GLLFAS (~69%) until 1996 when the difference became minimal (~94%) with a paired-t values changing from -6.92 to -2.80 (p<0.0001, p<0.006). The largest differences between the measures, which show as the spikes in the GLLFAS series (Fig. 4) corresponds to values in August (see Seasonality below) prior to 1996 but since has occurred in September and October. Nicholls and Hopkins (1993) reported that the change in methods at OMOE in 1985 from cellulose-nitrate filters to nylon filters increased values by 35%, however we did not see a strong difference compared to the GLLFAS values (where protocols were not changed) in the periods from 1977-1984 (8.18 $\mu g \cdot L^{-1}$, CHL_{MOE}=0.65*CHL_{GLLFAS}+1.13, r^2 =0.79) vs 1985-1995 (6.84 $\mu g \cdot L^{-1}$, CHL_{MOE}=0.89*CHL_{GLLFAS}+0.82, r^2 =0.88). The reason why the values became congruent after 1996 with differences of only 0.9 $\mu g \cdot L^{-1}$ is not clear. Given a lack of confirmation one way or another on which chlorophyll-a value may be closest to

the real value, and the fact that the two series are highly correlated for the entire time period (r>0.90) we decided to utilize the longer time-series from OMOE for our analysis, and ultimately will focus on the seston results.

When multiple series were available from different agencies, the longest continuous time-series was selected. Very short (e.g. chlorophyll_a_corrected_DSMO) or highly discontinuous series were not examined. The data were initially examined to determine if any outliers occurred beyond those found during standard QA/QC. In all, 8 values were removed as a result of implausibility (>5 SD units) or clear deviation from a concurrent measure at a similar station. Correlation between measures was done on monthly averages. Only values from May-Oct were used, though some years early in Project Quinte had data collected in April or November. Strongly non-normal data were transformed using log or reciprocal transformation (noted in text). All statistical analyses of the data series were completed using JMP® v10 (SAS Institute Inc. 2012) or R v3.0.1 (R Core Team 2013).

RESULTS AND DISCUSSION

The data has been assembled in 3 major groupings: 1) physical and climate measures 2) carbon and particulates and 3) chemical measures including nutrients (Fig. 2). The physical measures include values such as temperature, dissolved oxygen and Secchi depth. The carbon and particulates grouping includes the biological components such as chlorophyll-a and seston, but also dissolved carbon (inorganic and organic) and particulate fractions of nitrogen and carbon. The chemical fraction includes those dissolved fractions commonly done in water quality analysis: pH, conductivity, total hardness, and dissolved fractions of the major nutrients nitrogen and phosphorus and micronutrients (silica, magnesium etc.). For comparative purposes some values are combined (for instance total phosphorus, Secchi depth and chlorophyll-a together) into 2 groupings of "biological-physical" and "water chemistry", with "climate" treated on its own.

TIME SERIES

Physical Environment

While the collection of meteorological data is not specifically part of Project Quinte, it helps to explain some of the time series in this section. Data included in this report were collected from the National Climatic Data Center (NCDC) for Trenton Air Force Base (CYTR). In Fig. 5, mean, max and min annual air temperatures are plotted with annual total precipitation and snow accumulation. Climatic forcings and other related effects that are potential drivers of biogeochemical measures are summarized in Table 1. Extremely cold winters were experienced in 1976-1977, 1979, 1987, and 1994. The winter of 1994 was by far the coldest in the time-series with 25 days below a mean temperature of -15°C. The coldest winters often did not have increased snowfall, but the colder winter period in the 70s to early 80s had more high snowfall years. 1988 was the driest year in the series though the 2000s had many low precipitation years (2001, 2007 and 2010) along with many years with elevated summer temperatures. The period post-

1999 exhibits much greater temperature and precipitation variability year to year, though summers were typically hot and wet, interspersed with years of cooler temperatures and low precipitation. Compared to the 1972-1998 period, since 1999 the summers have been hotter, though interspersed with cold wet summers. Using yearly averages, the period from 1999-2012 is 1.2 °C warmer than 1972-1985, but it is not significantly different from this or the 1985-1998 period (t-test, unequal variances, p>0.2). However, a linear regression with date gives a significantly positive slope with r^2 =0.31 (F=17.366, p<0.001). This is in part due to the variability in temperature across the year. When months are considered separately, for the period 1999-2012, mean temperatures are elevated for June (+1.3 °C, p<0.001), Sept (+1.7 °C, p=0.004), Oct (+1.2 °C, p=0.01) and Nov (+1.5 °C, p=0.004).

Monthly data are plotted as an annual boxplot time-series of all of the measurements taken at B, HB and C for Project Quinte (Figs. 6-17).

Surface water temperature change tracks that of air temperature due to the shallow well-mixed riverine resemblance of the upper bay. During the summer, stratification at the middle and lower stations reinforces two layer flows so Hay Bay surface temperatures are very similar to Belleville and Conway is not as cool as conditions within Lake Ontario. Matching air temperature, there has been a slight increase (+1.3°C) in epilimnetic water temperature since the early 90s. Dissolved oxygen in the epilimnion is generally supersaturated in the BoQ (Minns et al. 2011) and since saturation is driven mostly by temperature it has declined slightly in the same period, but still remains well above hypoxic conditions.

The mixing depth at each site has changed little over time (Figs. 6-8) though the summer of 1998 or 1999 indicated slightly shallower mixed depths. The deeper mixed depth at Belleville during the 1970s is likely related to changes in water levels since this location is generally well mixed. It is also known however that the location of especially the middle and lower bay (HB and C) stations have changed periodically. The station location is marked by a spar-buoy that is installed annually by Environment Canada technical operations and is driven by how much cable has been installed onto the prefabricated mooring rigging. The correct depth within a geographical range is then chosen for the mooring location so the location can vary considerably over time. This might very well affect the mixed depth values, especially for Conway. This is confirmed by looking at the station Depth values which clearly vary over time with Conway being closer to 35 m some years and 29 m in others (Figs. 6-8).

It has already been determined that the stability (stratification) of the Bay of Quinte water column has increased over the sampling time-frame (Minns et al. 2011) in part due to the epilimnetic temperature increase of 1.3°C, as well as other physical environmental factors. The periodicity in the precipitation output is likely to change the flow rates in the major tributaries, thus changing the loadings of nutrients to the bay (Minns and Johnson 1979). For the 1999-2012 period, the March precipitation is lower (75% of 1985-1998), while the mid-summer July precipitation is significantly greater (170%, mean > 90mm) (one-way ANOVA, F=7.08, p=0.02). This recent increase in

summer precipitation could change the flow and exchanges within the bay since flushing rate is highly dependent on river inputs. Rates of remineralisation might also be affected since this increased flow occurs during the hottest period of the year.

The measurements of water clarity have undergone drastic changes in the BoQ at all sites (Figs. 6-8). Conway is much more transparent than B or HB, which are more similar to each other. The Secchi depth has increased at all sites from the murky low in the 1970s, to slightly higher values in the 80s to a high in the mid-90s and have been steady at a slightly lower value since. At all of the sites there was a climb in Secchi depth value starting in the early 1990s and peaking by 1997. After 1997, there is much greater annual variability at all sites, most clearly seen at the C and HB sites (Figs. 6-8). After 1994 the Secchi depth value increases till 1997 when it plateaus at this higher level though it has slightly declined during this period. This pattern occurs first and strongest at Conway, with Belleville the last station to increase in value. Prior to 1996, the B and HB sites Secchi values were not significantly different but begin to deviate beginning in 1986 and this difference becomes slightly greater after 1995. The Secchi depth values have declined slightly since the peak in 1997, but still remain deeper than earlier periods at all sites (repeated measures (RM) ANOVA, B (F=51.7), HB (F=98.2), C (F=236), p<0.001). For comparison to other values (e.g. correlations), the Secchi depth data was transformed by reciprocal (exponent -1) to account for the non-linearity in the data. The reciprocal transformation yielded a much better fit than logtransformation (Fig. 18). This is due to the fact that light forms an exponential relationship with depth so inversion resulted in a strongly linear relationship with light attenuation.

The similar measurement of PAR light attenuation (k_d , Figs. 6-8) (% light absorbed or scattered per meter) data shows a more steady decline than found in the Secchi data since the early 70s to a minimum in 2003 in early 2000s. There is significantly increased water transparency at all sites post-1996 (RM ANOVA, F=256, p<0.0001). The value of k_d reached a minimum in the period 2001-2003 and though it has increased since, this difference is not significant. The value of euphotic depth is calculated from values used to calculate k_d (based on 1% surface light) so it tracks the light attenuation data (Figs. 6-8) demonstrating a much smoother deepening of the euophotic zone starting in 1990, rather than a sharp increase in 1995. There is a gap in measurement of this parameter in the 1980s but euphotic depth post-1996 is significantly greater than found in the 1970s or early 1990s (repeated measures ANOVA, F=210, p<0.0001).

Carbon

The carbon-related measures that include organismal activity have changed considerably since the start of Project Quinte (Figs. 9-11). Seston and chlorophyll-a values are examined here in more detail, but other organic carbon partition measurements: ash-free dry weight (AFDW), total phytoplankton biomass, and particulate organic carbon (and particulate organic nitrogen) all indicate similar patterns over time. Total phytoplankton biomass has large gaps but corresponds very well with the measurement of seston and AFDW. Particulate organic carbon and nitrogen values are not significantly different between B and HB, but are significantly higher than at C

(RM ANOVA, F=288, p<0.0001) For all measures, Conway's biomass measurements are consistently lower than upper and middle bay sites and have shown a slower decline over time. Except for the early years (72-77) when Belleville had consistently higher values, generally, the middle bay (HB) and upper bay (B) sites are very similar, and pre-1995 values were not significantly different in chl-a (RM ANOVA, t-comparison, p>0.09), with one or the other having a slightly higher value on any given year. The upper bay (B) has more annual variability than HB for seston and AFDW resulting in increased highs and lows, but the signal for chlorophyll-a is slightly different and indicates that the middle bay (HB) has a greater annual range of values but less year-to-year variability (Figs. 9-11).

Though patterns are similar, the seston and chl-a time-series also differ in their breakpoints, with seston showing a much stronger change in 1994. This may be due in part to the fact that the Bay of Quinte has very high levels of hetertrophic flagellates (Munawar et al. 2011) which will not show up in the chlorophyll-a signal. For the chlorophyll-a series, naïve partition analysis (in JMP) using Akaike information criterion (AIC) indicated that the best model to separate years is 1978 for B and 1993 for HB and C (Fig. 19). For seston the best AIC model uses 1995 for B (RMSE 3.36, AICc 1022, Δmean 3.97), HB (RMSE 2.25, AICc 844, Δmean 3.35) and 1994 for C (RMSE 0.78, AICc 448, Δmean 1.42). The changes in time stanza can be seen when looking at deviations of each year from the overall mean (Fig. 20). Belleville's higher variability means that it is easier to delimit time stanzas at the lower and middle bay sites HB and C but positive deviations (above average) in chlorophyll, seston TP and kd all occur before 1995 and all negative deviations (below average) occur post-1995. The pre-1995 period exhibits the highest levels of biomass with a precipitous drop in 1995 following the record cold winter of 1994 with 1996 showing the lowest annual measurements. A similar drop in chl and seston is seen following the cold winters of 1978 and 1986 (See Table 1 and Figs. 9-11). The period from 1997 exhibits a rebound to conditions approaching the 1980s, and has been slightly elevated since (Figs. 9-11). The post-1995 period is significantly different from the pre-1995 period for both seston and chl (RM ANOVA (chl-a F=27.2, seston F=78.8) with Tukey-Kramer comparisons, p<0.001), but while the recent rebound period post-2000 is slightly elevated it is not significantly different than the 1995-2000 period.

For dissolved carbon fractions (Figs. 9-11), the time-series is much shorter (1995-2012) but while there is little change in organic carbon beyond a drop in 1997-1998 observed at all stations, there has been a steady increase in inorganic carbon (DIC) at all sites. At B, this accounts for 5 mg/L (20%) increase since 1995. This occurs concurrently with the modest increase in particulate carbon so may be related to remineralisation effects in the years following the dry and cold winter in 1994. The increased temperatures since this year could also have increased bacterial production, but the increase in Dreissenid mussel biomass after 1999 could have also contributed to increased DIC (Heath et al. 1995, Barnard et al. 2006), though a simultaneous increase in DOC would have also been expected.

Nutrients

Nutrients measured for Project Quinte are separated into phosphorus and nitrogen groups, including the total fractions: total phosphorus (TP) and total Kjeldahl nitrogen (TKN), which are often the only forms considered (Minns et al 1986, Millard et al. 1995, Nicholls 2012). While regularly ignored in many analyses, the other biologically available nutrient species including micronutrients are included here because they can have different geochemical or anthropogenic sources (Heathwaite and Johnes 1996). Both nitrogen and phosphorus are found in much higher concentrations at HB and B than occur at C (Figs. 12-14). The BoQ is effectively a widened river with respect to the transport of substances, but the sediment water interface can also increase persistence of biologically relevant compounds (Diamond et al. 1994, Minns et al. 2011). Most of the total phosphorus loadings to the BoQ is sourced from 3 sewage treatment plants and 2 rivers upstream of the upper bay Belleville site (Nicholls 1999). TP has shown a steady decline since the 1970s but has not changed significantly since 1990 with values ~ 0.04 mg·L⁻¹ at B and HB and 0.01 mg·L⁻¹ at C (RM ANOVA, F=43.1, p<0.0001).

Phosphorus has three major forms which together give total phosphorus (TP) to include all inorganic and organic phosphorus: soluble reactive phosphorus (SRP) which is an immediately biologically available form, soluble organic (unreactive) phosphorus and particulate phosphorus. While B and HB are generally higher in SRP, the difference is much less pronounced than for other forms of phosphorus since SRP exhibits much more variability from year to year. While SRP has declined in parallel to TP from high values in the 1970s, it occasionally shows periods of higher concentrations. This is relevant because an increase in SRP is considered an indication of reduced phosphorus limitation (Nürnberg and Peters 1984). Years of increased SRP seem to follow years of very cold winters and reduced precipitation (1978, 1994) exhibiting a large increase in 1996, which has been maintained at around 12% of TP since at the upper and middle bay locations. The increased SRP response at HB (and C to some extent) is lagged by a couple of years from the upper bay, perhaps due to the difference in stratification and nutrient transport at these sites. The proportion of SRP can be seen in the SRP:TP ratio showing very low relative SRP 77-79, 91-92 and 05-06, suggesting production in these years was highly phosphorus limited (Fig. 21). Peaks of higher relative SRP persist for much longer periods (72-75, 80-91, 94-04) suggesting a change in system function, likely due to changes in sediment remineralisation. If biological activity is reduced following the cold winter, remineralized SRP from the sediments could increase during the summer leading to peaks that occur for that year (Nicholls 1999). SRP recycling peaks during the warmer summer when regenerated from the sediments, so is expected to change over the season when TP load from inflows are high (Robinson et al. 1986; Nicholls 1999, Minns et al 2004). This process is supported by higher SRP:TP ratios at HB and C than found at B since the mid-1980s, sourced from stored sediment phosphorus.

Total particulate phosphorus (TPP) and total filtered phosphorus (TFP) was only measured for a period from the late 80s to the late 2000s. As expected, TPP follows the pattern shown by chl-a or seston since these are the major particles that contain phosphorus in the surface waters except under high flow conditions (not shown). TFP is

related to SRP and shows a similar pattern at B and HB with a few years not matching with apparent elevated concentrations at C.

The role of nitrogen in the BoQ has received much less attention than that of phosphorus (though see Liao 1977), but there are strong patterns in a variety of nitrogen forms. The nitrogen cycle is more complex than phosphorus, including an atmospheric component and nitrogen has more forms. Total Kjeldahl nitrogen is the sum of all forms: organic nitrogen, ammonia (NH₃) and ammonium (NH₄⁺), nitrate (NO₃⁻) and nitrite (NO₂). TKN has shown the same steady decline as TP since the early 70s for all sites in the BoQ (Figs. 12-14) and is similarly significantly lower post-1995 (RM ANOVA, F=50.4, p<0.0001). Nitrate and nitrite were both at very low levels in the BoQ in the 1970s, suggestive of nitrogen limitation (Liao 1977) but has been reasonably stable except for a period of exceptionally high nitrite values from 1980-1983 (with the increase at B in 1981) with multiple peaks in July 1981 of greater than 0.25 mgL⁻¹ in the upper bay. This value is extremely high and is at the toxicity level for salmonids (Lewis and Morris 1986). The source of this nitrite spike is unknown but it occurred at all the BoQ sites. The largest fraction of TKN in the upper bay is often the "other" fraction which includes particulate and organic forms (Fig. 22) but has reduced over time. The largest dissolved nitrogen fraction, nitrate, has increased steadily in the BoQ but most strongly at the lower bay C site (Figs. 12-14 and 22) as influenced by the historical buildup of excess nitrate in the Great Lakes (Winter et al. 2012). Nitrate also indicated large spikes in 1981-1982 at B and HB, and an additional one in 2010-2011 in years following nitrite spikes, presumably resulting from nitrification. The middle and upper bay nitrate values have been similar since 1999, prior to this HB values were usually considerably higher than at B. Ammonia concentration tracks TKN over time but ammonia exhibits more variability than other forms of nitrogen with regular peaks in the annual series including periods of high concentrations from 1982-1989, again in 2005-2006. Though ammonia can have a variety of sources, it is often associated with decomposition of organic nitrogen, animal excretion and releases from sewage treatment plants.

A couple of nutrient stoichiometry ratios are relevant to briefly consider. The ratio of total phosphorus to combined nitrate and nitrite (TP:NO $_{2+3}$) can indicate if nitrogen is a limiting nutrient and whether nitrogen-fixing algal groups may have an advantage (Liao 1977). The very large spike in nitrite in 1980-1983 for B and HB and the steady increase in nitrate at C clouds this relationship, but the ratio of TKN:TP can be used instead, though this ratio has the downside due to the excess organic nitrogen fraction in the upper bay (Fig. 21). In the 1970s phosphorus was in excess, so TKN:TP ratios were very low, and it was not until the large increase in nitrogen 1975-1980 that the ratio was above 15. Generally, seston in freshwater stoichiometrically require 20x the amount of nitrogen (Sterner 2011), so much of this phosphorus should be unutilized. The N:P ratio remained high from 1976-1985, then drops again precipitously in 1986-1987, raises again and drops again in 2000. While phosphorus is not in excess recently as it was in the 1970s, the ratio P:N is still higher at B and HB than would be expected for biological uptake (Redfield 1958). The TP:NO $_{2+3}$ ratio indicates 3 main time stanzas, best seen in the HB data with the 1970s having excess TP, the 1980s to mid-1990s with excess

nitrogen and a return to excess TP since 1999 (though there is some indication of reduced TP ratio in the last years of the time series). The (TP: NO_{2+3}) ratio is extremely low (below 2) in 1986-1987 and 1996-1997. This suggests nitrogen limitation might be particularly relevant in 1986/87, 1996/97 and 2000.

Two potentially limiting micronutrients are examined here: silicate and iron (Figs. 12-14). Silicate can be limiting to certain classes of phytoplankton since silica is used to create the external cell wall (frustule) of diatoms. Diatoms are an important component to the phytoplankton community in the Bay of Quinte and silicate limitation has been suggested during the very high productivity years in the 1970s (Nicholls et al. 2002). Silicate was at low concentrations at station B in the early 1970s but has been fairly steady near 1.5 mg/L, though a few years have seen strong drops: in 1988 at all stations (Sept and Oct near detection limit ~0.05mgL⁻¹) and at B in 1995 (Sept ~0.15mgL⁻¹) and to a lesser extent in 1997, 2007 and 2012. The values in 2012 (Oct ~0.02mgL⁻¹) correspond to high fall chlorophyll-a values (>25 µgL⁻¹). The major source of dissolved silicate is likely to be via riverine influx, so this might be related to an effect of loadings in preceding years since 1988 and 1994 were years with low precipitation. Silicate decreases from upper to lower bay so biological uptake may be reducing concentration as water moves along the bay since values in Lake Ontario are likely to be higher than found in the BoQ (~0.3 mgL⁻¹, Winters et al. 2012). It is unlikely that iron will be limiting to growth of phytoplankton since this generally only occurs in highly oligotrophic waters but dissolved iron declined since the 1970s. The series is highly intermittent and is cut off in 1994 so little can be determined about iron beyond a reduction in concentration in the 1990s compared to the 1970s.

Dissolved water chemistry

Water chemistry reporting contains a range of measurements that include physical water characteristics, but are generally dissolved ions, including biologically important ones such as micro-nutrients. Many important water chemistry values have only been measured since 1995 including pH, total hardness, total calcium, whereas chloride and sodium, alkalinity and conductivity have been measured back to the 1970s (Figs. 2, 15-17). Other than the nutrient ions, the lower bay site C has higher values of dissolved fractions than occurs in the upper and middle bay sites. This is due to evaporation that takes place within the lake which concentrates the substances and additive loadings of conservative constituents (those trivial to biological reactions) from the rivers upstream in all of the Great Lakes (Chapra et al. 2012).

Alkalinity and conductivity (and pH for a shorter period) were relatively stable for much of the study, but exhibited decreasing values beginning in 1993 (B and HB) and recent increases starting in 2000 at all stations (Figs. 15-17). A drop in alkalinity, total hardness, calcium, pH was seen in 1999 during the very hot dry summer (Figs. 5, 15-17). There was also an increase in chl-a and seston values in 1999, so part of the chemical change could be due to increased algal production (Brewer 1975). The BoQ acts as an elongated freshwater estuary with layered flow in the middle and lower bay, so reduced flows and increased evaporation are more likely to concentrate substances rather than to reduce them. The 1980s was a period of stable precipitation compared to

the 2000s which has been much more variable in rainfall and warmer during the summer. This increase in alkalinity and conductivity is still low however, so buffering capacity has changed very little. The measurement of total hardness and total calcium only occurs post-95 but shows a similar pattern of increase of alkalinity at station B, though this increase is much less at the other sites. At site C, calcium and hardness decreased until 2006, then indicated an increase until sampling ended in 2009. Calcium hardness is the major source of total hardness in the BoQ, which is expected since the area has a foundation of limestone bedrock (Sly 1986). Hardness is sourced from the upper bay and the total hardness values of the lower and middle bay are now comparable, even though values in Lake Ontario have been dropping over this period (Chapra et al. 2012). Some calcium is also likely to be sourced from road salting activities but is likely a minor source.

Potassium, magnesium and sulphates show little discernable pattern over time, though these have only been measured since the regime shift in the BoQ which occurred post-1995. There was a drop in the potassium and magnesium values in 2008 at B and HB driven by values in Sept-Oct which are only 50% of the typical values. This might be related to 2008 being a very high precipitation and snow year, but the pattern does not show up in other dissolved constituents. Potassium and magnesium salts are sourced from weathering, but are also constituents of fertilizers and road salts, and there is some indication that there has been an increase in recent years which might match increases in other dissolved components (Ramakrishna et al. 2005; Chapra et al. 2012).

One pattern that is very clear for the dissolved ions in the upper bay is for chloride and sodium, both of which have significantly increased continually at all sites since the 1970s (most intensely at B and narrowly at HB) since the 1970s (RM ANOVA, F=58.8, p<0.0001). In the last years of the time series, there is a very sharp upturn in the concentration of both sodium and chloride at both B and HB. This is worth continuing to monitor. There is very little change at the lower bay site but there is a (non-significant) pattern of decline of chloride during the 1980s-1990s and some indication of a slight increase in sodium in recent years, which matched the pattern from coastal Lake Ontario (Winter et al. 2012). Since industrial activities have declined during this period around the Bay of Quinte, the only likely source of the increased loadings of sodium and chloride is from salting activities as have been seen in other parts of Lake Ontario (Winter et al. 2012). The major loadings from urbanized areas are sourced by the major rivers above the Belleville site which matches the pattern of increased concentrations of these salts down the axis of the Bay of Quinte.

MULTIVARIATE ANALYSIS

Correlations

A Pearson correlation analysis was undertaken to discern the major relationships between all of the measurements taken (including meteorological) for Project Quinte. Monthly averages were used to take into account that biological (and some chemical or geological) processes have an inherent lag in reaction to a driver. This allows seasonality to be incorporated and makes it more likely that the data are more normally

distributed than for measurements taken on a single day every two weeks. Since there was an expectation of differences in relationship between sites, each site (B, HB and C) was run separately (Table 2a-c). Correlation plots are also supplied for each pair of the correlation matrix to note the scatter in the relationships, and in addition, a histogram of values for each measurement to visualize the normality of the data (Figs. 23-25). There is considerable disagreement over how to effectively interpret when a correlation is relevant (James and McCulloch 1990; Prairie 1996). As a result, a cautionary approach was taken when interpreting the Pearson correlation coefficient where only values of r>|0.7| (very strong) were considered relevant for monthly averages, though some borderline relationships were flagged above r>|0.6| (Table 2a-c).

In the upper bay at Belleville (Table 2a, Fig. 23), some correlations consistently clustered as expected: the major total nutrients TP and TKN, the major organic particulate carbon measures (seston, chlorophyll-a), and the water column light characteristics (Secchi⁻¹, kd). It is worth noting that without taking the reciprocal, Secchi depth had a much poorer relationship to other measures (reduced ~10%), sometimes dropping below r=0.7. Nitrate, nitrite, SRP and chlorophyll-a distributions were fairly non-normal (Fig. 23) but log-transformation did not significantly change any of the correlations so the untransformed values were used. TP was strongly correlated with TKN, chl-a, seston, Secchi and kd, and euphotic depth (Zeu1%). Euphotic depth is negatively correlated to kd the other biological values because the value of kd decreases as transparency (thus photic depth) increases. Surprisingly, TKN had even stronger correlations with all these values (Table 2a). This suggests that nitrogen may play and important role as a co-limiting nutrient in the upper bay. This is supported by partition analysis of the time series where the best AIC model for the upper bay B was TKN>=0.68 for seston (RMSE 2.76, AICc 975, Δmean 5.69) and chl-a (RMSE 9.33, AICc 1701, Δmean 17.39) and TKN>=0.58 for seston (RMSE 1.98, AICc 796, Δmean 4.44) and chl-a (RMSE 7.35, AICc 1597, Δmean 14.47) for the middle bay HB station. Other nutrient sub-components in the upper bay were rarely correlated with any other measurement, with only SRP-TP (r=0.61) and nitrate-sulphate (r=0.67) at a borderline level. This indicates that the total fractions of nutrients are much more reliable for underlying relationships to the biological processes than individual constituents which are likely driven by conversion processes at much different time scales.

The light measurements at Belleville were strongly correlated to major nutrients (TP, TKN) and the organic particulates (seston, chl-a, r>0.8). Within the dissolved fraction (Figs. 23-25, Table 2a), DIC, alkalinity, conductivity, and total hardness and total calcium were also strongly correlated. As expected, total hardness was exceptionally correlated to calcium since this is the largest component to hardness. Chl-a and seston were also negatively correlated with total hardness and calcium (r=-0.7) likely due to the negative correlation between hardness and TKN and TP (r<-0.6). This is likely in part due to the fact that calcium will bind with nitrogen and phosphate ions removing them from biological availability. Chloride, sodium (r>0.9) and magnesium (r>0.8) were very strongly correlated, which is expected since the primary source of chloride in the bay is expected to be from road salting. Unlike Winter et al. (2012) we did not see significant correlations with chloride and precipitation or snow accumulation, however, the highest

values for these measurements are during the freshet in months that are not sampled during Project Quinte (Dec-Apr), and even using just the month of May did not provide any significant correlations.

The middle bay station Hay Bay (Table 2b, Fig. 24) has similar relationships to those found in the upper bay, though some are weaker (Chl-TKN, Chl-TP, AFDW-TP and TKN-Secchi⁻¹). The TKN correlations with the biologically driven measures (chlorophyll, seston, AFDW, kd etc.) are still greater than values for TP as they were in the upper bay. The Secchi-1 correlations with seston, chl and attenuation are higher at HB compared to B, likely due to reduced turbidity or resuspension at HB which is often stratified during the summer (Table 2b). While the values are not significant the correlations of ammonia with the biological measures are much greater at HB indicating that this might be playing a greater role in primary production compared to the upper bay. Some of the dissolved water chemistry relationships are no longer correlated or much weakened (total hardness, calcium, alkalinity), particularly to DIC, and are no longer related to chl-a or light as they were in the shallower upper bay. This is likely due to the effect of stratification at Hay Bay which concentrates primary production in the epilimnion and separates some of the chemical drivers within the hypolimnion. One difference in dissolved ions is that sulphate is becoming an important ion at HB with much stronger relationships (negative and positive), especially to magnesium, which both strongly increase from upper to lower bay. The sulphate time series is very short however, so the interpretation of the relationship is limited. A few dissolved constituents become correlated with the month number (i.e. effectively increase or decrease over the sampling period of May-Oct). Total calcium is strongly negatively correlated with month (r=-0.77), while hardness and DIC have weaker negative relationships, while TP is weakly positive. The positive relationship with TP-month is a result of the fact that the highest values of TP occurs late in the season (see: Seasonality section below for more information) but this association was strongest at HB compared to station B.

At the lower bay site Conway (Table 2c, Fig. 25) the relationships are similar to those in the middle bay (HB), but many of the relationships are now not significant. One interesting difference is the increased negative correlations of nitrate to TP, the organic particulate measures (chl and seston) and light. This result may seem to be counterintuitive since it runs against the gradient of lower chl-a and increased clarity in the lower bay, but is due to the proximity of excess nitrate pool found in Lake Ontario of 0.35-0.4 mgL⁻¹ vs. 0.2-0.25 mgL⁻¹ at Conway (Winter et al. 2012). This supports previous findings that Conway has a strong influence of mixing with water masses from outside of the bay (Freeman and Prinsenberg 1986). DOC also has relationships at C that are not found in the other sites, with chloride (r=-0.60), sulphate (r=-0.69) and month# (r=-0.63). A negative correlation exists at both HB and C for DOC and magnesium, but it is stronger at C (r=-0.60 and r=-0.79 respectively). A borderline positive correlation also exists for DOC and alkalinity (which may be an extension of the relationship with DIC). Sulphate is also slightly correlated with sodium and chloride at Conway, which is likely driven by the higher values of all of these measurements in Lake Ontario.

Discriminant Analysis

A linear Discriminant Analysis (LDA) canonical plot (Fig. 26) was prepared in JMP for all of the sites and selected groups of biological/nutrient/physical and dissolved fraction variables. The groups were chosen based on those which indicated potential for high correlation values in Table 2a-c. The biological/nutrient/physical groupings included: seston, chl-a, TKN, TP, secchi⁻¹ and kd. The dissolved ion groupings included: total hardness, calcium, magnesium, potassium, sulphate, sodium, chloride, alkalinity, pH and specific conductivity. The rays on the biplots give the Mahalanobis distance of the observation from the site centroid with direction in the canonical space. The biplot for the biological/nutrient/physical grouping indicates that the CA1 axis accounts for 98.2% of the variance to separate the BoQ sites (B,HB,C), dominated by TKN (30%), chl-a (21%) and kd (18%) (MANOVA, F=124.6, p<0.0001). The CA2 axis is dominated by the transparency values (Secchi⁻¹ and kd). There is considerable overlap with B and HB sites. The symbols on the biplot designate the time stanza with the post-1995 data indicated by open symbols on Fig. 26 which are shifted to the left on CA1 for B and HB but less for C which shifts down on the CA2 axis. This matches what are seen in the time-series plots with lower TKN, TP, seston and chl-a values post-1995 at B and HB but much clearer condition (Secchi) at C. The biplot for dissolved fractions indicates that the CA1 axis accounts for 95.2% of the variance to separate sites, dominated equivalently by Ca (23%) and Mg (22%) and by hardness (14%) (MANOVA, F=196, p<0.001). The CA1 axis separates the sites very effectively with much less overlap than found in the biological measures. Most of the dissolved components were only measured after 1995 so only open symbols appear on this biplot. The CA2 axis has similar dominants with hardness and Ca and the HB sites partially separates from B and C on the CA2 axis. This means that effectively the sites can be discriminated by the gradient of their calcium total hardness values.

SEASONALITY

To illustrate the seasonality associated with the measures of Project Quinte, monthly boxplots from May to Oct at B, HB and C are plotted in Figs. 27-29. A few important measures (seston, TP and Secchi) have been selected in Fig. 27 to demonstrate differences in the seasonality for the time stanzas of post-95 and pre-95. The complete set of seasonal plots for these time stanzas are shown in Figs. 28-29 for all other measures. It is also useful to see the entire time-series for each month without grouping into time-stanzas which are shown in Figs. 30-31. Generally the B and HB stations are similar for most parameters, but are usually different for C versus B or HB. The upper and middle bay sites generally also show more seasonality than the lower bay site.

Seasonally, seston, AFDW and chl-a peak in August post-95 whereas the peak was in September pre-95 and are now significantly reduced with the seston peak of 12 mg/L down to 7 mg/L. Summer chl-a is reduced to 8 µgL⁻¹, which is 70% of pre-95 values and seston, POC and AFDW are at 55-60% of their previous values. The lack of change for May-June but a large change in July-Sept can be seen more effectively in the individual monthly time-series (Fig. 30). This differs from the findings of Winters et al. (2012) for coastal Lake Ontario which showed reduced fall and spring blooms with a slight

increase in summer. This reinforces the idea that the dynamics of the coastal Great Lakes may be considerably different than found in the more eutrophic embayments.

The water clarity values (Secchi depth, 1% euphotic depth and light attenuation) show similar patterns with the most transparent period in spring (May-June) with the least clear month being Aug (Figs. 28, 30). The seasonality is similar at all sites but B and HB have very similar values while Conway's values and timings are slightly different. The secchi depth has deepened by 40-50% at all sites indicating considerably clearer conditions (Figs. 27,30) with considerably more variability in the values from B in the upper bay, which is expected since there is more likelihood for sediment resuspension and river-based turbidity input. The greater variability in Secchi depth post-95 is very clear in the size of the whiskers on the box plots (Figs. 6-8) especially at C which shows very large ranges in Secchi depth recently (3-9 m). The difference in Secchi depth post-95 is most apparent in the spring and fall when there is the greatest change over time whereas July-Aug values have changes little since the 1970s (Fig. 30).

The impact of phosphorus on the BoQ ecosystem has been extensively discussed in a number of previous publications (Millard and Sager 1994, Minns et al. 1986, Nicholls 2012), so will not be repeated here other than some comments on seasonality. The seasonal pattern of phosphorus closely follows that of the TKN with these nutrients building up from lows in the spring to peaks in the fall (Figs. 28,30). Both of these total nutrients have shown a significant reduction to 70% for peak values from pre-95 time stanza but these reductions are mostly in the months of Aug-Oct with very little difference over time in May-June (Fig. 28). While Belleville (B) shows the highest TP values, the values in the middle bay (HB) are equal to or exceed those of B for Sept-Oct, though the values at B show more variability so the values are not statistically different. The maximum measured value of TP (TPmax) at B has decreased since the early 1970s to 1986, and while it has remained at a lower value since (0.05-0.1 mgL⁻¹) there is still considerable annual variability (Fig. 32). Belleville also experienced two abrupt drops in TPmax (77-79 and 84-86) which correspond to years with very cold winters and summers. Post-95 the Julian day of peak TP at B occurs approximately 3 weeks earlier during the first week of August (Julian day 219) rather than the last week of August (Julian Day 239) in the 1970s and 80s (Fig 32). In recent years, the TPmax peak at station B has been on a trend to even earlier in the year (< Julian Day 200). The earlier timing of peak phosphorus may likely be due to warmer summer temperatures increasing bio-mediated release of iron-bound phosphorus from sediments since mineralization processes are temperature dependant (Jensen and Andersen 1992). While the maximum chlorophyll-a value has seen a decline similar to that of TP at Belleville, the same analysis of timing for the chlorophyll-a peak generates the opposite result, with the post-95 peak occurring later in the year at the end of August (Julian day 242), whereas it was in early August (Julian day 225) for the 1970s and 80s (Fig. 32).

The other nutrient constituents are quite variable over the time series with respect to seasonality (Figs. 28,30). The seasonal pattern of SRP is similar to TP, but is much more variable year to year though peaks are likely to be in September and peaks in October (where HB often has the highest concentrations) are less common post-95.

Silicate is seasonally variable with higher concentrations during the July-Sept period and is elevated at HB and B compared to C, though the concentrations are identical for all sites in May. For the nitrogen components, nitrite and ammonia can be spikey at any month of the year with no real pattern though ammonia is at higher concentrations July-Oct. Nitrate values tend to be highest in the spring (May-June) at B and HB whereas C tends to be consistent across the season and, as mentioned previously, is continually increasing over time. Post-95 the nitrate values in July-Sept at B and HB are at extremely low concentration. Since TP is increasing in value during this time, this is again suggestive of nitrate limitation during the late summer months.

There is much less seasonality in the dissolved water chemistry values (Figs. 29,31). Alkalinity and specific conductivity change little over the year and have changed little over the time-series. Though the series is shorter, there is also little or no seasonality for DIC, DOC, magnesium, or sulphate. Seasonality in iron suggests elevated values in Aug-Oct at B but the series is variable. Total hardness and calcium patterns are similar with a slight minimum in Aug-Sept and the greatest change in the upper bay. One chemical property that changes over the year clearly is pH which is similar in the spring and fall with identical values for all of the sites across the bay, but B and HB are elevated during July-Sept. This might be related to the algal productivity which can affect pH through changes to the bicarbonate equilibrium (Schindler 1971; Brewer and Goldman 1996).

The trend over time for increased sodium and chloride is clearly seasonal, though the monthly pattern is weakest in the upper bay (Fig. 31). The overall change is very small at Conway (and to a lesser extent HB) most of the year but is best seen in May, whereas in the upper bay the trend is strong each month of sampling for both sodium and chloride. The reduced seasonality in the upper bay station suggests that there is storage of chloride that is released more gradually over the year. This is supported by the loss of the deviation between HB and B values after 1997 especially for the months of June-Sept. There was a corresponding decline over time in chloride at Conway from June-Sept which may now be showing an increase since 2000. This suggests that when tracking of patterns of chloride increase within the Bay of Quinte we should use values from early in the year to track the pattern over time.

While there has been an overall change in temperature and precipitation (Fig. 33), the changes in seasonality are strongest during the summer for the climatic variables over the last 40 years. The total increase in temperature since 1999 is evident in Fig. 33 which is a significant increase for both summer (+ 0.59 °C July, Tukey HSD, p<0.0001) and even larger for winter (+1.78 °C January, Tukey HSD, p<0.0001) though the change in January temperature took place by 1985. The change in seasonality of precipitation occurs after 1999. From 1972-1999 the lowest precipitation month is July (53 cm) with August (or June) having the highest precipitation (78 cm) during the growing season. After 1999, the rainy and dry months are reversed with July becoming the highest precipitation month (93 cm) and August now the lowest (78 cm). The result of this pattern is hotter, wetter Julys and dry Augusts after 1999.

CONCLUSION

Project Quinte is an example of a long-term ecological research (LTER) program with measurements being continually taken on the physical environment, nutrients, water chemistry, phytoplankton and zooplankton composition, fish populations and fish habitat that is extremely rare, on par with the Experimental Lakes Area, Lake Geneva or Lake Windermere studies (see Vasseur et al. 2014). The Bay of Quinte is a unique and important embayment of Lake Ontario which is a historically important fish nursery habitat. While its importance as a commercial fisheries has faded over time, the Bay of Quinte still continues to support a very important recreational fishery (Hurley and Christie 1977). Historical studies on the Bay of Quinte ecosystem date back to Pritchard (1931) who detailed Cisco spawning to the charming hand-drawn figures found in Tucker (1948) documenting the phytoplankton community temperature profiles and wind conditions. Unfortunately, historical scientific research in the BoQ is very patchy and a considerable gap occurs after these studies until the documentation of deteriorated conditions in the late 1960s. Project Quinte has produced a dataset of biweekly sampling from May-Oct where we have observed significant long-term changes in biogeochemical measures in the Bay of Quinte since 1972 and many of these changes have been well documented (see Millard and Sager 1994, Minns et al. 1986b; Minns et al. 2011; Nicholls 2012). Some locations within the Bay were only sampled for short periods of time and stations were often dropped because of lack of funds or staffing reductions. The resulting dataset is the result of a truly collaborative relationship among a variety of federal and provincial agencies, but while results come from different analytical labs, the data is guite comparable, even with methodological differences. This is very important because it permits researchers to extend the data series since some measures were only done by one agency or another for a period of time.

In examining the resulting data, it becomes clear that while there was often a difference in absolute value, many of the measures show remarkable synchrony across the stations from the upper to lower bay and some trends are striking. In particular, there has been a steady increase in clarity, resulting in deeper euphotic zones throughout the bay. This is to some degree due to decreased algal biomass (chlorophyll-a) and seston which are in turn driven by lower nutrient values of total phosphorus and nitrogen as suggested by high correlation values, particularly for TKN and TP. While total nitrogen (TKN) has decreased over time, nitrite has occasionally experienced peaks, including a huge upsurge in 1981 that persisted for some years, the source of which we could not explain. Nitrate has increased over time within the BoQ, though the largest increase at Conway in the lower bay is likely driven by the much larger increases seen in Lake Ontario over the same time period (Winters et al. 2012). There is some suggestion of co-limitation of algal biomass by nitrogen as suggested by the highest correlations being with TKN and the recent trend of nitrate depletion during the summer high production months which could promote nitrogen-fixing cyanobacteria (McQueen and Lean 1987; Nicholls et al. 2002; Munawar et al. 2012).

The clarity related measures of Secchi depth and light attenuation (kd) were highly correlated, though Secchi depth was slightly less correlated to productivity measures

than kd, particularly at the upper bay site which is more likely to be influenced by resuspension events and turbidity. The sharp change in clarity around 1994 was most likely triggered by the extremely cold winter and the accelerating macrophyte expansion (Fig. 34) in the upper bay (Leisti et al. 2006) shifting the system from a turbid to a clearphase alternative stable state (Scheffer and Carpenter 2003). While this is still a regime shift, this break in the time-series has previously been suggested to be driven by "pre and post zebra mussels" (Nicholls et al. 2002; Miehls et al 2009; Nicholls et al. 2011; Johannsson and Bowen 2012) but in examining the zebra mussel adult densities across the upper and middle bay (Fig. 34) we do not see an increase in the benthic surveys until 1999 (Dermott and Bonnell 2000). Veligers are found in surveys back to the early 1990s but settled zebra mussels were only reliably found on hard surfaces (e.g. intakes for the water treatment plant) at a few coastal sites in the upper bay before the 2000s. Most of the benthic habitat in the upper bay is composed of shifting, very soft sediment or silt and sand (Damiani and Thomas 1974) which is a poor settlement surface for zebra mussels. It is likely that the expansion of macrophytes in the upper bay provided a fixed surface which in turn helped to foster the invasion of zebra mussels into the Bay resulting in the sharp increase in biomass occurring in 1999 in the lower and middle bay (Dermott and Bonnell 2000).

Within the dissolved constituents, there have been fewer major changes over the Project Quinte time-series beyond decreases in the major nutrients, though there were strong differences between the lower bay site Conway and the middle and upper bay stations (B and HB) in water chemistry. The major ions were highly correlated with each other, with alkalinity, conductivity, total hardness and calcium having high correspondence. The minor ions magnesium and potassium were correlated with one another at the lower bay site, but magnesium was related to sodium at the upper bay site suggesting probable loading from urban sources (see Minns et al 2004). While we did not see the relationships of chloride with precipitation or snow accumulation seen in other studies (Winter et al. 2012) this is likely due in part to the fact that our measurements begin in May after the freshet. We do however see a strong increase in chloride and sodium over time at the upper and middle bay sites. Temperature and precipitation appeared to be tied with changes to productivity, particularly following very cold winters (eg. 1978-79 and 1994) but these relationships were not significant in the annual means correlation matrix due to the fact that very few data points are available. Any further analysis will likely require higher temporal resolution data to resolve them, including lag times and modeling to include the temperature extremes which drive these relationships. Likewise, a further analysis of the changes in climatic forcing would be helpful, including the most recent years since 2000 which exhibit higher summer temperatures with high precipitation, interspersed with occasional colder or dry summers.

The Project Quinte dataset shows very clear seasonality for some measurements, though it is constrained to the months of May-Oct which limits its ability to examine impacts of events such as the freshet or ice-covered periods. The very early spring and late fall unstratified periods are also not well represented. With regards to the major nutrients, in the upper bay, while the overall pattern has been a decrease over time,

seasonal nutrients peak several weeks earlier at the beginning of August rather than the end of August post 1995. Conversely, the seston and chlorophyll-a values peak several weeks later in August post1995. There has been no major change to the timing of the transparency maximum despite the overall change in clarity. The overall chlorophyll-a values have decreased post 1995, and are similar for the May-June period, but are much reduced from July-October, resulting in reduced summer-fall phytoplankton biomass. This pattern is different than found by Winter et al. (2011) for coastal Lake Ontario, emphasizing the disparity between embayments and the main lake. Care should be taken when applying patterns found in the main lake to nearshore protected waters. An increase in DIC during most of the year post1995 may be due to recirculation behaviour of Dreissenid mussels (Heath et al. 1995; Barnard et al. 2006; Miehls et al. 2009) or heterotrophic microbial activity (Munawar et al. 2011), but DIC measurements were only taken after 1995 so caution must be employed in the interpretation of this pattern. The timing of the phosphorus peak might also be mediated by Dreissenid mussels, with the timing of the phosphorus peak occurring approximately 3 weeks earlier in recent years, but since this pattern is strongest in the 2000s it is suggestive that it may be due to the increase in summer temperatures found in the upper bay during this period.

Project Quinte has provided a long-term, continuous source of biological, chemical and physical data for an aquatic ecosystem undergoing a series of stressors ranging from nutrient controls to a series of invasive species. Ecosystem studies are often hampered by gaps in data or termination of data collection before associations can be ascertained. The Project Quinte dataset allows researchers to examine relationships between trophic levels and environmental drivers over time with very good temporal sampling resolution in a way that is not available for almost any other location in the Great Lakes. Future work linking findings from the Bay of Quinte to other locations will illustrate how valuable this extensive and detailed dataset can be to determine relationships not only for a single ecosystem, but rather in the application of these findings to similarly impacted ecosystems around the world.

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Table 1: Noteworthy meteorological, climatic, biological or societal anomalies, forcings, changes or events. *

Date	Meteorological / Climatic	Biological or Societal Changes
1972	High precip (>85mm) & snow (>250mm)	5
1973-1974	La Niña	High planktivorous fish biomass
1976	Cold summer (<20°C mean July & Aug) and extreme cold winter (see text), high	3 ,
	snowfall (>200 mm)	
1977	High snowfall (>200 mm), extreme cold	Phosphate controls ↓TP (28-38%), ↓TN
	winter (see text)	(13-20%) (Minns et al. 2004)
1978-1979	1979 extreme cold winter	↓ Phytoplankton biomass ↑P/B
		↓ Predaceous zooplankton biomass
1980	Mt. Saint Helen's eruption	↓ Herbivorous zooplankton and copepod biomass
1980-1982	Cold winter, ↑ ice winters	↑ Cormorants, ↑ <i>Bosmina</i> (1981)
1982-1983	El Niño, very mild winter (≤5°C, Jan min >-10°C), Hot summer (>22°C)	↑↑ zooplankton biomass ↓↓ planktivores Macrophytes start return to BoQ
1984-1985 1985-1986	Moderate winter, ↑ ice winters, cool summer (<20°C mean July & Aug), 1985 snowfall (>250mm)	Record high Walleye YOY recruitment (Ridgway et al. 1990)
1987	Extreme cold winter Dec 1987-winter 1988 (see text)	BoQ listed as Area of Concern (AOC) under the Great Lakes Water Quality Agreement
1988-1989	La Niña, Hot summer (>22°C), very low precipitation (<60 mm)	Planktivore and Piscivore biomass
1991	Mt. Pinatubo volcanic eruption (June 15), 2 nd largest terrestrial eruption of the 20 th century, ↓global sunlight by 10%, ↓temp 0.5°C in northern hemisphere	Dreissenid mussels (DM) first recorded BoQ Last year of ↑ Gizzard Shad, alewife absent after this year
1991-1992	El Niño, Cold summer (<20°C July & Aug)	
1993	↓global temp 0.73°C, wet cold summer in US and flooding	Chiad and 7 lietine
1993-1994	1994 extreme cold winter (25 days mean temp below -15°C), record ice cover on Great Lakes (>90%)	Beginning of large recent increase of macrophyte density in the BoQ, high White Perch then ↓↓ till 2003.
1996	Very high precipitation (>85mm), but low runoff and BoQ outflow	Begin ↑ DM at Conway, first adult DM in benthic surveys in Big Bay, ↓ Phytoplankton biomass but no P/B change, ↓ Alewife
1997	Very high snowfall (>200 mm)	↑ DM veligers in plankton
1997-1998	Strong El Niño, very mild winter (≤5°C), Jan 1988 min >-8°C	
1998		Bythothrephes reported in the BoQ at Conway
1999	Hot summer (>22°C), start new climatic phase of oscillating wet/dry years.	Cercopagis and Round Goby reported in BoQ, begin ↑↑ DM biomass adults

2000	The summer that wasn't. Cold summer (<20°C mean July & Aug), very high precipitation (>85mm)	↓↓ Phytoplankton biomass ↑P/B, ↓↓ all zooplankton, DM adult biomass peak
2001	Very low precipitation (<60 mm)	Near record high zooplankton (Daphnia)
2002	Very mild winter (≤5°C, Jan min >-8°C), hot summer (>22°C)	
2003	Very high precipitation (>85 mm)	↑ Round Goby
2004	Very high precipitation (>90 mm)	
2005	Hot summer (>22°C)	
2006	Very mild winter (≤5°C Jan min >-8°C), hot summer (>22°C), very high precipitation (>90 mm)	
2007	Very low precipitation (<60 mm)	
2008	Very high precipitation (>90 mm), high snowfall (>275 mm)	↑ Zebra mussel veligers 25% of zooplankton biomass for all sites
2009	El Niño, very high precip (>85 mm)	
2010	Very mild winter (≤5°C Jan min >-8°C), Hot summer (>22°C), low precipitation	
2011	Hot summer (>22°C), high precipitation (>90mm)	
2012	Hot summer (>22°C), very mild winter (≤5°C Jan min >-8°C)	

^{*}Meterological measurements downloaded from NCDB for Trenton AFB. Other sources for biological and climatic forcings are noted.

Climatic summary general trends:

1972-1975 decreasing precipitation from high in 72, moderate winters and summers 1976-1982 cold winters and no hot summers, several high snowfall years (72,76,77) 1983-1988 moderate winters, warm summers, moderate precipitation except low in 88. 1989-1994 cold winters (89,93,94) including coldest (94) and coldest summer (92) 1995-1998 mild conditions

1999-2012 increasing temperatures and variability: very hot summers (except cool summers 00,04,09), and much more variable rainfall including highs (03,04,06,08,09), interspersed with low precipitation years (01,07,10), no high snowfall years (except 08) including the record low (06)

Table 2a: Pearson correlation matrix for the Project Quinte measurements at the upper bay site Belleville (B). Significant, extremely strong correlations (r>|0.9|) are marked in bold red, strong correlations (r>|0.7|) are marked in bold dark blue, while borderline weaker correlations (r>|0.6|) are marked in bold green.

3	T KN	NH3	NO3	NO2		ը	SRP		Seston	AFDW	Т		2	000	¥	Cond		Fe Fe						804		В	Sec	Zmix	Zeu1%	#Month	mMax	тетр	mMin	XMax	XMin	rain	snow	precip	WindDir	WindSpd	тМах	mMin	Precip	tSnow
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NH3		1.00			T																																							
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Seston	0.78	0.32	-0.2	7 -0.0	13	0.71	0.14	0.11	1.00)																																		
FDW	0.80	0.46	-0.2	6 0.0	15	0.65	0.13	0.18	0.94	1.00)																																	
hl	0.78	0.34	-0.2	3 -0.0	15	0.73	0.33	0.11	0.77	0.77	7 1.0	00																																
OIC		_			_	_				-0.56	_		.00																															
ОС										0.42				1.00																														
ιlk										-0.02					1.00																													
Cond	-0.02															1.00																												
Н										0.42		_	_	_			1.00																											
e	0.39	0.07	-0.1	3 -0.1	0 (0.58	0.35	-0.07	0.38	0.17	7 0.3	34 0.	.00	0.00	0.06	-0.22	0.00	1.00																										
l a	-0.08	-0.18	-0.0	3 -0.0	19 -(0.19 -	0.29	0.24	-0.04	0.02	2 0.0	03 0.	.00	0.20	-0.01	0.43	0.40	-0.12	1.00																									
3	0.04	-0.20	-0.1	5 -0.1	8 (0.00 -	0.24	0.09	-0.04	-0.07	7 0.	16 -0.	.18	0.18	-0.13	0.24	0.34	-0.16	0.93	1.00																								
hard	-0.58																																											
`a	-0.60	-0.17	0.3	2 -0.2	9 -(0.53 -	0.26	-0.03	-0.69	-0.68	-0.7	71 0.	.86 -	0.22	0.90	0.71	-0.23	0.00	-0.30	-0.40	0.98	1.00																						
Лg	0.33	-0.08	-0.3	2 -0.0	19 (0.31	0.04	0.15	0.52	0.45	5 0.3	31 0.	.05	0.13	-0.09	0.28	0.28	0.00	0.85	0.66	-0.05	-0.21	1.00																					
3O4	-0.38	-0.10	0.6	7 -0.0	12 -(0.49 -	0.20	0.00	-0.34	-0.37	7 -0.4	41 0.	.15 -	0.16	0.15	0.06	-0.49	0.00	-0.25	-0.23	0.34	0.33	-0.22	1.00																				
(0.01	0.01	0.2	0.0	7 -(0.09 -	0.12	0.02	0.12	0.01	1 -0.0	04 0.	.09	0.01	0.11	0.20	-0.13	0.00	0.15	0.04	0.14	0.11	0.29	0.21	1.00																			
(d	0.84	0.43	-0.2	2 0.0	0	0.80	0.38	0.04	0.86	0.84	4 0.7	78 -0.	.51	0.33	-0.10	-0.13	0.32	0.46	-0.20	-0.09	-0.61	-0.64	0.25	-0.43	-0.06	1.00																		
/Secchi																											1.00																	
Zmix																								-0.06				1.00																
Zeu1%	-0.82																																											
Month			_			_					_	_												-0.20																				
nMax	0.06	0.08	-0.2	3 0.0	15 (0.13	0.09	0.13	0.07	0.12	2 0.	11 -0.	.05	0.20	0.03	-0.01	0.40	-0.05	0.00	-0.06	-0.10	-0.10	-0.06	-0.53	-0.41	0.07	0.04	-0.07	-0.10	-0.33	1.00													
nTemp	0.07	0.08	-0.2	3 0.0	15 (0.13	0.09	0.14	0.08	0.12	2 0.	11 -0.	.03	0.21	0.04	-0.01	0.40	-0.05	0.00	-0.05	-0.08	-0.08	-0.07	-0.52	-0.40	0.07	0.04	-0.04	-0.09	-0.32	0.99	1.00												
nMin	0.08	0.09	-0.2	3 0.0	15 (0.14	0.10	0.16	0.09	0.13	3 0.	11 -0.	.01	0.23	0.05	0.00	0.39	-0.04	0.00	-0.04	-0.06	-0.06	-0.07	-0.50	-0.39	0.07	0.04	-0.02	-0.09	-0.29	0.98	0.99	1.00											
(Max	0.01	0.06	-0.1	9 0.0	14 (0.06	0.03	0.09	-0.01	0.03	3 0.0	08 -0.	.05	0.15	0.05	0.00	0.37	-0.07	0.03	-0.03	-0.08	-0.08	0.01	-0.45	-0.37	-0.01	-0.05	-0.11	-0.04	-0.39	0.89	0.88	0.85	1.00										
(Min	0.01	0.02	-0.1	8 0.0	15 (0.09	0.09	0.14	0.05	0.07	7 0.0	06 0.	.01	0.25	0.05	-0.02	0.38	-0.04	-0.01	-0.04	-0.02	-0.02	-0.11	-0.46	-0.40	0.03	0.00	0.01	-0.03	-0.32	0.92	0.94	0.95	0.77	1.00									
ain		_	_	_	_	_				_	_		_							_	_	_		_						0.10		_	_			1.00								
now																														0.11							1.00							
recip																																						1.00						
																																						0.01						
VindSpd		_									_																													1.00				
nMax																																								-0.08	1.00			
		_	_		-	_				_	_		_							_	_	_																_		-0.08	_	1.00		
		-	-	_	_	_				_	_	_	-							_	_	_		_														_		-0.06		_	1.00	
Snow		_		_	_					_	_		_																											0.11				1.0

Table 2b: Pearson correlation matrix for the Project Quinte measurements at the middle bay site Hay Bay (HB). Significant, extremely strong correlations (r>|0.9|) are marked in bold red, strong correlations (r>|0.7|) are marked in bold dark blue, while borderline weaker correlations (r>|0.6|) are marked in bold green.

3	Z¥.	NH3	NO3	NO2	٩		SRP	iΩ	Seston	Ž	AFDW	당	DIC	000	<u> </u>	¥	Sond	ī	Fe ,	ā.		Thard				*	g	Sec	Zmix	Zeu1%	#Month	mMax	mTemp	mMin	ХМах	XMin	rain	snow	precip	WindDir	WindSpd	тМах	mMin	Precip	Snow
ΓKN	1.00				-	+	0)	0)	0)	-	Q.	0	ш	-	-		0	ο.	-		0	-	0	_	(0)	×	×	92	1/4	N	41:	-			^	^		o	0.	>	>	_	_	=	#3
NH3	0.40																																							-					
NO3	-0.41		1.00		+	+			+	+																														-					
NO2	0.07				,	+			+	+																														-					
P	0.84					00																																		-					
RP	0.40			_	_	_	1 00																																	-					
i Si	0.19								1																															-					
	0.78									00																																			
.FDW	0.73										1.00																													+					
hl	0.70								_	_	_	1.00																												+					
IC	-0.45								_		_		1.00)																															
OC	0.33				-				_	_					0																									-					
lk	-0.12												_	_		00																								-					
ond	0.12												_				1.00																												
H	0.44				-				_	_								1 00																						-					
e	0.48			_	_	_			_	_	_			-	_	_																								-					
a	-0.07					_					_				_	_				1.00	1																			-					
	0.14			_	_	_			_	_	_			-	_	_				_	_	,																		+					
nard	-0.47			_	_	_			_	_	_			-	_	_					_	_																		_					
a	-0.52												_		_	_						_																		-					
la I	0.24				-				_	_			_		_	_				_	_	_	_		1															+					
9 04	0.06																				-	_		-	-															_					
•	-0.14																							_		1.00														-					
d	0.75					_																					1 00													-					
/Secchi					_	_			_	_																		1.00												_					
mix					_				_		_														0.01		_			1										-					
	-0.68				_	_			_																						1									+					
Month	0.55)								_					
Max	-0.30				-				_	_																						_)							+					
Temp	-0.29				-				_	_																						_													
Min	-0.27																															_	_												
Max	-0.35				-				_	_																						_	_	_	_										
Min	-0.29				-				_	_																						_	_	_	_	_									
ain					-				_	_					_									_								_	_	-0.10						_					
now					-				_	_																						_	_	-0.26				1.00		_					
recip					-				_	_																						_	_	-0.10			_								
/indDir																																					_			1.00					
/indSpd				_	_	_			_	_				_		_					_	_	_	_	_					_	_	_	_	_	_				_	_					
nMax				_	_	_			_	_	_			_	_	_						_	_	_						_	_	_	_	_	_					_	-0.08	1.00			
nMin				_						_					_									_																	-0.08		1.00		
Precip				_	_	_			_	_	_			_	_	_						_	_	_						_	_	_	_	_	_					_	-0.06			1.00	
Snow				_	_	_			_	_	_			_	_	_					_	-	_	_	_				_	-	_	_	_	_	_				_	_	0.11				1 0

Table 2c: Pearson correlation matrix for the Project Quinte measurements at the lower bay site Conway (C). Significant, extremely strong correlations (r>|0.9|) are marked in bold red, strong correlations (r>|0.7|) are marked in bold dark blue, while borderline weaker correlations (r>|0.6|) are marked in bold green.

3	TKN	SH2	NO3	NO2			SRP	ίδ	Seston	AFDW			000	¥	Cond	퓝				Thard			SO4		Σ	Sec	Zmix	Zeu1%	#Month	mMax	mTemp	mMin	XMax	XMin	rain	snow	precip	WindDir	WindSpd	mMax	mMin	tPrecip	Snow
ΓKN	1.00				+		0)	0)	0)	_		-	-	1		<u>.</u>	-	_		-		_	0,				IN	14	445	_	-	_	^	^	-	0)		_	_	_	_	-	
NH3		2 1.0)																																								
VO 3	-0.40	0.3	1.0	0																																							
I O2	0.00	0.0-	-0.0	8 1.0	00																																						
ГР	0.60	0.3	-0.6	3 0.0)7	1.00																																					
SRP	0.46	0.3	-0.4	4 0.1	12	0.69	1.00																																				
Si	0.23	3 0.1	l -0.1	8 0.1	19 (0.38	0.41	1.00																																			
Seston	0.37	7 0.2	-0.5	5 0.1	18 (0.48	0.26	0.22	1.00																																		
FDW	0.29	0.3	-0.5	3 0.2	24 (0.40	0.26	0.19	0.86	1.00																																	
Chl	0.37	7 0.2	-0.5	4 0.0)5 (0.47	0.35	0.23	0.52	0.53	1.00)																															
DIC	0.37	7 0.3	0.4	8 -0.1	18 -(0.07 -	0.15	0.38	-0.25	-0.25	-0.16	1.00																															
OC	0.55	0.19	0.4	9 -0.1	19 -(0.10 -	0.14	0.57	-0.25	-0.31	-0.27	0.54	1.00)																													
Λlk	0.22	2 0.1	0.1	4 0.0)2 -(0.18 -	0.30	0.00	0.20	0.13	-0.01	0.61	0.63	1.00)																												
Cond	0.10	0.20	-0.5	8 0.1	15 (0.37	0.35	-0.01	0.41	0.49	0.40	-0.14	-0.43	0.04	1.00																												
Н	0.14	4 -0.0	-0.0	1 0.2	25 -(0.07 -	0.24	-0.14	0.21	0.23	0.05	-0.12	0.1	0.26	0.22	1.00																											
e	0.22	2 0.09	-0.1	8 -0.0)7 (0.34	0.15	0.34	0.33	0.26	0.11	0.00	0.00	-0.02	0.08	0.00	1.00																										
la	-0.26	-0.1	-0.1	7 0.0)9 (0.10	0.19	-0.05	-0.06	0.04	0.07	-0.23	-0.59	-0.3	0.51	0.10	0.09	1.00																									
i l	-0.10	0.1	-0.6	0.3	30 (0.34	0.39	0.07	0.27	0.43	0.32	-0.25	-0.60	-0.2	0.75	0.11	0.16	0.73	1.00																								
hard	0.06	0.0	-0.0	4 0.0)4 (0.02 -	0.22	-0.19	0.01	0.04	-0.20	0.02	-0.08	0.09	0.08	0.13	0.00	-0.20	-0.17	1.00																							
`a	0.40	0.2	0.3	1 -0.2	25 -(0.10 -	0.28	0.18	-0.23	-0.25	-0.47	0.29	0.46	0.44	1 -0.26	0.07	0.00	-0.71	-0.68	0.73	1.00																						
Лg	-0.52	2 -0.2	-0.4	7 0.3	37 (0.14	0.16	-0.49	0.33	0.41	0.45	-0.46	-0.79	-0.58	0.50	0.04	0.00	0.83	0.82	0.03	-0.67	1.00																					
SO4	-0.36	-0.1	-0.3	8 0.2	29 (0.20	0.20	-0.24	0.21	0.26	0.32	-0.52	-0.69	-0.5	0.32	-0.05	0.00	0.66	0.64	-0.13	-0.51	0.68	1.00																				
(-0.14	4 0.0	-0.1	4 0.0)9 -(0.01 -	0.07	-0.22	0.09	0.10	0.09	-0.12	-0.18	-0.12	0.10	-0.05	0.00	0.24	0.21	0.01	-0.18	0.27	0.43	1.00																			
(d	0.52	0.4	-0.5	8 0.1	10 (0.57	0.33	0.39	0.63	0.63	0.53	0.14	0.28	0.12	0.28	0.18	0.28	-0.19	0.18	-0.13	-0.07	-0.07	-0.17	-0.13	1.00																		
/Secchi	0.43	0.3	-0.5	8 0.1	18 (0.49	0.29	0.26	0.76	0.72	0.62	-0.14	-0.09	0.09	0.41	0.23	0.18	-0.10	0.29	0.00	-0.13	0.16	0.10	0.04	0.79	1.00																	
Zmix	0.11	1 -0.1	-0.0	3 -0.1	13 (0.07	0.11	0.15	-0.09	-0.19	0.03	0.05	0.39	0.0	-0.16	-0.20	-0.20	-0.21	-0.28	-0.22	0.11	-0.40	-0.21	-0.16	0.02	-0.11	1.00																
eu1%	-0.53	-0.4	0.5	9 -0.1	11 -(0.57 -	0.32	-0.35	-0.61	-0.62	-0.54	1 -0.26	-0.40	-0.19	-0.33	-0.18	-0.43	0.19	-0.11	0.12	-0.07	0.27	0.26	0.16	-0.93	-0.80	-0.03	1.00															
Month	-0.24	4 -0.20	-0.3	6 0.0)6 (0.20	0.27	0.13	0.04	0.10	0.27	-0.48	-0.63	-0.33	0.38	-0.10	0.09	0.57	0.50	-0.06	-0.53	0.70	0.61	0.11	-0.09	-0.02	0.11	0.13	1.00														
nMax	-0.14	4 0.18	0.1	0.0)6 -(0.19 -	0.20	-0.28	0.06	0.16	-0.03	0.02	-0.24	1 -0.07	0.12	0.20	0.05	0.16	0.22	0.15	-0.05	0.25	0.16	0.14	-0.02	0.11	-0.74	0.03	-0.33	1.00													
nTemp	-0.15	0.18	0.0	9 0.0)7 -(0.19 -	0.19	-0.28	0.05	0.16	-0.03	-0.01	-0.25	-0.09	0.13	0.22	0.04	0.18	0.23	0.12	-0.08	0.26	0.16	0.15	-0.02	0.11	-0.74	0.03	-0.32	0.99	1.00												
nMin	-0.16	0.1	0.0	8 0.0)8 -(0.18 -	0.19	-0.28	0.05	0.16	-0.02	2 -0.05	-0.27	7 -0.1	0.14	0.23	0.03	0.19	0.24	0.10	-0.11	0.28	0.16	0.15	-0.02	0.12	-0.72	0.03	-0.29	0.98	0.99	1.00											
(Max	-0.11	1 0.1	0.1	5 -0.0)2 -(0.21 -	0.19	-0.26	0.02	0.09	-0.08	0.03	-0.18	3 -0.0°	0.01	0.24	0.01	0.06	0.11	0.24	0.03	0.21	0.14	0.15	-0.06	0.05	-0.62	0.04	-0.39	0.89	0.88	0.85	1.00										
(Min	-0.14	4 0.1	0.1	2 0.1	11 -(0.21 -	0.19	-0.29	0.02	0.10	-0.05	-0.04	-0.2	1 -0.1	0.09	0.25	0.06	0.14	0.18	0.11	-0.06	0.21	0.13	0.11	-0.05	0.08	-0.68	0.08	-0.32	0.92	0.94	0.95	0.77	1.00									
ain	-0.11	1 -0.1	0.0	9 0.0)6 -(0.06	0.05	0.09	-0.13	-0.08	-0.05	-0.26	0.0	1 -0.08	-0.07	0.08	-0.11	0.04	0.00	-0.10	-0.05	-0.02	0.11	-0.05	-0.09	-0.11	0.20	0.11	0.10	-0.19	-0.15	-0.10	-0.22	-0.10	1.00								
now	0.08	0.0	-0.0	6 -0.0)6 (0.09	0.06	-0.05	0.04	-0.01	0.01	-0.20	-0.10	-0.0	0.03	-0.10	-0.06	0.01	-0.02	-0.07	-0.13	0.12	0.15	0.04	-0.01	-0.06	0.17	0.00	0.11	-0.23	-0.25	-0.26	-0.18	-0.23	0.00	1.00	i						
recip	-0.11	1 -0.1	0.0	9 0.0)6 -(0.06	0.05	0.09	-0.13	-0.08	-0.05	-0.26	0.00	-0.08	-0.07	0.08	-0.11	0.04	0.00	-0.10	-0.06	-0.02	0.11	-0.05	-0.09	-0.11	0.20	0.11	0.10	-0.19	-0.15	-0.10	-0.22	-0.10	1.00	0.01	1.00						
VindDir	0.01	1 -0.0	0.0	2 -0.0)4 (0.04 -	0.01	0.12	-0.14	-0.08	0.06	0.11	0.00	-0.04	1-0.06	-0.02	0.07	-0.03	-0.02	0.04	0.12	-0.11	-0.28	-0.07	-0.01	-0.08	0.06	0.03	0.03	-0.05	-0.04	-0.03	-0.09	-0.01	0.01	-0.15	0.01	1.00					
VindSpd	0.09	0.0	-0.0	8 -0.0)3 (0.10	0.08	0.01	0.05	0.04	-0.06	6 -0.11	-0.03	0.10	0.06	-0.10	-0.13	-0.04	-0.01	-0.08	-0.04	-0.03	-0.01	-0.11	0.02	0.01	0.23	-0.09	0.06	-0.17	-0.18	-0.18	-0.17	-0.19	-0.02	0.10	-0.02	0.12	1.00				
nMax	-0.01	1 -0.0	0.0	2 0.0)7 -(0.02	0.06	0.11	-0.05	-0.03	-0.09	-0.05	-0.10	-0.02	2 -0.13	0.04	0.13	0.06	0.09	-0.05	-0.17	0.16	0.10	0.15	-0.05	-0.11	-0.09	0.06	0.00	0.16	0.14	0.12	0.28	0.07	-0.12	0.00	-0.12	0.02	-0.08	1.00			
nMin	-0.09	-0.1	0.1	5 -0.1	18 -(0.16 -	0.08	0.02	-0.10	-0.16	-0.09	-0.16	-0.08	0.04	1 -0.31	0.06	0.18	0.01	-0.12	0.02	-0.05	0.08	0.06	-0.16	-0.13	-0.15	-0.03	0.19	0.03	0.05	0.05	0.05	0.14	0.03	0.04	-0.07	0.04	-0.03	-0.08	0.29	1.00		
Precip	-0.10	-0.0	0.1	7 0.0)1 -(0.15 -	0.01	0.03	-0.15	-0.06	-0.07	-0.01	0.19	-0.12	2 -0.11	0.05	0.02	0.02	-0.07	-0.29	-0.11	-0.13	-0.24	-0.20	-0.11	-0.13	0.05	0.12	0.01	-0.08	-0.05	-0.02	-0.16	0.04	0.36	0.05	0.36	-0.05	-0.06	-0.39	0.03	1.00	
Snow	0.06	0.0	-0.1	6 -0.1	12 (0.08	0.03	0.01	0.02	-0.06	0.12	0.06	0.07	7 -0.09	0.14	-0.14	0.07	-0.06	-0.07	-0.10	0.10	-0.19	0.08	-0.33	-0.01	-0.04	0.06	-0.02	0.01	-0.06	-0.07	-0.08	-0.12	-0.04	0.00	0.15	0.00	-0.02	0.11	-0.33	-0.32	0.14	1.0

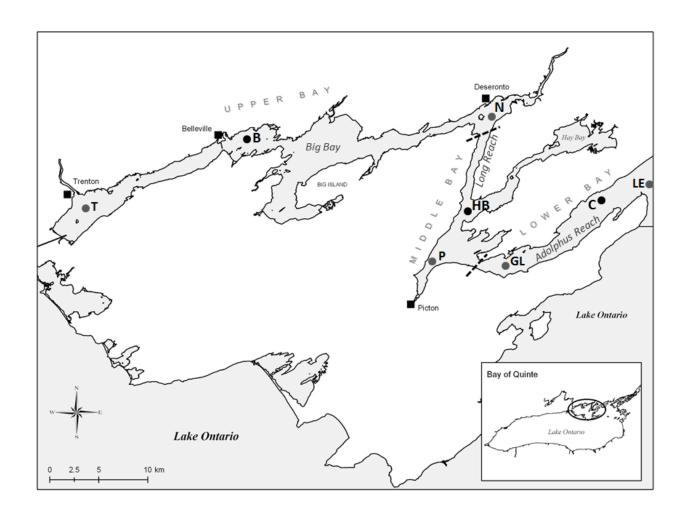
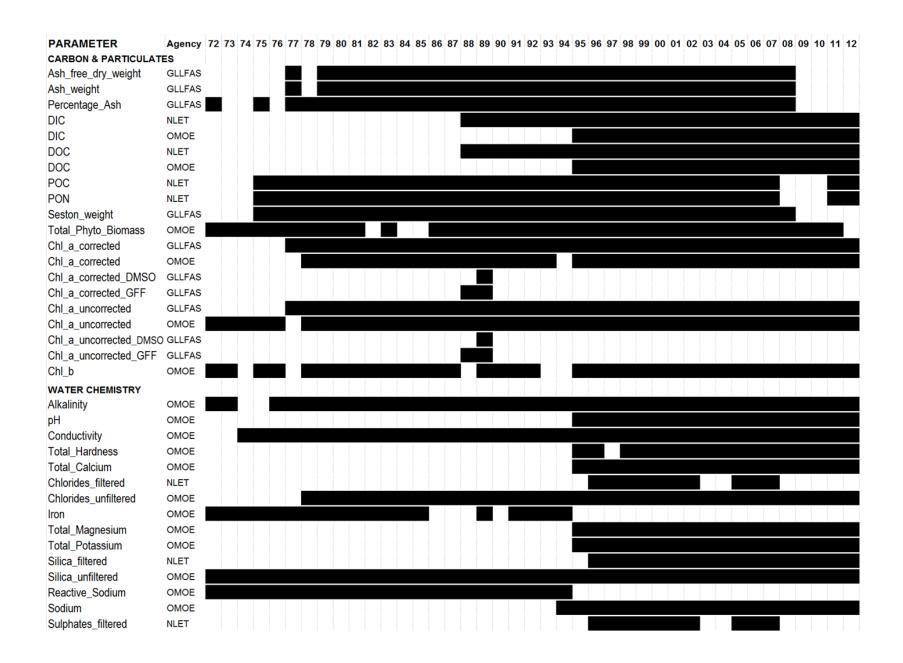


Figure 1: The Bay of Quinte location on Lake Ontario (inset) and long-term sampling locations for Project Quinte. The stations with solid black circles: Belleville (B), Hay Bay (HB) and Conway (C) are sites with complete time-series found in this report. Stations with grey circles: Trenton (T), Napanee (N), Picton (P), Glenora (GL) and Lennox (LE) are sites with partial time-series. Dashed lines delimit the upper, middle and lower bay sectors.



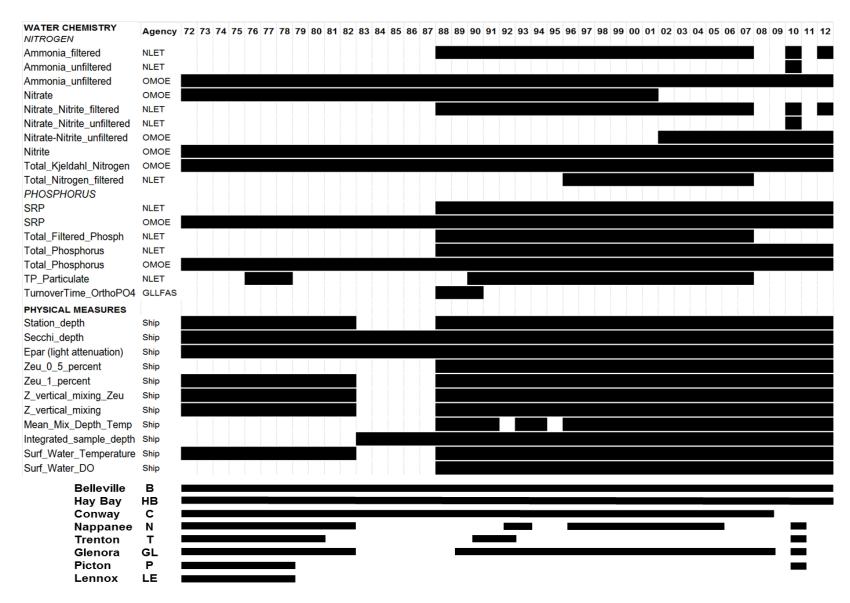


Figure 2: Biogeochemical properties measured for Project Quinte for 1972-2012. Solid bars indicate years in which data are available for that parameter. Locations sampled by year are indicated at the bottom.

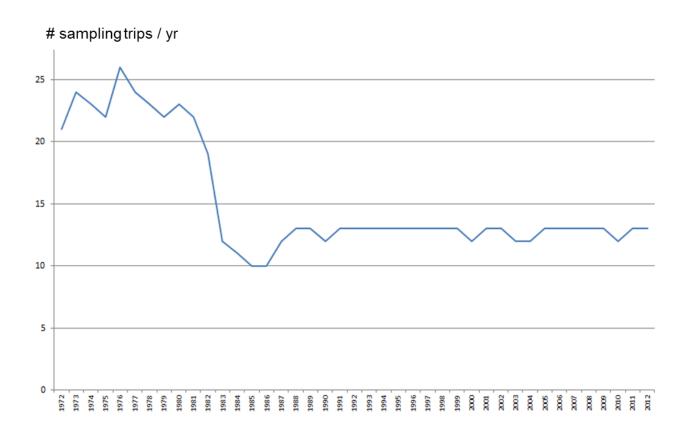


Figure 3: Number of sampling trips per year for Project Quinte 1972-2012. For the stations sampled refer to Fig. 2.

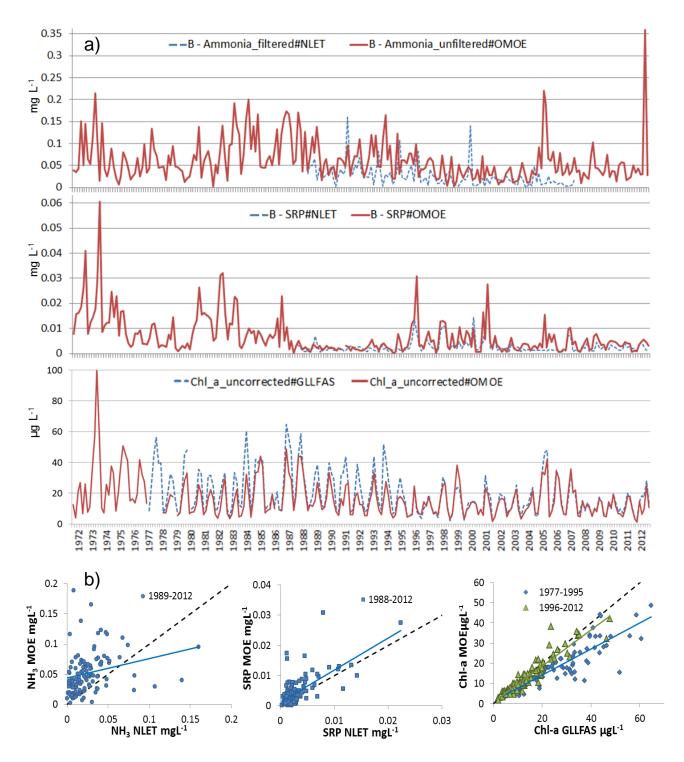


Figure 4: a) Differences between Ontario Ministry of the Environment (OMOE), National Laboratory for Environmental Testing (NLET) and Great Lakes Laboratory for Fisheries and Aquatic Sciences (GLLFAS) analytical labs time-series for ammonia (top), soluble dissolved phosphorus (SRP, middle) and chlorophyll-a (bottom). b) Plots of the same comparisons of year-ranges ammonia and SRP and for chl-a. The 1:1 is shown as dashed line. Regression equations are found in the text.

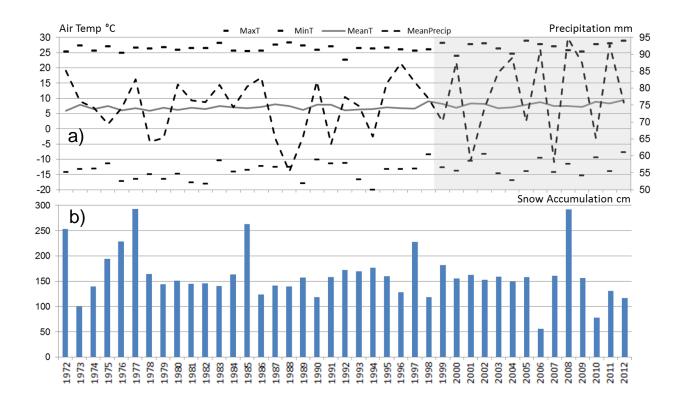


Figure 5: Climate measurements (from NOAA-NCDC) for Trenton Air Force Base (1972-2012) of (a) air temperatures (annual mean (solid line) with upper and lower bars indicating min and max), annual precipitation (dashed line) in mm and (b) annual snow accumulation in cm. The shaded area in (a) represents the period of greater climactic variability post 1999 noted in the text and in Table 1.

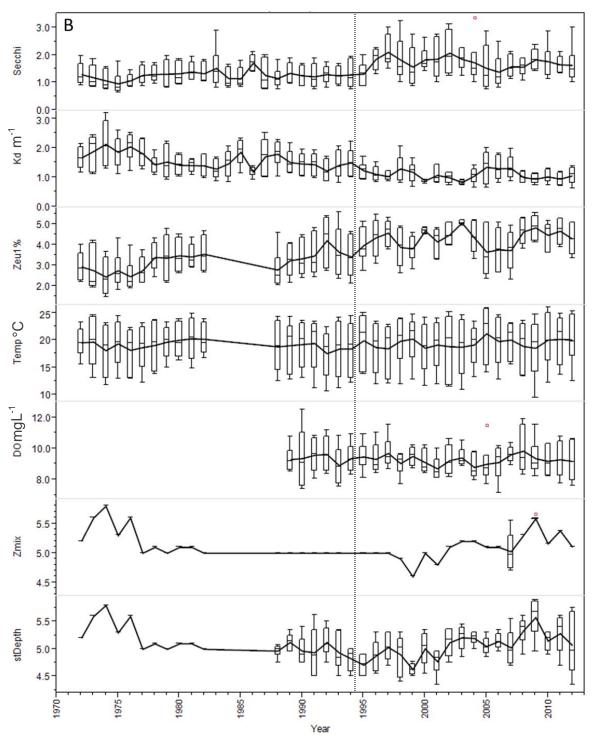


Figure 6: Belleville (B) annual box plots (1972-2012) of the monthly physical environment measurements. Clarity values: Secchi depth, light-attenuation (k_d) and euphotic depth of 1% surface light (Zeu1%). Water column: epilimnetic temperature, dissolved oxygen, mixed depth (Zmix) and station depth (stDepth). Measures without units are m. Boxes are 25th and 75th quartiles with whiskers 1.5 of quartile range, median box line and outliers as points. Bold line connects the annual means. Vertical fine-dotted line separates time groupings of pre and post-1995.

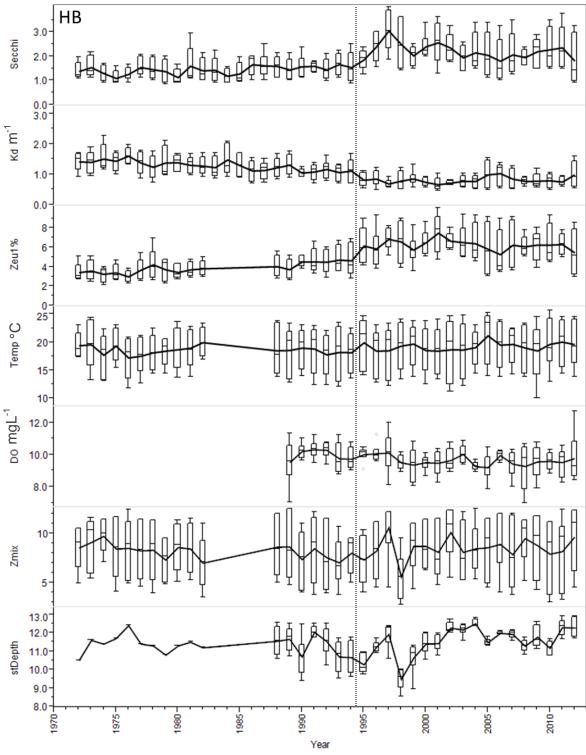


Figure 7: Hay Bay (HB) annual box plots (1972-2012) of the monthly physical environment measurements. Clarity values: Secchi depth, light-attenuation (k_d) and euphotic depth of 1% surface light (Zeu1%). Water column: epilimnetic temperature, dissolved oxygen, mixed depth (Zmix) and station depth (stDepth). Measures without units are m. Box plots as in Fig. 6.

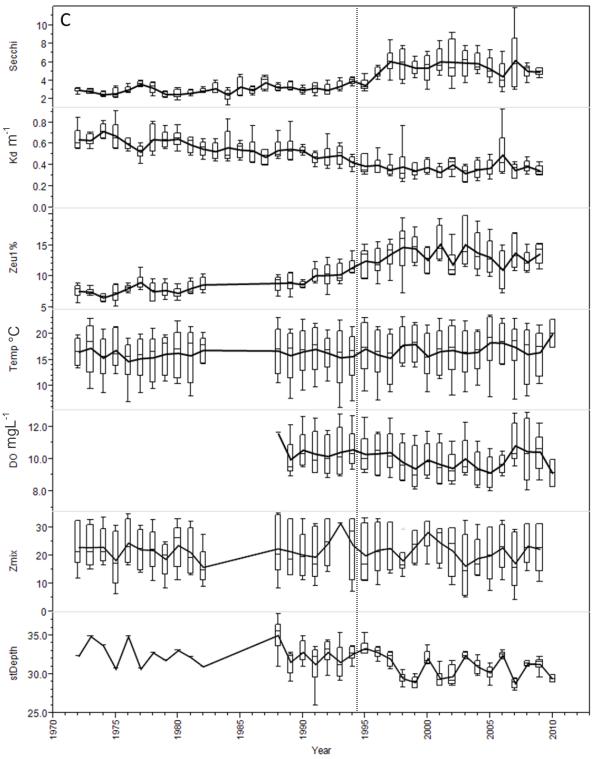


Figure 8: Conway (C) annual box plots (1972-2012) of the monthly physical environment measurements. Clarity values: Secchi depth, light-attenuation (k_d) and euphotic depth of 1% surface light (Zeu1%). Water column: epilimnetic temperature, dissolved oxygen, mixed depth (Zmix) and station depth (stDepth). Measures without units are m. Box plots as in Fig. 6.

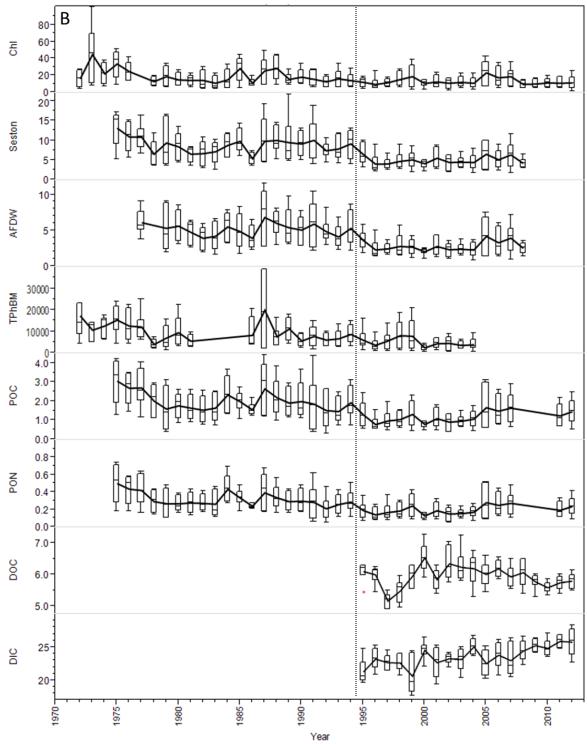


Figure 9: Belleville (B) annual box plots (1972-2012) of the monthly carbon particulates and dissolved fractions. Series includes: chlorophyll-a, seston, ash-free dry-weight (AFDW), total phytoplankton biomass (TPhBM), particulate organic carbon (POC), particulate organic nitrogen (PON), dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC). Units are mgL⁻¹ except chlorophyll-a (μgL⁻¹) and phytoplankton biomass (mg·m⁻³). Plots are as Fig. 6.

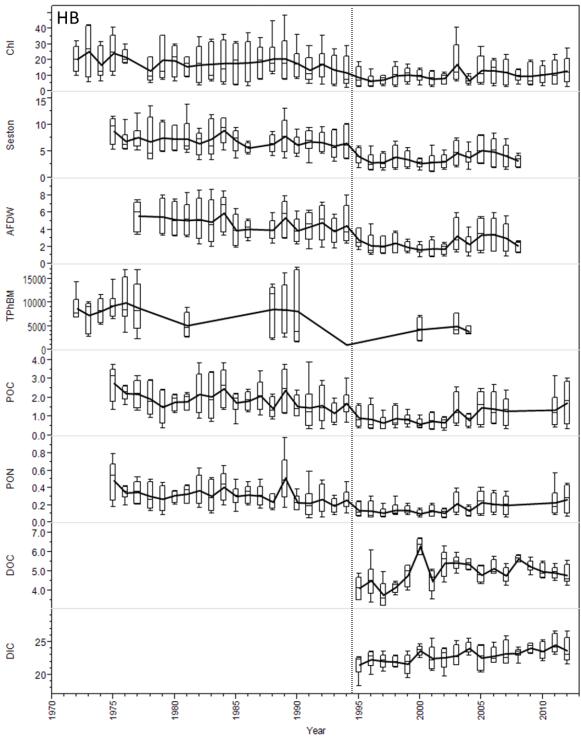


Figure 10: Hay Bay (HB) annual box plots (1972-2012) of the monthly carbon particulates and dissolved fractions. Series includes: chlorophyll-a, seston, ash-free dryweight (AFDW), total phytoplankton biomass (TPhBM), particulate organic carbon (POC), particulate organic nitrogen (PON), dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC). Units are mgL⁻¹ except chlorophyll-a (μgL⁻¹) and phytoplankton biomass (mg·m⁻³). Plots are as Fig. 6.

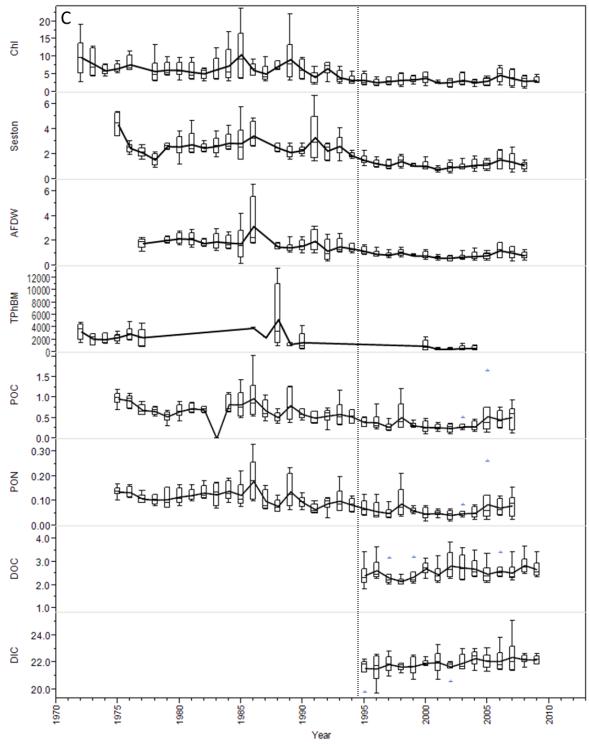


Figure 11: Conway (C) annual box plots (1972-2012) of the monthly carbon particulates and dissolved fractions. Series includes: chlorophyll-a, seston, ash-free dry-weight (AFDW), total phytoplankton biomass (TPhBM), particulate organic carbon (POC), particulate organic nitrogen (PON), dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC). Units are mgL⁻¹ except chlorophyll-a (μgL⁻¹) and phytoplankton biomass (mg·m⁻³). Plots are as Fig. 6.

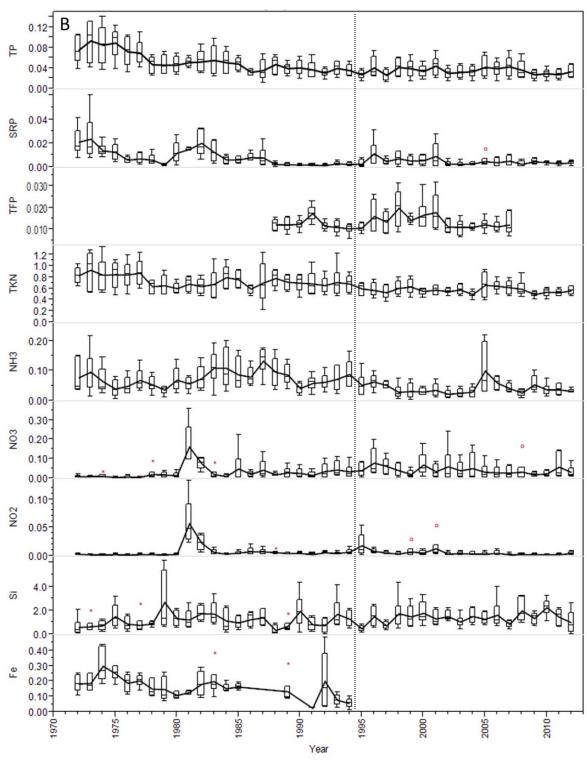


Figure 12: Belleville (B) annual box plots (1972-2012) of the monthly nutrient constituents including: total phosphorus (TP), soluble reactive phosphorus (SRP), total filtered phosphorus (TFP), total Kjeldahl nitrogen (TKN), ammonia (NH $_3$), nitrate (NO $_3$), nitrite (NO $_2$), silicate (Si) and iron (Fe). All units are mgL $^{-1}$. Plots are as Fig. 6.

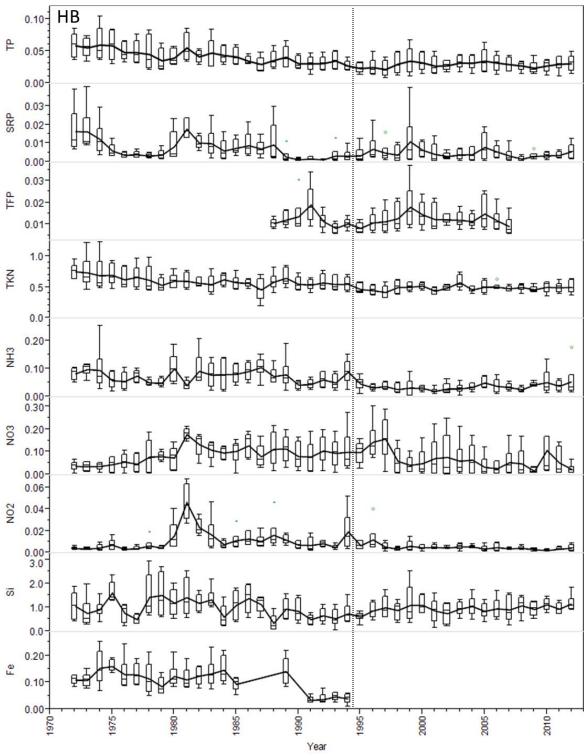


Figure 13: Hay Bay (HB) annual box plots (1972-2012) of the monthly nutrient constituents including: total phosphorus (TP), soluble reactive phosphorus (SRP), total filtered phosphorus (TFP), total Kjeldahl nitrogen (TKN), ammonia (NH $_3$), nitrate (NO $_3$), nitrite (NO $_2$), silicate (Si) and iron (Fe). All units are mgL $^{-1}$. Plots are as Fig. 6.

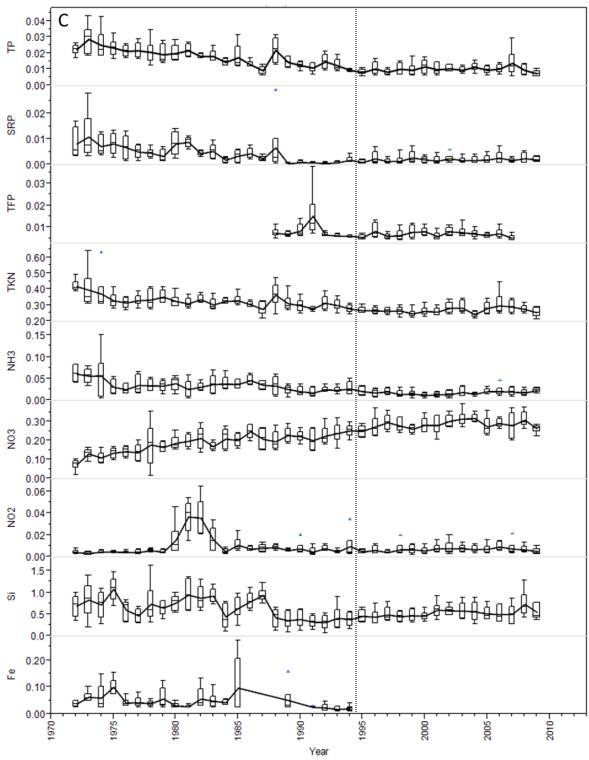


Figure 14: Conway (C) annual box plots (1972-2012) of the monthly nutrient constituents including: total phosphorus (TP), soluble reactive phosphorus (SRP), total filtered phosphorus (TFP), total Kjeldahl nitrogen (TKN), ammonia (NH₃), nitrate (NO₃), nitrite (NO₂), silicate (Si) and iron (Fe). All units are mgL⁻¹. Plots are as Fig. 6.

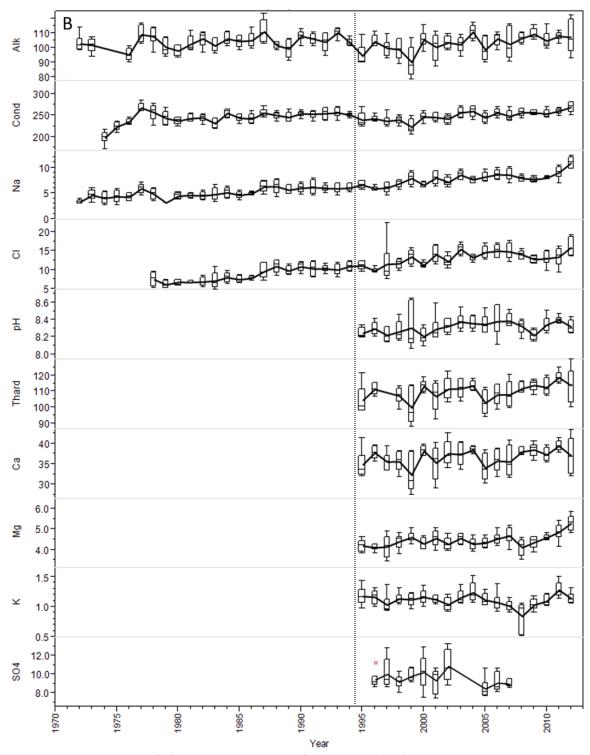


Figure 15: Belleville (B) annual box plots (1972-2012) of the monthly dissolved constituents of water chemistry including: Alkalinity, specific conductivity, sodium, chloride, dissolved inorganic carbon, dissolved organic carbon, total hardness, total calcium, magnesium and sulphate. All units are mgL^{-1} except for specific conductivity (μScm^{-1}) and pH. Plots are as Fig. 6.

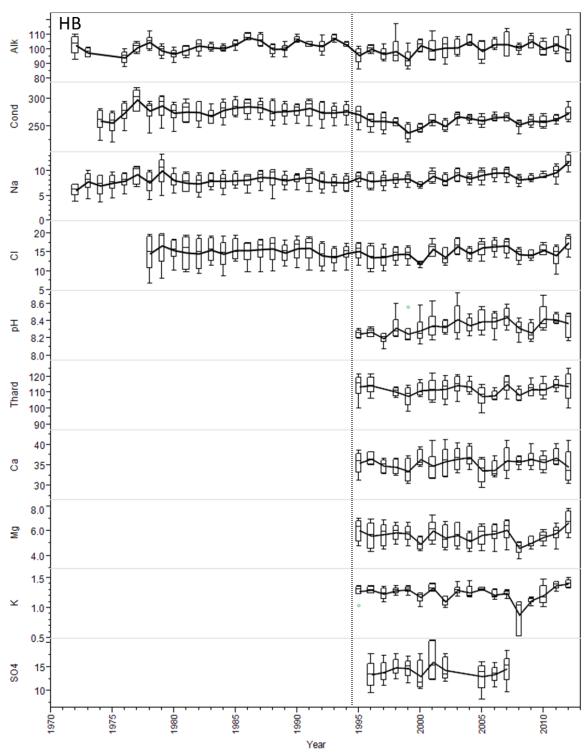


Figure 16: Hay Bay (HB) annual box plots (1972-2012) of the monthly dissolved constituents of water chemistry including: Alkalinity, specific conductivity, sodium, chloride, dissolved inorganic carbon, dissolved organic carbon, total hardness, total calcium, magnesium and sulphate. All units are mgL^{-1} except for specific conductivity (μScm^{-1}) and pH. Plots are as Fig. 6.

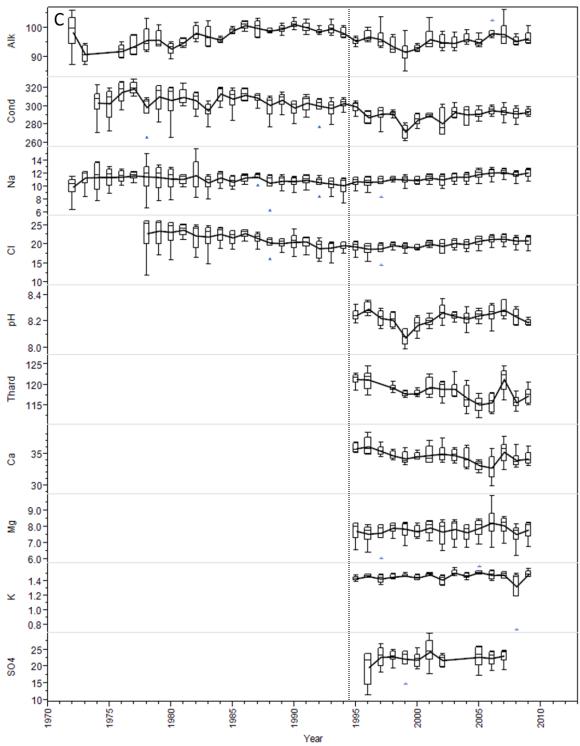


Figure 17: Conway (C) annual box plots (1972-2012) of the monthly dissolved constituents of water chemistry including: Alkalinity, specific conductivity, sodium, chloride, dissolved inorganic carbon, dissolved organic carbon, total hardness, total calcium, magnesium and sulphate. All units are mgL⁻¹ except for specific conductivity (μScm⁻¹) and pH. Plots are as Fig. 6.

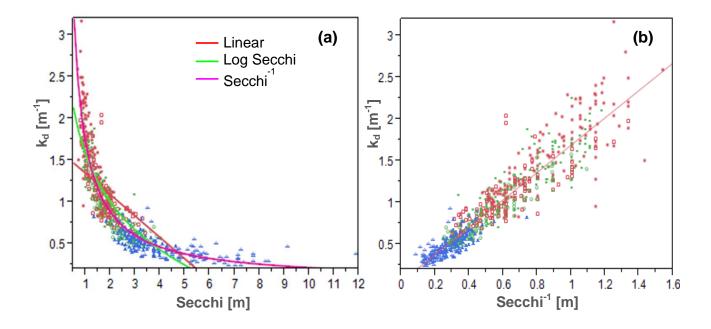


Figure 18: Regression of Secchi depth with light attenuation (k_d or εpar) for the Project Quinte data. Values from the upper bay Belleville are shown with red squares, middle bay Hay Bay with green circles and lower bay Conway with blue triangles. Solid symbols indicate pre1995 values. (a) Lines of best fit for a linear, log-Secchi, and inverse Secchi relationship. (b) The best overall fit is for the inverse relationship (refer to text for explanation).

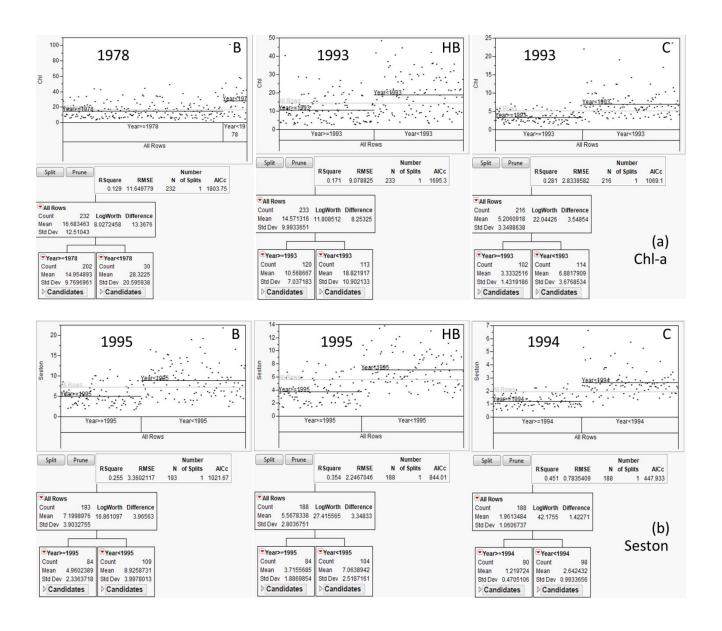


Figure 19: Partition AIC analysis output from JMP v.10 using year as the predictor for the (a) chlorophyll-a and (b) seston time-series for Belleville (B), Hay Bay (HB) and Conway (C) sites. The output gives the plot of values based on the AIC model split, and values for the difference in the means is given in the boxes below. The HB and C sites have the best split model for chlorophyll-a at 1993 and 1978 for B, while the B and HB sites have the best model split for seston at 1995 and 1994 for C.

	CHL			Seston			TP			Kd		
YEAR	В	НВ	C	В	НВ		В	НВ	С	В	НВ	c
1972	_	*	*	-	-	-	*	*	*	*	*	*
1973	*	*	*	-	-		*	*	*	*	*	*
1974	*	*	*	-	-	-	*	*	*	*	*	*
1975	*	*	*	*	*	*	*	*	*	*	*	*
1976	*	*	*	*	*	*	*	*	*	*	*	*
1977	-	-	-	*	*	*	*	*	*	*	*	*
1978					*			*	*		*	*
1979		*	*	*	*	*			*	*	*	*
1980		*	*	*	*	*			*		*	*
1981		*			*	*	*	*	*		*	*
1982		*			*	*	*	*	*		*	*
1983		*	*	*	*	*	*	*	*		*	*
1984		*	*	*	*	*	*	*		*	*	*
1985	*	*	*	*	*	*			*	*	*	*
1986		*	*			*					*	*
1987	*	*		*	-	-				*	*	
1988	*	*	*	*	*	*			*	*	*	*
1989		*	*	*	*	*				*	*	*
1990		*	*	*	*	*				*		*
1991				*	*	*						
1992		*	*	*	*	*					*	
1993		*		*	*	*						
1994				*	*					*	*	
1995												
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1997												
1998												
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2003		*										
2004												
2005	*											
2006												
2007												
2008												
2009												
2010												
2011												
2012												

Figure 20: Yearly deviations from the overall mean of the time-series (1972-2012) for chlorophyll-a, seston, total phosphorus, and light attenuation for Belleville (B), Hay Bay (HB) and Conway (C) sites. Sites marked with an asterisk (*) or no symbol are not significantly different from each other (repeated measures ANOVA with Tukey HSD comparisons at p<0.05). Cells marked in pink are significantly greater than the mean while blue cells are significantly lower than the overall mean of the time-series.

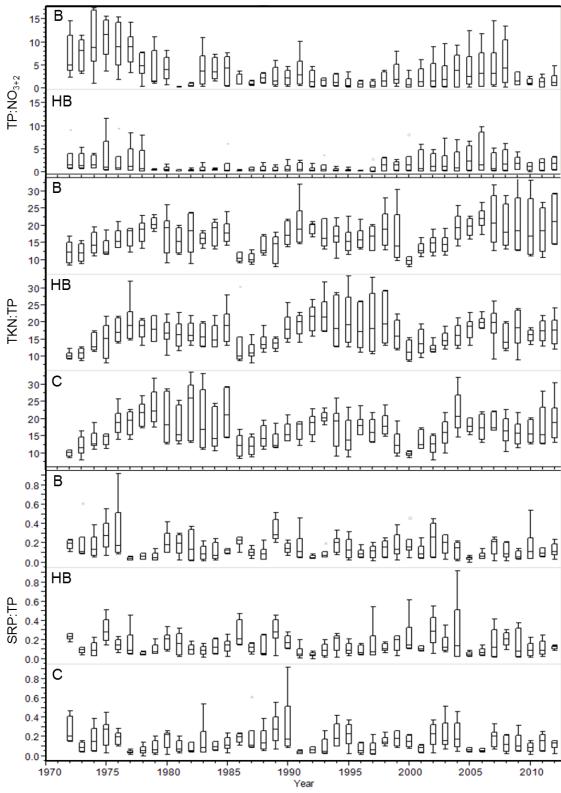


Figure 21: Annual box-plot time-series (1972-2012) for nutrient ratios from Belleville (B), Hay Bay (HB) and Conway (C) sites for total phosphorus to nitrate+nitrite (TP:NO $_{3+2}$), total Kjeldahl nitrogen to total phosphorus (TKN:TP) and soluble reactive phosphorus to total phosphorus (SRP:TP). No plot for C site TP:NO $_{3+2}$ (see text). Box plots as Fig. 6.

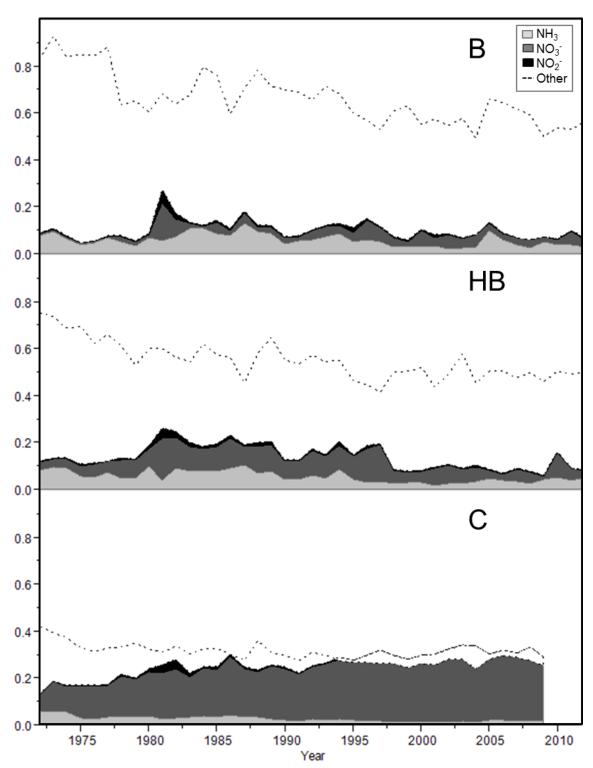


Figure 22: Fractions of nitrogen constituents given by a stacked area graph (1972-2012) from the OMOE dataset of Project Quinte for Belleville (B), Hay Bay (HB) and Conway (C). Ammonia is given in light grey, nitrate in darker grey and nitrite in black. The dotted line gives the rest of the nitrogen constituents to add to the value of total nitrogen from TKN. The larger fraction of nitrate can be seen at C compared to the B and HB sites.



Figure 23: Correlation plots of Table 2a with the 95% confidence ellipse (shaded) for each pair of measurements at Belleville (B). Histograms for each measurement illustrate the underlying distribution so that a deviation from normality can be determined.

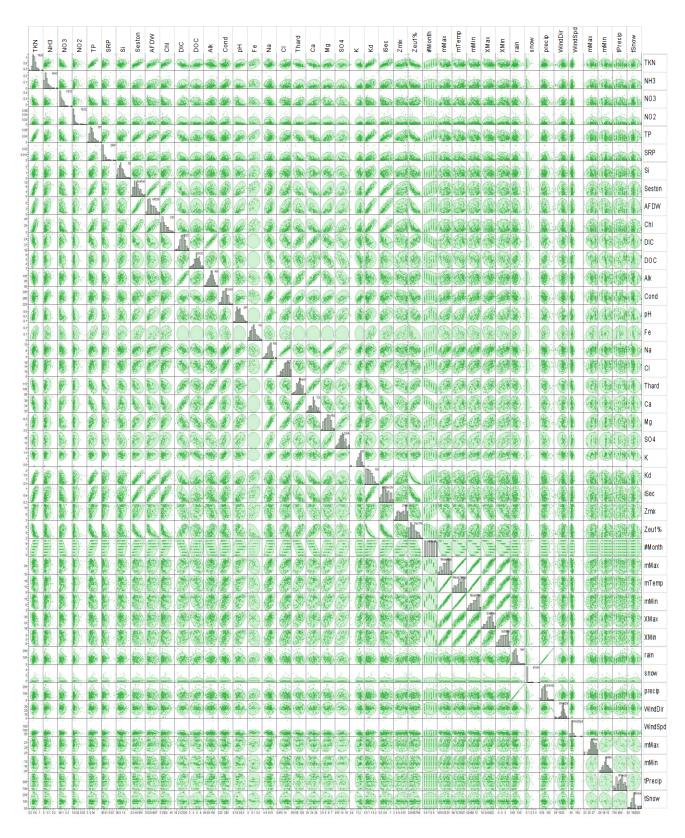


Figure 24: Correlation plots of Table 2b and the 95% confidence ellipse (shaded) for each pair of measures at Hay Bay (HB). Histograms for each measurement illustrate the underlying distribution so that a deviation from normality can be determined.

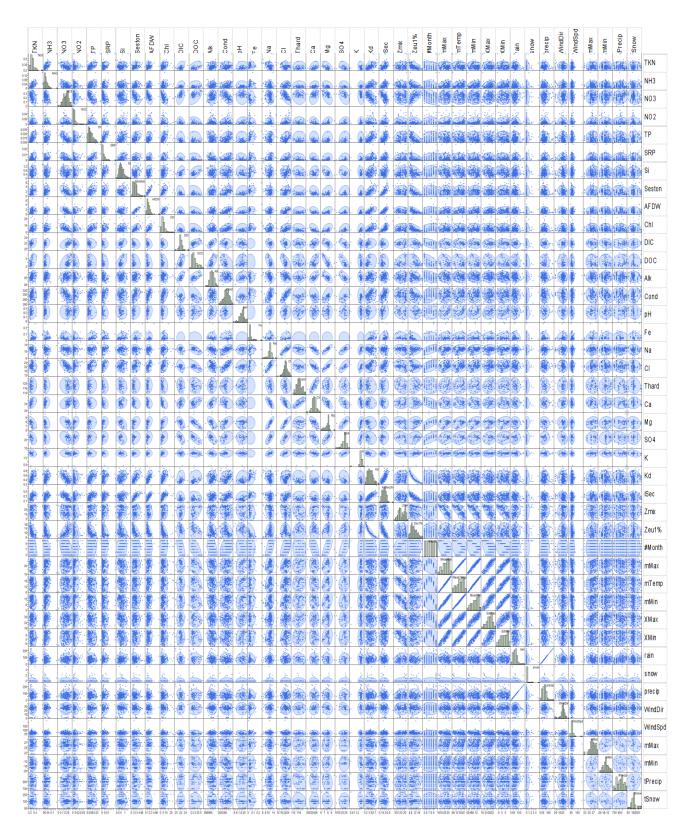


Figure 25: Correlation plots of Table 2b and the 95% confidence ellipse (shaded) for each pair of measures at Conway (C). Histograms for each measurement illustrate the underlying distribution so that a deviation from normality can be determined.

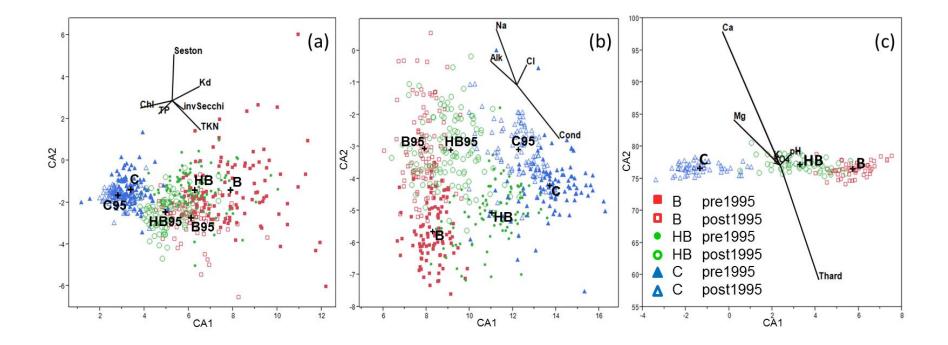


Figure 26: Linear Discriminant Analysis (LDA) canonical plot output from JMP v10 showing biplot rays and sites for a) biological/nutrient/physical measures: seston, chlorophyll-a (Chl), total Kjeldahl nitrogen (TKN), total phosphorus (TP), secchi⁻¹ (invSecchi) and light attenuation (kd); b) dissolved constituents having a long time-series: alkalinity (alk), specific conductivity (Cond), sodium (Na) and chloride (Cl); and c) for dissolved series with data limited to post-1995 only: total hardness (THard), calcium (Ca), magnesium (Mg), potassium (K), sulphate (SO4) and pH. All graphs use the same symbols of Belleville (B, red squares), middle bay Hay Bay (HB, green circles) and lower bay Conway (C, blue triangles) with solid symbols indicating pre-1995 values. Each site and time-stanza centroid is labeled using a + with post-1995 centroids marked 'Site'95. The rays on the biplots give the Mahalanobis distance of the observation from the site centroid and direction in the canonical space.

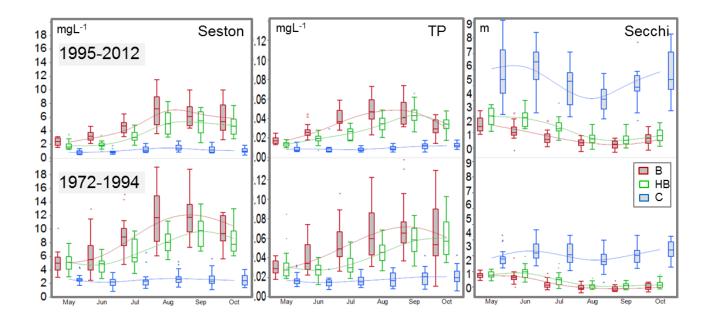


Figure 27: Monthly box plots for the time-stanza of pre1995 (bottom) and post1995 (top) for seston, total phosphorus and Secchi depth. Outlier values are shown as points. Line is the smoothed spline fit of monthly means. Box plots are as Fig. 6.

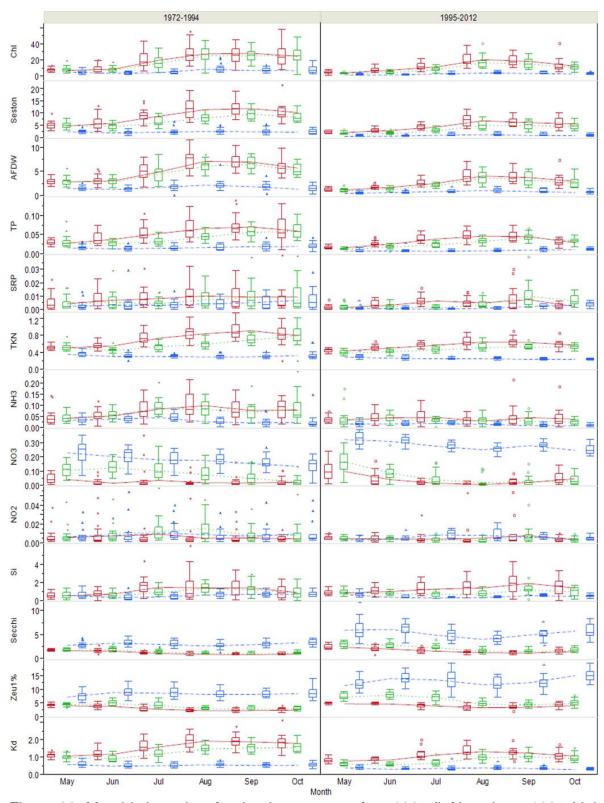


Figure 28: Monthly box plots for the time-stanza of pre1995 (left) and post1995 (right) for selected biological/nutrient/clarity measures. Boxplots are for Belleville (B, red), Hay Bay (HB, green) and Conway (C, blue) and outliers are shown as points. Lines connect the monthly means. Box plots are as Fig. 6.

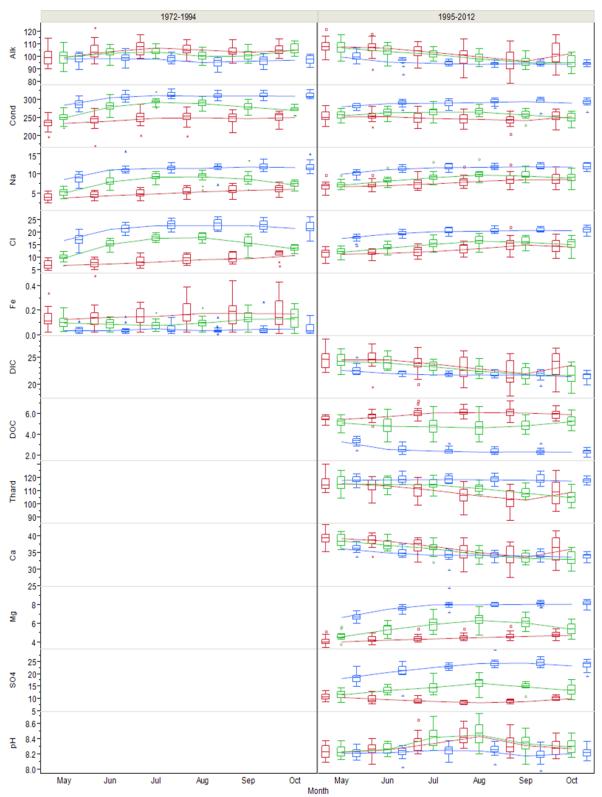


Figure 29: Monthly box plots for the time-stanza of pre1995 (left) and post1995 (right) for selected dissolved and water chemistry measures. Boxplots are for Belleville (B, red), Hay Bay (HB, green) and Conway (C, blue) and outliers are shown as points. Lines connect the monthly means. Box plots are as Fig. 6.

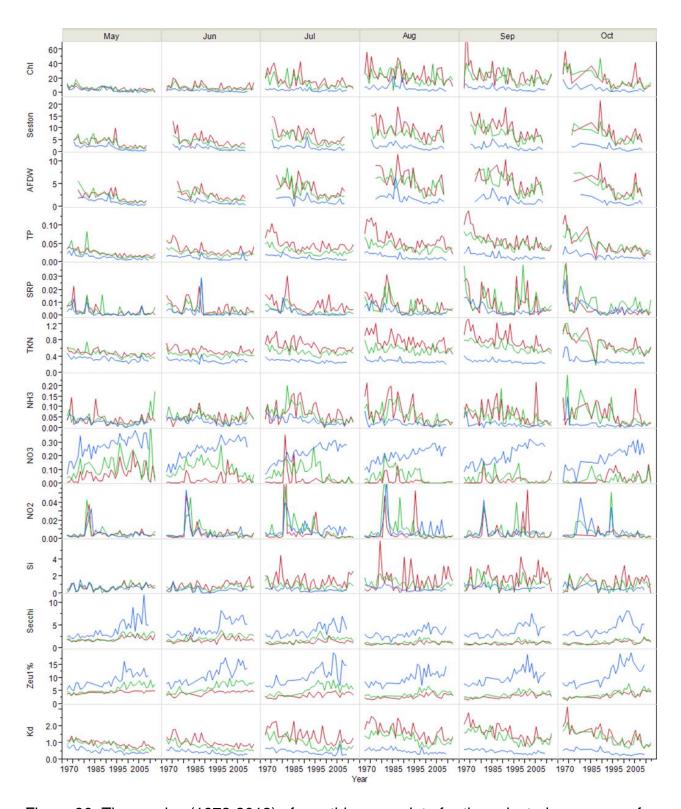


Figure 30: Time-series (1972-2012) of monthly mean data for the selected measures of biological/nutrient/clarity for Belleville (B, red), Hay Bay (HB, green) and Conway (C, blue). Lines connect the monthly means.

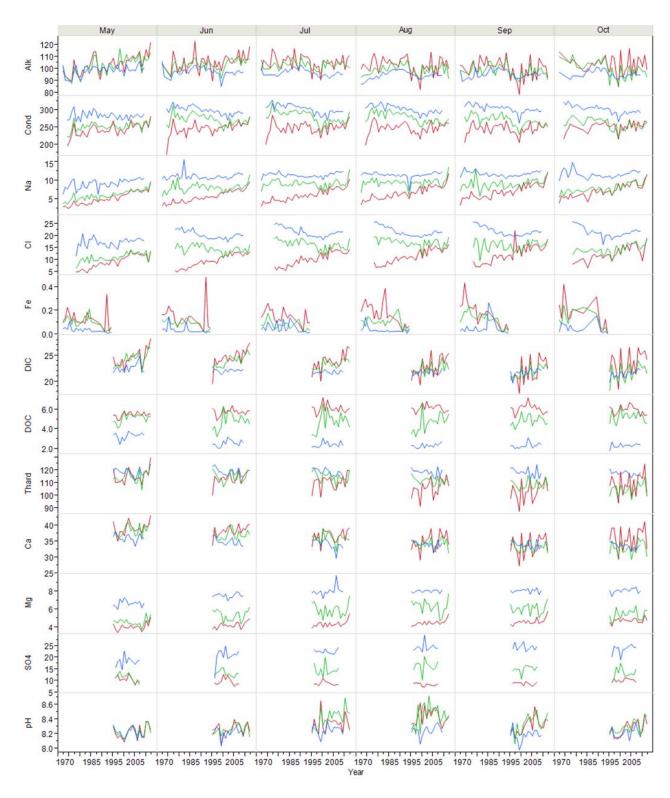


Figure 31: Time-series (1972-2012) of monthly mean data for selected measurements of biological/nutrient/clarity for Belleville (B, red), Hay Bay (HB, green) and Conway (C, blue). Lines connect the monthly means.

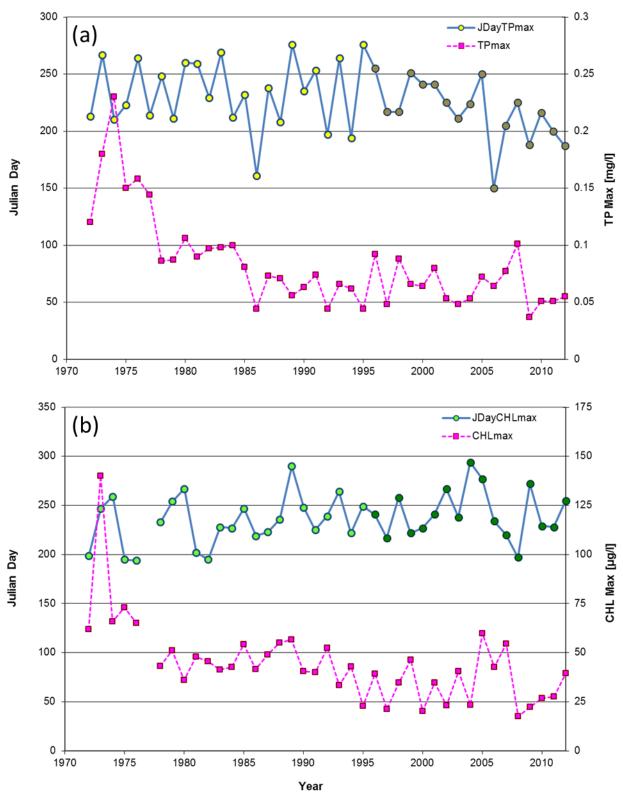


Figure 32: Time-series (1972-2012) for Belleville of the (a) maximum total phosphorus (TPmax) and b) chlorophyll-a with the corresponding Julian date (solid blue line) of the sample. The decline in TPmax Julian date post1995 is marked with dark filled circles.

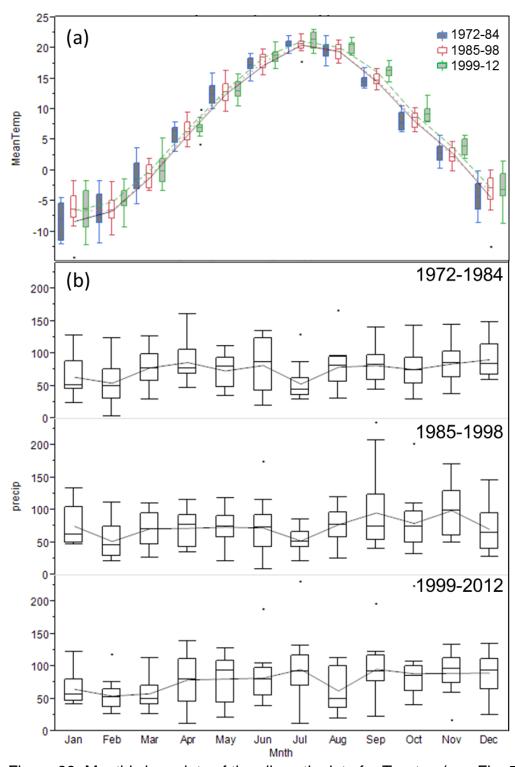


Figure 33: Monthly box plots of the climactic data for Trenton (see Fig. 5) for time stanzas of 1972-1984 (blue solid line, dark grey filled boxes), 1985-1998 (red dotted line, unfilled boxes), and 1999-2012 (green dashed line, light grey filled boxes) for mean temperature (top) and precipitation (bottom). Lines connect the monthly means.

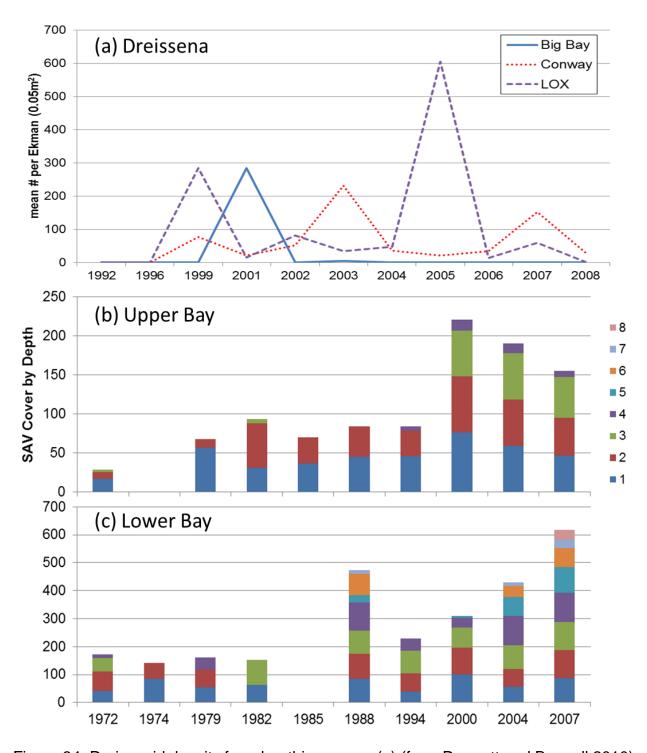


Figure 34: Dreissenid density from benthic surveys (a) (from Dermott and Bonnell 2010) and submerged aquatic vegetation (SAV) cover by depth interval for (b) upper and (c) lower bay during surveys from 1972 and 2008 (from Leisti et al. 2012).