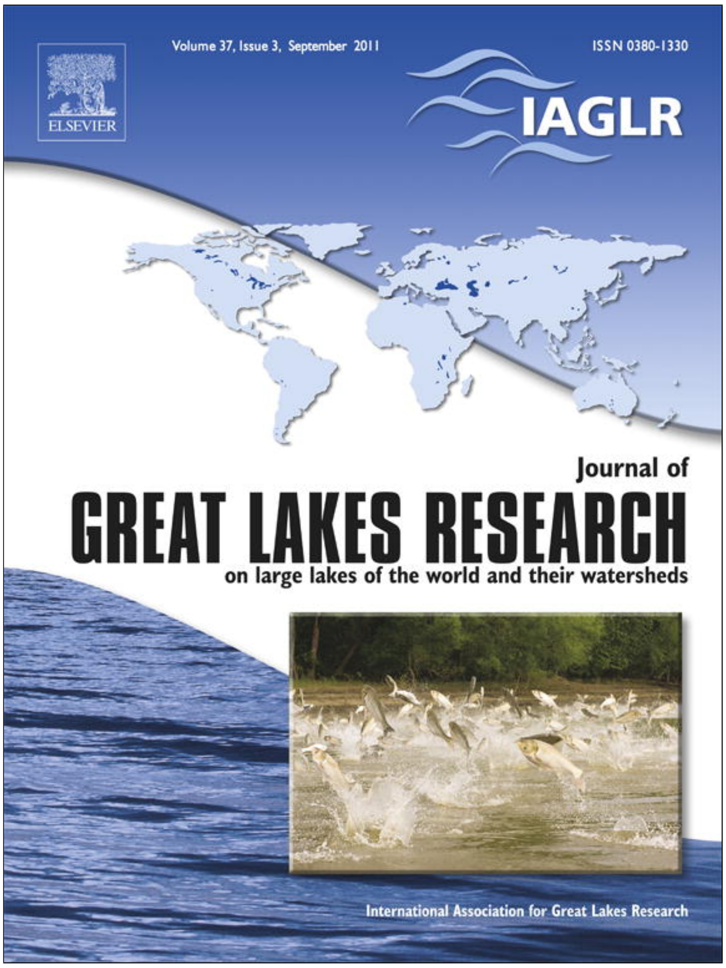
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Predicting the response of Hamilton Harbour to the nutrient loading reductions: A modeling analysis of the “ecological unknowns”

Alex Gudimov [a], Maryam Ramin [a], Tanya Labencki [b], Christopher Wellen [a], Milind Shelar [a], Yuko Shimoda [a], Duncan Boyd [b], George B. Arhonditsis [a,*]

[a] *Ecological Modeling Laboratory, Department of Physical & Environmental Sciences, University of Toronto, Ontario, Canada M1C 1A4*
[b] *Water Monitoring & Reporting Section, Environmental Monitoring and Reporting Branch, Ontario Ministry of Environment, Toronto, Ontario, Canada M9P 3V6*

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ABSTRACT

We examine the likelihood of delisting the Hamilton Harbour as an Area of Concern, if the nutrient loading reductions proposed by the Remedial Action Plan are actually implemented. Our analysis suggests that the chl *a* criterion of 10 μg L^{-1} is achievable, but the water quality setting process should explicitly accommodate the natural variability by allowing for a realistic percentage of violations, e.g., exceedences of less than 10–15% of the weekly samples during the stratified period should still be considered as compliance of the system. The current epilimnetic total phosphorus criterion of 17 μg L^{-1} is probably stringent and therefore a somewhat higher value (e.g., 20 μg L^{-1}) may provide a more realistic goal. Phosphorus dynamics in the sediment–water column interface need to be revisited, as the internal nutrient loading can conceivably be a regulatory factor of the duration of the transient phase and the recovery resilience of the Harbour. We also pinpoint two critical aspects of the system dynamics that invite further investigation and will likely determine our predictive capacity to assess compliance with the chlorophyll *a* criterion of 10 μg L^{-1}, i.e., the nutrient recycling mediated by the microbial food web and the structural shifts towards a zooplankton community dominated by large-sized and fast-growing herbivores. The latter prospect highlights the notion that the bottom-up (i.e., nutrient loading reduction) approach historically followed in the Harbour was sufficient to bring the system in its present state, but any further improvements should be viewed in the context of a combined bottom-up and top-down (i.e., alleviation of the zooplanktivorous pressure) control.

Introduction

The International Joint Commission (*IJC*) identified 43 Areas of Concern in the Great Lakes basin where the water quality and ecosystem integrity were considered impaired. Hamilton Harbour was designated as one of 17 Canadian Areas of Concern (*AOC*) due to a number of Beneficial Use Impairments (BUIs), including those related to eutrophication or undesirable algae (Great Lakes Water Quality Agreement or GLWQA, 1978 — as amended 1987). Having the mandate of restoring and protecting environmental quality and beneficial uses, the Hamilton Harbour Remedial Action Plan (*RAP*) was formulated through a wide variety of government, private sector, and community participants (Hall et al., 2006). The foundation of the remedial measures and the setting of water quality goals reflect an ecosystem-type approach that considers the complex interplay among abiotic variables and biotic components pertinent to its beneficial uses (Hamilton Harbour Technical Team — Water Quality or HHTT—WQ, 2007). Specifically, local stakeholders have selected the warm water fishery as a priority use for the Harbour which was then related to a critical total phosphorus (*TP*) level following a “mental model” that dissected the eutrophication problem in the Harbour into a sequence of causal associations, i.e., fish need aquatic plants for shelter and reproduction, aquatic plants need light to grow, light will only penetrate the water column if chlorophyll *a* levels are sufficiently low, low chlorophyll *a* levels are achieved through sufficiently low *TP* concentrations (Charlton, 2001).

The substantial reduction of total phosphorus from the sewage effluents of the four wastewater treatment plants (*WWTPs*) and the steel mills that discharge into Hamilton Harbour, led to a significant decrease of the total phosphorus (*TP*) concentrations and to an improvement of the water clarity. In particular, Hiriart-Baer et al. (2009) recently showed that the soluble reactive phosphorus (*SRP*), total phosphorus (*TP*), and total ammonia (*TNH3*) concentrations have substantially decreased over the course of a 20-yr period (1987–2007), accompanied by a 15–20% decline of the average chlorophyll *a* levels in the system. Importantly, the same study provided evidence that phosphorus limiting conditions for phytoplankton growth are gradually prevailing in the Hamilton Harbour, and therefore further phosphorus loading reductions should trigger faster rates of water quality improvement (Hiriart-Baer et al., 2009). Yet, the system is still

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[*] Corresponding author. Tel.: +1 416 208 4858.
E-mail address: georgea@utsc.utoronto.ca (G.B. Arhonditsis).

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characterized by systematic spatial water quality gradients, reflecting the higher nutrient concentration in nearshore sites adjacent to major exogenous nutrient sources: (*i*) the Windermere basin where the non-point nutrient loads from Red Hill Creek along with the Hamilton–Wentworth *WWTP* effluents are being discharged; and (*ii*) the west end of Hamilton Harbour which receives substantial amounts of outflow water from Cootes Paradise; a productive system with very high chl *a* ($>30\ \mu g\ L^{-1}$) and *TP* ($>50\ \mu g\ L^{-1}$) concentrations. Further, the system arguably remains quite far from attaining the delisting water quality goals ($TP<17\ \mu g\ L^{-1}$, chl *a* $5–10\ \mu g\ L^{-1}$, Secchi Disk Transparency >3 m) set by the Stage 2 Update 2002 Report (Hamilton Harbour RAP Stakeholder Forum, 2003), while the uncertainty of the empirical relationships used to link reductions in nutrient mass loadings with the corresponding improvements in Harbour water quality cast doubt on the feasibility of the timeframe projected to achieve the anticipated conditions. Acknowledging the significance of the latter issue, the Hamilton Harbour *RAP* underscores the need of continuously tracking the system response to the variability associated with the exogenous loading and refining the nutrient loading targets and/or water quality goals accordingly (HHTT-WQ, 2007).

In this regard, aside from the regular monitoring of the system, mathematical modeling has been an integral part of the Hamilton Harbour restoration efforts. Ramin et al. (2011) recently developed a process-based eutrophication model that aimed to reproduce the interplay among eight state variables (i.e., nitrate, ammonium, phosphate, phytoplankton, cyanobacteria, zooplankton, organic nitrogen and organic phosphorus) within a relatively simple two-compartment vertical segmentation representing the epilimnion and hypolimnion of the Harbour. The planktonic food web model was subsequently calibrated with Bayesian inference techniques founded upon a statistical formulation that explicitly accommodated measurement error, parameter uncertainty, and model structure imperfection (Ramin et al., 2011). The model was then used to address several critical questions regarding the present status and the future response of the system, such as: How possible is it to meet the eutrophication delisting goals of the *AOC*, if the Stage 2 nutrient loading reduction targets of the Hamilton Harbour *RAP* are actually implemented? How frequently would the Stage 2 water quality goals be violated and what is the confidence level that the exceedance frequency of these goals will remain lower than the U.S. EPA endorsed 10% level? Ramin et al.'s (2011) projections suggested that the epilimnetic *TP* concentrations will decrease in response to the reduction of the external nutrient loadings and that the proposed quality goal of 17 μg *TP* L^{-1} will likely be met, if the Hamilton Harbour *RAP* phosphorus loading target of 142 kg day^{-1} is achieved. The attainment of the water quality goal related to the summer chlorophyll *a* concentrations ($5–10\ \mu g\ L^{-1}$) though was not unequivocally demonstrated, as the central tendency of the predictions can exceed the $10\ \mu g\ L^{-1}$ threshold level depending on the assumptions made about the strength of the top-down control as well as the importance of the internal nutrient sources (e.g., phosphorus release from the sediments, nutrient mineralization).

Concurrently with the Ramin et al. (2011) study, Gudimov et al. (2010) conducted a second (independent) modeling exercise based on an upgraded model structure that differs from the previously described eutrophication model in that: (*a*) the spatial segmentation consisted of three compartments representing the epilimnion, mesolimnion, and hypolimnion; (*b*) a third functional phytoplankton group (labeled as "Green Algae") was added to provide an intermediate competitor and to more realistically depict the continuum between diatom and cyanobacteria-dominated communities; and (*c*) a third trophic level was considered to account for the role of omnivorous zooplankton in the system. The predictions of the more complex model with regards to the attainment of the water quality goals for *TP* and chlorophyll *a* concentrations were very similar to the projections obtained from the Ramin et al. (2011) study. The same exercise also provided evidence that the anticipated structural shifts of the zooplankton community will determine the restoration rate as well as the stability of the new trophic state in the Harbour. Moreover, it was advocated that the level of planktivory should be a focal point of the remedial actions and may shape the response rate of the system to the nutrient loading reductions, since the larger zooplankton taxa (preferentially consumed by planktivorous fish) are particularly efficient in suppressing the standing phytoplankton biomass. The success of the fish restoration efforts has been traditionally perceived as being dependent upon the water quality improvements, but the two management actions at this stage should rather be viewed as having a recursive relationship that will likely modulate the success of the restoration efforts in the Harbour. Finally, both Ramin et al. (2011) and Gudimov et al. (2010) emphasized that all the predictions are dependent upon the assumptions made regarding the contemporary nutrient loading estimates along with what was perceived as present "average" water quality conditions in the Harbour.

To this end, the present analysis revisits two critical assumptions of the aforementioned modeling studies and examines their effects on the projected responses of the system to the targeted nutrient loading reductions.

- The first point involved the practice followed during the calibration of the two eutrophication models, aiming to reproduce the recent average water quality conditions along with the actual magnitudes of the major ecological processes and cause–effect relationships that underlie the Harbour dynamics. While this approach was rationalized as a pragmatic means to overcome the substantial uncertainty characterizing the exogenous nutrient loading estimates (see discussion in Gudimov et al., 2010), it entails the risk of misrepresenting the actual range of system dynamics experienced when misleadingly phasing out short-term shifts of the year-to-year variability. In particular, the Gudimov et al. (2010) and Ramin et al. (2011) calibration exercises revolved around an average summer epilimnetic *TP* level of $30\ \mu g\ L^{-1}$, which was on par with Hiriart-Baer et al.'s (2009) seasonal Kendall trend analysis (see the corresponding solid line in their Fig. 2). Yet, the same study reported a positive (but statistically non-significant) reversal of the *TP* trends since the year 2000 (Seasonal Kendall slope estimator $\approx 0.48\ \mu g\ L^{-1}\ yr^{-1}$), and recent monitoring evidence suggests that summer epilimnetic *TP* concentrations of $35–38\ \mu g\ L^{-1}$ are fairly typical at the offshore areas of the Harbour. Thus, the question arising is what is the likelihood of the system to still meet the *TP* water quality goal, if the starting point is higher by 5–8 μg *TP* L^{-1} relative to the reference conditions used from the earlier modeling studies?
- The second assumption involved the ecological parameterization of the two eutrophication models and more specifically the high values assigned to the fractions of plankton metabolism (80%) that are returned into the system as dissolved phase phosphorus. While this strategy was proven effective to simultaneously match the typically high summer chl *a* levels ($>15\ \mu g\ L^{-1}$) and low phosphate concentrations ($<2–3\ \mu g\ L^{-1}$) in the system, it may have disengaged the summer phytoplankton growth from the exogenous nutrient loading reductions as it postulated increased reliance on internal nutrient fluxes. Thus, the question arising is how realistic is the latter ecological parameterization? Should we expect higher frequency of compliance with the chlorophyll *a* criterion of $10\ \mu g\ L^{-1}$, if the assumption on the importance of the nutrient regeneration mechanisms is relaxed?
- In addition to the previous critical questions, the present study challenges the historical notion that the phosphorus release from the sediments is minimal and examines the potential ramifications to the future system responses.

- Finally, our analysis offers insights into the optimal configuration of the zooplankton community for achieving faster recovery rates by assessing the relative importance of the zooplankton abundance vis-à-vis the zooplankton community composition.

Methods

We conducted a series of modeling experiments based on the eutrophication model presented by Gudimov et al. (2010). The conceptual design of the model is presented in Fig. 1, and the model equations and the new parameterization are provided in Tables 1 and 2 of the Electronic Supplementary Material or ESM. Detailed model description and sensitivity analysis have been presented in Gudimov et al. (2010), and thus we briefly highlight the basic model features in the Electronic Supplementary Material. In our numerical experiments, the intra-annual variability associated with the weather conditions was accommodated by inducing weekly perturbations sampled independently and uniformly from the range [−20%–20%]. The intra-annual variability associated with the exogenous nutrient loading was similarly treated stochastically by inducing weekly perturbations for both concentrations and relevant flows. Because of the lack of significant correlations ($r<0.4$) between the concentrations of the different nutrient forms and the flows in the Hamilton Harbour creeks (Wellen and Arhonditsis, 2010), the corresponding

Table 1
Goodness-of-fit statistics for the Hamilton Harbour eutrophication model, based on the monthly values (2000–2009) of total phosphorus (*TP*), phosphate (PO_4), nitrate (NO_3), total ammonia (TNH_3), chlorophyll *a*, and total zooplankton biomass.

Water quality variables	Model summary statistics	Units	Epilimnion	Mesolimnion	Hypolimnion
	r^2[a]	–	0.41	0.94	0.98
TP	*AE*[b]	μg L^{-1}	2.26	7.14	5.58
	MEF[c]	–	−1.51	−3.74	−0.68
	r^2	–	0.84	0.76	0.67
PO_4	*AE*	μg L^{-1}	1.09	1.89	0.75
	MEF	–	0.57	0.31	0.28
	r^2	–	0.87	0.79	0.69
NO_3	*AE*	mg L^{-1}	−0.40	−0.47	−0.56
	MEF	–	−1.54	−2.02	−2.38
	r^2	–	0.99	0.99	0.99
TNH_3	*AE*	mg L^{-1}	−0.09	−0.09	−0.09
	MEF	–	0.93	0.93	0.93
	r^2	–	0.95		0.85
Chlorophyll *a*	*AE*	μg L^{-1}	2.21		1.98
	MEF	–	0.73		0.53
Zooplankton	r^2	–	0.92		
biomass[d]	*AE*	μg L^{-1}	−13.11		
	MEF	–	0.77		

[a] Coefficient of determination.
[b] Average error.
[c] Modeling efficiency (Stow et al., 2003).
[d] Goodness-of-fit statistics calculated using volume-weighted concentrations.

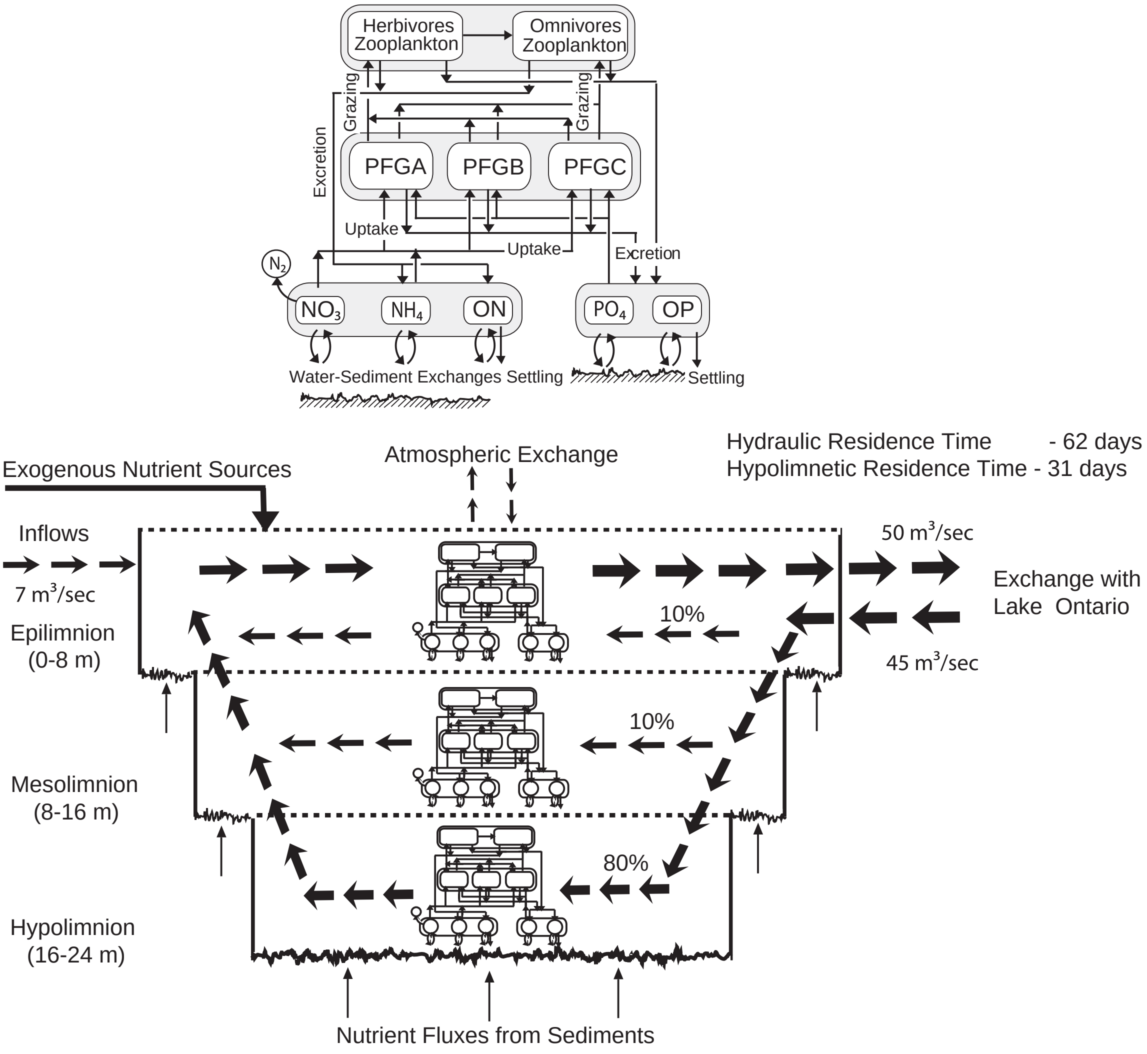

Fig. 1. Flow diagram and spatial segmentation of the Hamilton Harbour eutrophication model. The inflow, outflow and residence time values reported in the diagram correspond to the summer stratified period.

Table 2
Estimates of the nutrient loading variability from the Hamilton Harbour watershed creeks using Beale's ratio method (Study period: 1988–2008).

Creek name	Nutrient	Beale's average concentration (mg/L)	Average daily flow (L/s)	Average daily loading[a,b] (kg/day)	Daily loading Root Mean Squared Error (kg/day)[c]	Average yearly loading (kg/yr)	Yearly loading Root Mean Squared Error (kg/yr)
Grindstone Creek	Phosphate	0.06	745.0	4.01	8.40	144	302
	Nitrate	1.93		124.01	119.11	4464	4288
	Total Phosphorus	0.31		20.17	25.79	726	928
	Total Nitrogen	3.84		247.61	232.77	8914	8380
Spencer Creek	Phosphate	0.03	1960.0	5.02	10.76	1832	3927
	Nitrate	0.97		164.45	260.65	60,024	95,138
	Total Phosphorus	0.09		15.50	24.21	5657	8837
	Total Nitrogen	1.79		302.33	427.15	110,351	155,911
Red Hill Creek	Phosphate	0.04	632.8	2.11	1.34	769	488
	Nitrate	1.74		95.32	63.90	34,790	23,324
	Total Phosphorus	0.10		5.38	3.43	1965	1253
	Total Nitrogen	2.61		142.45	92.60	51,996	33,799

[a] Flows are averaged over the entire year.

[b] Beale's Ratio method for calculating loadings:

$$L_d = \frac{\overline{Q}\overline{l}}{\overline{q}}\left(\frac{1+\frac{1}{n}\frac{S_{lq}}{\overline{l}\,\overline{q}}}{1+\frac{1}{n}\frac{Sq^2}{\overline{q}^2}}\right)$$

L_d is the estimated daily loading rate; $\overline{Q}$ is the mean daily flow for the year; $\overline{l}$ is the mean daily load for the days when concentrations were measured; $\overline{q}$ is the mean daily flow for the days when concentrations were measured; n is the number of days when concentrations were measured;

$$S_{lq} = \frac{\sum_{i=1}^{n} q_i l_i - n\overline{q}\overline{l}}{n-1}, \quad S_q^2 = \frac{\sum_{i=1}^{n} q_i^2 - n\overline{q}^2}{n-1}$$

where q_i is an individual measured flow when a concentration was measured; and l_i is the daily load on each day a concentration was measured.

[c] The root mean squared error of the L_d term was calculated as: $RMSE(L_d) = \sqrt{\frac{\Sigma_{i=1}^{n}(L_d - l_i)^2}{n}}$.

perturbations (weights) were treated independently and were uniformly sampled from the [−30%–30%] range. [It should also be noted that the lack of correlation is likely due to lack of wet weather sampling in the database, as recently collected information from the system suggests a moderately strong correlation between peak flows during storms and nutrient concentrations (T. Labencki, unpublished data).] Serial correlation coefficients of 0.4–0.6 were also assigned to more realistically mimic the week-to-week variability associated with the inflows from the local creeks (Oracle Crystal Ball™).

We examined the exceedance frequency of the delisting *TP* and chlorophyll *a* goals under an assortment of abiotic conditions and food web interactions; that is, the parameters and/or factors controlling the phosphorus release from the sediments, the fraction of plankton metabolism recycled as phosphate, and the zooplankton abundance were each assigned high or low levels. Specifically, the parameter representing the fraction of inert phosphorus buried into deeper sediment layers was set equal to 75% and 90%, which approximately correspond to phosphorus sediment release of 3.2–3.8 mg m^{-2} day^{-1} and 1.2–1.6 mg m^{-2} day^{-1}, respectively. In a similar manner, the fraction of plankton metabolism resupplied to the water column as dissolved-phase inorganic phosphorus, and thus more readily available for phytoplankton uptake, was assigned values of 25% and 80% to reproduce conditions of slow and fast nutrient regeneration in the water column. Adopting one of Gudimov et al.'s (2010) recommendations for model augmentation, we also considered an alternative scenario under which herbivorous zooplankton feeding relies not only on the three phytoplankton groups and detritus, but also on allochthonous particles and/or types of food that are not explicitly accounted for by our model, e.g., benthic algae and macrophytes. Our numerical experiments analyzed nutrient concentrations and plankton patterns to the resulting eight (2^3) permutations of bottom-up and top-down control mechanisms of the planktonic food web dynamics in the Harbour. The exogenous nutrient loading was assumed equal to the Hamilton Harbour *RAP* loading targets (see Gudimov et al., 2010; Table 4-ESM), while our Monte Carlo experiments also accommodate the intra- and interannual variability in the system. Prior to the analysis, we present recent empirical estimates (and associated errors) of the non-point nutrient loading stemming from the three major creeks in the Hamilton Harbour watershed, which subsequently are used to determine the related forcing of the eutrophication model.

Results and discussion

The first step of our analysis was to revisit the parameterization presented in Gudimov et al. (2010) and represent the higher *TP* summer levels (35–38 μg L^{-1}) that typically characterize the Hamilton Harbour epilimnion. In particular, the new calibration involved the values assigned to the fraction of plankton mortality becoming phosphate, the fraction of inert phosphorus buried into deeper sediment, the allochthonous particle settling velocity, and the maximum nitrification rate at optimal temperature (see Table 2 in ESM). The discrepancy between model outputs and observed monthly averages from 2000 to 2009 was assessed by calculating the coefficient of determination (r^2), the absolute error (*AE*), and the modeling efficiency (*MEF*) values (Table 1). In Fig. 1-ESM, we illustrate the model performance combined with the 95% uncertainty bounds that depict the propagation of the intra- and interannual variability associated with the exogenous nutrient loading and meteorological forcing through the calibrated model. Notably, the width of the uncertainty zones of the different model endpoints were significantly narrower than those presented in Gudimov et al. (2010), reflecting the different Monte Carlo sampling schemes adopted by the two studies. While our earlier study treated stochastically the annual loading from the different exogenous sources (i.e., one constant perturbation implemented over the entire annual cycle for each Monte Carlo run) and then examined the compliance of the *TP* and chla summer averages with the corresponding water quality criteria in the Harbour (see Figs. 6 and 8 in Gudimov et al., 2010), our focus herein is to more realistically reproduce the week-to-week variability in the system and subsequently use the daily predictions to draw inference on the expected responses to nutrient loading reductions. Thus, the present study places more emphasis on the intra-annual variability, while the annual loadings examined to force the model revolve more closely around the average values examined in the Gudimov et al. (2010) study (see Tables 2 and 4 in their ESM).

Generally, the model closely reproduces the average total phosphorus (*TP*), phosphate (PO_4), total ammonia (TNH_3), chlorophyll *a*, and total zooplankton biomass patterns. In particular, relative to the Gudimov et al. (2010) calibration exercise, the model accurately captures the seasonal variability of the TNH_3 concentrations as well as the summer *TP* levels. We also found significant agreement between predicted and observed winter and spring nitrate concentrations, but the model still underestimates the summer nitrate levels in the Harbour. Nitrate/nitrite concentrations have been increasing at an exponential rate for almost four decades in the Harbour (Hiriart-Baer et al., 2009), but evidently this accumulation of nitrate is a more general pattern in the Great Lakes, as similar increasing trends with substantial decline of the summer NO_3 drawdown have been reported in Lakes Erie, Superior, and Ontario (Charlton et al., 1999; Finlay et al., 2007; Dove, 2009). One logical strategy to improve the model fit to the observed nitrate data would have been to increase the nitrification rates, although the current calibration vector already predicts relatively high nitrification levels both in the water column (5–15 mg m^{-3} day^{-1}) and the sediment interface (8–20 mg m^{-3} day^{-1}). A parameterization that postulates high nitrification rates in the system will also be consistent with Finlay et al.'s (2007) assertions that the accumulating NO_3^- in Lake Superior is almost entirely derived from nitrification occurring within the system. Thus, if we also consider its implications on the hypolimnetic oxygen dynamics of the system (Snodgrass and Ng, 1985; Roy et al., 1996; Sterner et al., 2007), we believe that the most parsimonious next step would be to obtain in situ measurements of nitrification in the Harbour and to reparameterize the model accordingly. Aside from the nitrification levels in the water column and/or the sediment, another hypothesis proposed to explain the recent increasing nitrate trends involves the inflows from the sewage treatment plants and the fertilizer residues that are directly discharged to the system, as well as the atmospheric deposition of the remnants of fossil fuel combustion, fertilizer use, and other local activities in the Great Lakes basin (Bennett, 1986; Gudimov et al., 2010). That is, one plausible explanation for the misrepresentation of the summer nitrate concentrations may be the underestimation of the exogenous loading, as we are lacking reliable information with regards to the nitrate/nitrite concentrations in all the major point and non-point sources; especially after the upgrading of the nitrification facilities in the local wastewater treatment plants. Yet, we note that further refinement of the nitrate loading forcing of the model could potentially lead to a better agreement with the epilimnetic data, but cannot adequately address the hypolimnetic mismatch. The latter problem may be addressed if we assume substantial contribution from groundwater discharges or most likely that the density differences between the nitrate-rich wastewater effluents and the Harbour water could result in direct disposal of water masses in the hypolimnion; a process that is not explicitly accounted for by our model.

Similar to Hiriart-Baer et al.'s (2009) reported patterns (see their Fig. 6), our model predicts a weakly positive *Chla-TP* relationship under the present loading conditions, while the corresponding chlorophyll *a* predictive distributions for different *TP* levels consistently exceed the targeted level of 10 μg L^{-1} (Fig. 2a). When the model is forced with the Hamilton Harbour *RAP* nutrient loading propositions, the epilimnetic *TP* concentrations dramatically decrease (<24 μg L^{-1}), while *TP* levels lower than 20 μg L^{-1} significantly decrease the exceedance frequency of the 10 μg L^{-1} chl *a* goal (Fig. 2b). Further, the relatively discontinuous drop of the chlorophyll *a* predictive distributions around the level of 20 μg *TP* L^{-1} implies a severe accentuation of the phosphorus limitation of the algal growth in the system, given the parameterization of the three phytoplankton functional groups simulated ($PH_{i = PFGA,\ PFGB,\ PFGC} < 20\ \mu g\ PO_4\ L^{-1}$; see Appendix 2 in ESM). The third panel of the same figure illustrates the predictive distributions of chlorophyll *a* and epilimnetic *TP* concentrations derived from the entire pool of the Monte Carlo runs examined. Generally, our analysis provides evidence that the chl *a* criterion of 10 μg L^{-1} is achievable, but the water quality setting process should explicitly accommodate the natural variability by allowing for a realistic percentage of violations, e.g., exceedances of less than 10% of the weekly samples during the stratified period should still be considered as compliance of the system. Likewise, the current epilimnetic total phosphorus criterion of 17 μg L^{-1} is probably too stringent if the current summer epilimnetic *TP* concentrations are set to an average level of 35–38 μg L^{-1}; thus, a somewhat higher value (e.g., 20 μg L^{-1}) may provide a more realistic goal. Yet, we also emphasize that the accuracy of our projections is contingent upon the credibility of the contemporary nutrient loading estimates in the Harbour. The latter point also raises the question of how reliable are the current loading estimates and to what extent the efficacy of the empirical causal relationships historically used to

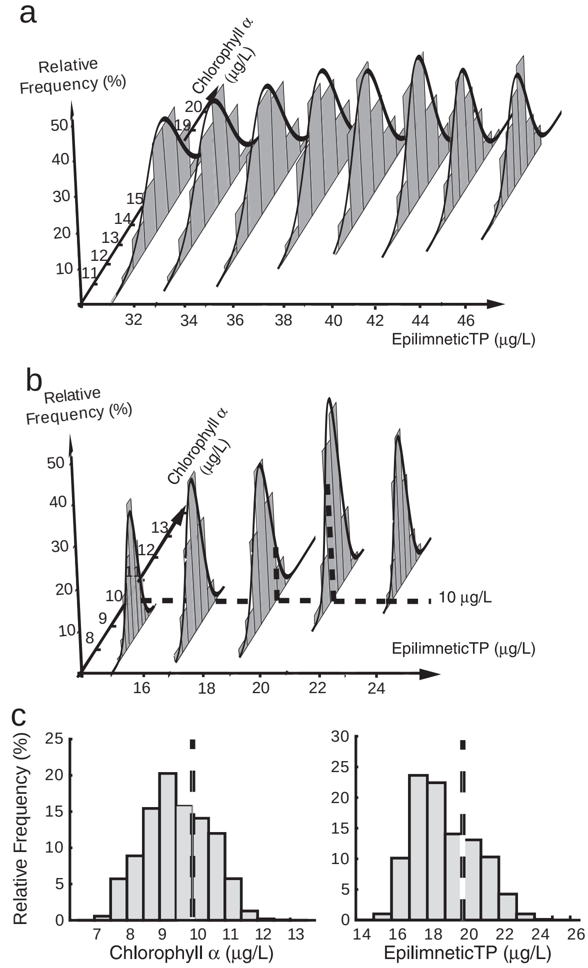

Fig. 2. Chlorophyll *a* predictive distributions for different levels of *TP* concentrations under (a) the present and (b) the Hamilton Harbour RAP loading propositions. The third panel illustrates the predictive distributions of chlorophyll *a* and epilimnetic *TP* concentrations derived from the entire pool of the Monte Carlo runs examined. Note that these modeling experiments refer to the updated loading targets for the Woodward (*TP* = 74 kg/day) and the Skyway (*TP* = 17 kg/day) Wastewater Treatment Plants.

link *P* loading with *TP* and chlorophyll *a* levels in the Harbour are undermined by the relevant error?

Exogenous nutrient loading: how confident are we about the current non-point loading estimates?

Gudimov et al. (2010) examined the relationships between the chlorophyll α and total phosphorus summer averages in the Harbour and the *TP* loadings from the different sources, which primarily highlighted the critical role of the Woodward *WWTP* discharges (see their Fig. 10). In particular, the corresponding linear regression models explained about 65% of the overall chlorophyll α ($Chla_{Harbour} = 0.193 \times TP_{Woodward} + 13.071$; $r^2 = 0.656$) and total phosphorus ($TP_{Harbour} = 0.058 \times TP_{Woodward} + 16.899$; $r^2 = 0.659$) variability generated by the model. The same study also showed the relatively small proportion of the variability associated with the effluent loads from the Skyway *WWTP* ($<2\%$), although existing evidence from the actual system suggests that the degradation in its performance can significantly impact the water quality (Charlton, 1997). On the other hand, the most important non-point loading source was Cootes Paradise accounting for 15% and 23% of the ambient *Chla* and *TP* variability in the Harbour. The nutrient loadings from Red Hill and Grindstone Creeks appear to play a secondary role, but the substantial uncertainty associated with the corresponding estimates along with the major nutrient inflows stemming from episodic rainfall events could potentially influence the exceedance frequency and the confidence of compliance with the water quality standards during the summer stratified period (Gudimov et al., 2010). Thus, the need for improving the tributary (i.e., non-point source/watershed) loading estimates to Hamilton Harbour for key water quality variables (e.g., total phosphorus, total nitrogen, suspended solids) is critical for projecting future system responses to nutrient loading reductions.

Hamilton Harbour's drainage basin is about 500 km^2 in area and encompasses three major creeks — Grindstone, Spencer, and Red Hill Creeks (Fig. 2a in ESM). The land uses of each of the major watersheds are mixed, but Grindstone Creek and Spencer Creek are dominated by agriculture and Red Hill Creek is dominated by urban area (Fig. 2b in ESM). Red Hill Creek's watershed stands out as more poorly drained than either Grindstone Creek's or Spencer Creek's, and consequently experiences higher surface saturation and runoff potential for most part of the growing season (Wellen and Arhonditsis, 2010). The Water Survey of Canada has maintained stream gauges along the courses of the three creeks (Fig. 2a in ESM), while Ontario's Provincial Water Quality Monitoring Network has been monitoring the concentrations of various contaminants, i.e., all major nitrogen and phosphorus species, metals, and suspended solids (Wellen and Arhonditsis, 2010). Our focus herein is placed on the general flow trends, nutrient concentrations, and associated loading estimates during the 1988–2008 period.

The flows of Grindstone Creek, Spencer Creek, and Red Hill Creek at their downstream locations are provided in Fig. 3, in which the red lines connect the median monthly values. Grindstone Creek follows a pattern of high flows in the months of March and April associated with the snowmelt followed by a summer period of low flows

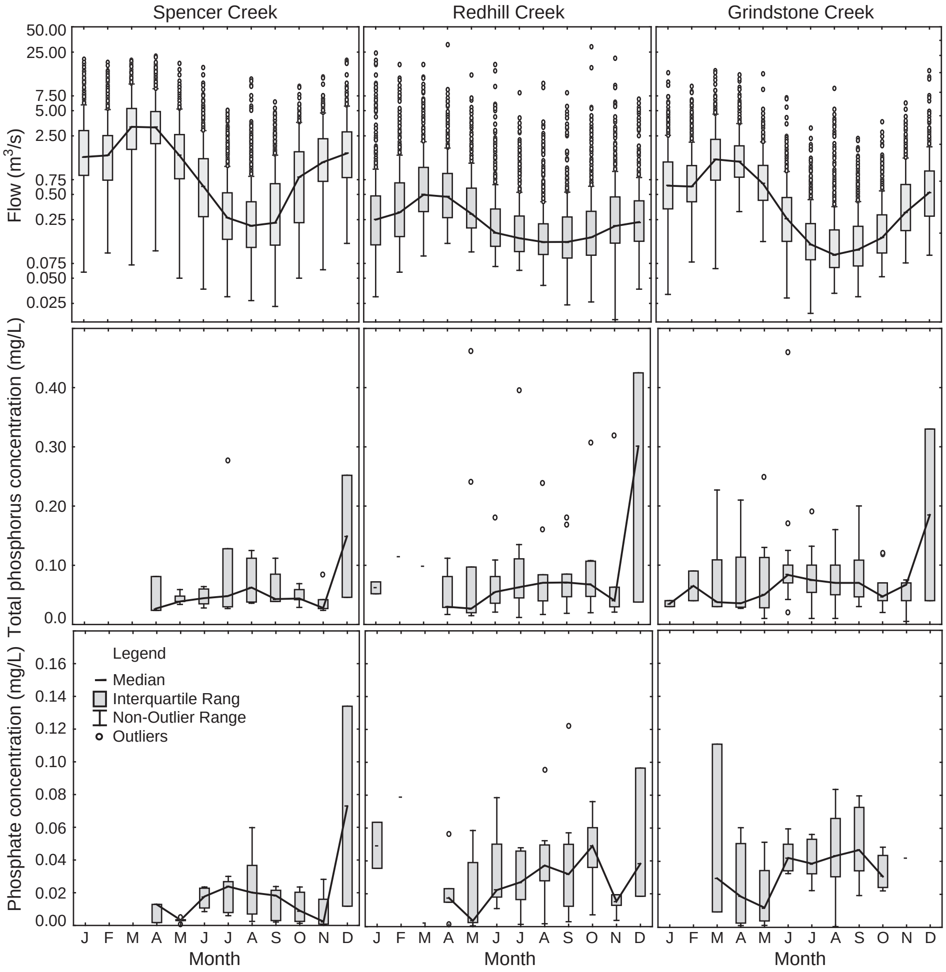

Fig. 3. Box plots of average daily flows and concentrations of total phosphorus and phosphate for Red Hill Creek, Spencer Creek and Grindstone Creek. Flows are plotted in logarithmic scale.

punctuated by episodic flow events. The fall season is characterized by higher flows, though it is also punctuated by larger events. Similar to the fall season, the winter is also characterized by extreme events, possibly due to extreme freezes and snap thaws. Spencer Creek follows a pattern similar to Grindstone Creek. Spencer Creek's fall flow regime is more variable than its winter flow regime. There is considerably more variability in Red Hill Creek relative to Grindstone and Spencer Creeks. Namely, Red Hill Creek's median flows are much lower than Grindstone or Spencer Creeks, but Red Hill Creek's extreme flows are as high as the extreme flows of Spencer Creek and substantially higher than the extreme flows of Grindstone Creek. This significant variability is consistent with what is known about urban catchments and so is not particularly surprising. Urban catchments are characterized by substantial amounts of impervious surface so rather than seeping into soils, nearly all of the rainfall on impervious surfaces runs off immediately. This results in much faster rainfall response, much higher peak flows, and lower levels of soil moisture when compared to similar non-urban catchments (Groffman et al., 2003).

We also examined the downstream temporal variability of water quality for each creek, as it can be used to infer the "hot moments" – times of high concentration – that can be targeted for future monitoring or remediation efforts. Characteristic examples of such "hot moments" are the flushing events, when the water table moves closer to the surface in response to precipitation or meltwater inputs and gets in contact with the nutrient-laden upper layers of the soil. The extra soil water removes dissolved nutrients from the soil and thus contributes nutrients to stream baseflow. Runoff generation due to saturation excess occurs when the water table is at or near the surface, so flushing events correspond to times of saturation excess. Any precipitation received during saturation cannot infiltrate and so must run off of the surface, possibly carrying particulate nutrients to the stream. In a modeling study, Valeo and Moin (2000) showed that the saturation excess flow can account for as much as 10% of annual streamflow in Ancaster Creek, a subwatershed of Spencer Creek. If the water table remains near the surface for an extended period of time, like in the spring thaw, the baseflow gradually shifts from high to very low concentrations of nutrients, as all the available nutrients are leached away. This trend has been shown for dissolved nutrients, though it is not likely true for particulate and therefore for total nutrients (Creed et al., 1996).

In Grindstone Creek, particulate phosphorus tends to be highest in the month of December (Fig. 3). Higher phosphate concentrations are also experienced in August and September, suggesting that end of summer storm flushing drives phosphate dynamics. In Spencer Creek, the highest phosphate concentrations are measured in December, though no measurements were taken in January, February, or March. Because the snowmelt events tend to occur in early spring, the low concentrations of nutrients observed in April indicate that the main fraction of the non-point loading likely occurs in March, when the catchment begins flushing. The cause for the high phosphorus concentrations in December in Spencer, Grindstone and Red Hill Creeks is not clear, but it is unlikely that local farmers apply fertilizer or manure in December or late November.

Daily and yearly loadings are reported for phosphate, nitrate, total phosphorus, and total nitrogen in the three creeks in Table 2. Nutrient loading estimates were calculated using Beale's ratio method, which assumes a constant ratio between flow and concentration (Richards and Holloway, 1987). While this has not been the case for the three creeks examined, Beale's ratio has been shown to give acceptable yearly estimates for loads of total phosphorus and ammonium to the Great Lakes (Preston et al., 1989). When calculating Beale's ratio, it was assumed that the concentrations measured represented daily concentration values, and therefore the daily load could be calculated as the daily average flow times the concentration measured that day. Using the root mean squared error (*RMSE*), uncertainties for the loadings were calculated as the discrepancy between the estimated daily loading rate with Beale's ratio and the mean daily load for the days on which concentrations were determined (Wellen and Arhonditsis, 2010). Our error estimates are always larger than the daily loading values and substantially higher than those generated with similar methods reported elsewhere (Richards and Holloway,1987; Macrae et al., 2007). Preston et al. (1989) obtained *RMSE* values between 6% and 16% of yearly load for total phosphorus, while all our *RMSE* values are greater than 100%. The *RMSE* values presented here, especially for yearly loads, are simply not comparable to the Preston et al. (1989) study, which had reliable estimates of the true loading calculated from daily water quality samples. Our analysis has solely the difference between the calculated Beale ratio estimator value of daily loading and actual daily loading measurements to calculate error. Further, the Preston et al. (1989) study reported *RMSE* values for simulated bimonthly sampling and phased out the inter-annual variability by concentrating on only one year. By contrast, the present study examined loadings over roughly ten years for each creek, and so greater variability is to be expected.

The Hamilton Harbour Remedial Action Plan's Stage 2 Update 2002 had initial and final goals for total phosphorus loading to Hamilton Harbour from the streams of the watershed. Merely adding the total phosphorus loadings from the three streams here, we get 41 kg day^{-1}. This is well below the initial goal of 90 kg day^{-1} and possibly below the final goal of 65 kg day^{-1}, assuming that the loading originating from the streams not monitored by this dataset is negligible. Taking the total *RMSE* into account, however, we see that the total of 41 kg day^{-1} is subjected to an uncertainty of approximately 35 kg day^{-1}. Thus, it is not possible to infer from these loading estimates alone whether either the initial or final total phosphorus loading goals are met. Averaging the values estimated by the Hamilton Harbour Remedial Action Plan's Contaminant Loadings Report across the study period of 1996–2007 (Contaminant Loadings and Concentrations to Hamilton Harbour: 2003-2007 Update or CLCHH, 2010), Grindstone Creek has a daily loading of about 15 kg P day^{-1}, Spencer Creek of 24 kg P day^{-1}, and Red Hill Creek of 22 kg P day^{-1}. The values reported here agree with these earlier loading estimates within the *RMSE*, but our study does however call attention to the significant uncertainties associated with our best estimates of the stream loadings into the Hamilton Harbour. Finally, in the Electronic Supplementary Material, we present numerical experiments designed to examine separately the effects of the episodic meteorological events (e.g., spring thaw, intense summer storms) and short-term variability at the local wastewater treatment plants on the water quality conditions of the system.

What is the "ideal" zooplankton community for promoting the restoration of the system?

A basic feature of the recent modeling studies in the Harbour was the absence of a simulated carbon cycle due to the lack of reliable estimates of exogenous particulate carbon loading (Gudimov et al., 2010; Ramin et al., 2011). Yet, one of the ramifications of such model structure involves the zooplankton feeding exclusively on endogenous sources (algae and detritus) and therefore the coupling of the phytoplankton-zooplankton relationship may have been unrealistically tight. The latter pattern was particularly evident in Gudimov et al.'s (2010) analysis of the seasonal plankton variability, in which the phytoplankton and zooplankton trajectories projected in response to the gradual reduction of the exogenous nutrient loading were parallel to each other (see their Fig. 7). While recent studies render support to this assumption downplaying the role of allochthony (Brett et al., 2009), we have relaxed the zooplankton reliance on algal-related diet by introducing an alternative food source into the model that may represent the terrestrial organic matter inputs and/or other (potentially important) autochthonous carbon pools, e.g., benthic algae and macrophytes. To overcome the lack of relevant data, the amount of allochthonous carbon (*t-POC*) in the system was adjusted by an inverse solution approach, whereby the total particular organic carbon (terrestrial + biogenic) was consistently lying within the observed range (0.8–2.0 mg L^{-1}) in the system (Burley, 2007). The same source was also assumed to be grazed with equal preference ($Pref_{herbi,t\text{-}POC}$) and to have similar nutritional value ($FQ_{t\text{-}POC}$) with biogenic detritus; an assumption that deviates from Brett et al.'s (2009) findings, who showed that *t-POC* typically represents an inferior quality food and may only be catabolized for metabolic demands for energy. Using the food limitation term, i.e., total food abundance/(half saturation constant for grazing + total food abundance), as the regulatory factor for inducing changes on the zooplankton feeding patterns, we designed two scenarios regarding the importance of terrestrial carbon to zooplankton production. In the first scenario, zooplankton does not switch to allochthonous organic material, unless the food limitation term falls below 0.4. That is, we effectively postulate a zooplankton that opts for an algal-based diet of superior nutritional quality to enhance somatic growth and reproduction, but may at times experience starvation due to the wax-and-wane cycles of phytoplankton. The alternative scenario assumes that zooplankton is not willing to starve and therefore once the food limitation gets lower than 0.9, *t-POC* become part of its diet; a scenario that effectively examines the impact of a quantitatively adequate but qualitatively (nutritionally) variant diet on the planktonic food web patterns.

Forced with the *RAP* exogenous nutrient loading targets (HHTT-WQ, 2007), our model predicts that an increased reliance upon allochthonous *POC* does not make a significant difference on the compliance of the system with the chlorophyll *a* target of 10 μg L^{-1} under conditions of high phosphorus release from the sediments and high recycling rates of phosphate, i.e., regardless of the zooplankton diet, the system consistently demonstrates chlorophyll *a* concentrations higher than 10 μg L^{-1} (Fig. 4 and Fig. 3-ESM). When lower recycling rates are assumed, a mixed zooplankton diet appears to effectively control the phytoplankton biomass and ultimately results in an acceptable exceedance frequency (<2%) of the chlorophyll *a* target; a prediction that differs dramatically from the one supported by the combination of low recycling rates and algal-dominated diet of zooplankton (>50%). By contrast, the scenario of low phosphorus release from the sediments suggests a more straightforward ecosystem functioning in that the zooplankton diet (and consequently abundance) plays a minimal role, while the phytoplankton levels are predominantly regulated by the rates of the regeneration mechanisms of organic matter (Fig.4 and Fig. 4-ESM). Further, the exceedance frequency of the *TP* criterion of 20 μg L^{-1} is also influenced by the zooplankton abundance, although the release of phosphorus from the sediments is clearly the primary regulatory factor (see also following discussion). Notably, the scenario of mixed zooplankton diet appears

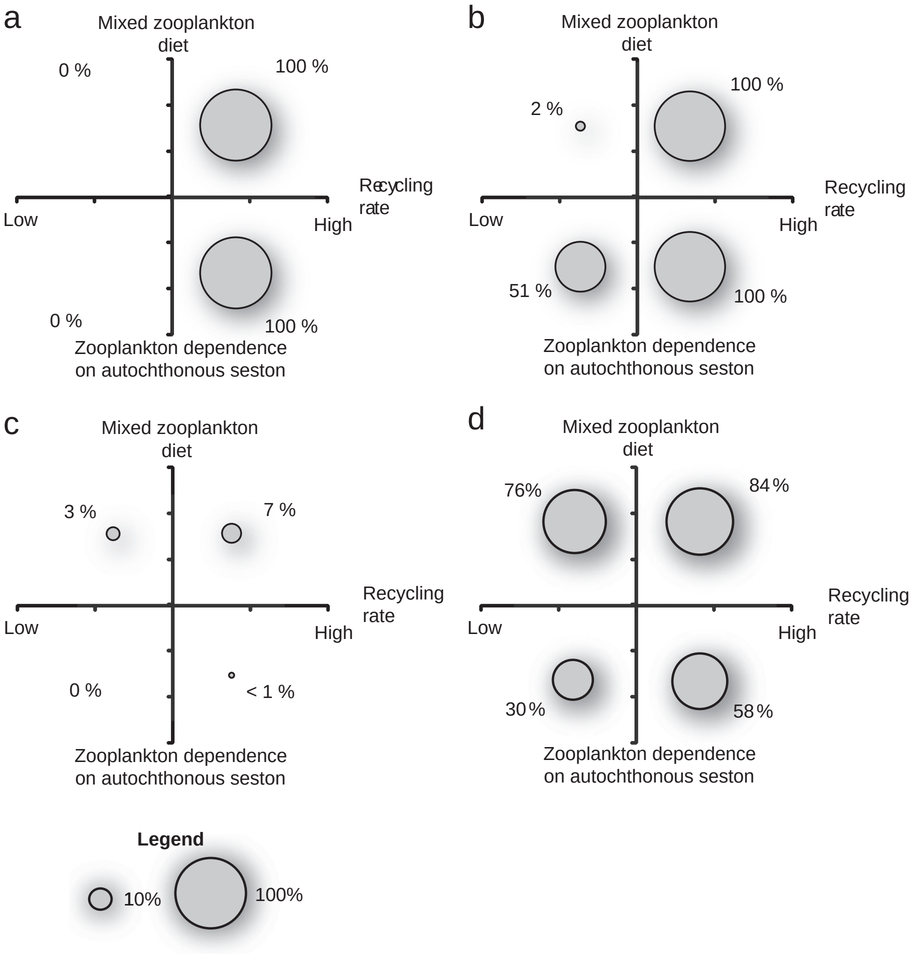

Fig. 4. Exceedance frequency plots of the chlorophyll α (10 μg L^{-1}) and epilimnetic *TP* (20 μg L^{-1}) water quality criteria under the Hamilton Harbour *RAP* nutrient loading propositions and different levels of (i) *nutrient recycling*: the fraction of plankton metabolism resupplied to the water column as dissolved-phase inorganic phosphorus ($\alpha_{PO4i,j}$) is 25% or 80%; (ii) *phosphorus sediment release*: the fraction of inert phosphorus buried into deeper sediment layers (β_P) is equal to 75% or 90%; and (iii) *zooplankton abundance levels*: reliance only on autochthonous food sources (three phytoplankton groups and detritus) or supplementary feeding on allochthonous particles and types of food that are not explicitly accounted for by our model, e.g., benthic algae and macrophytes.

to (plausibly) promote the frequency of violations of the *TP* standard, given that the consequent lower phytoplankton biomass increases the amount of dissolved-phase phosphorus that remains unutilized in the water column.

Generally, our analysis suggests that the assumptions made about the zooplankton diet (reliance upon allochthonous versus autochthonous food sources) make little difference with regards to the inference drawn on the compliance of the system with the existing water quality goals. Yet, it should be emphasized that an implicit idea underlying the present modeling experiments is that there will be no structural changes in the zooplankton community following the progression of the system to a mesotrophic status; an assumption that most likely does not hold true, given the well-documented changes in the zooplankton community since the early 70s (Gerlofsma et al., 2007). In particular, starting from a zooplankton community in the late 1970s that was primarily dominated by large rotifers *(Keratella quadrata*, *Brachionus angularis*, *Filinia terminalis* and *Trichocera cylindrical)* and the cladoceran *Bosmina longirostris* (Harris et al., 1980), the Harbour has gradually experienced shifts in composition with recent decline in rotifers and consistent presence of *Daphnia* species (e.g., *Daphnia retrocurva, Daphnis galeata mendotae, Ceriodaphnia lacustris*) and copepods (e.g., *Diacyclops thomasi, Cyclops vernalis, Leptodiaptomus siciloides, Skistodiaptomus oregonensis*) (Gerlofsma et al., 2007). The continuing elimination of rotifers may partly reflect the concurrent improvement of the water quality conditions, although other factors such as the competition associated with the increasing presence of *Daphnia* in the system and the predation by the increasing populations of copepods could not be ruled out (MacIsaac and Gilbert, 1991). A structural shift of the zooplankton community towards large cladocerans is desirable due to their capacity to strongly suppress algal biomass, and evidence of the potential importance of the top-down control in Hamilton Harbour was observed in 1997, when a prolonged and unusually high zooplankton abundance resulted in Secchi depth measurements of greater than 5 m (Charlton, 2001). Further, Ramin et al. (2011) offered insights into the optimal features (maximum grazing rates, half saturation constant for grazing, zooplanktivory levels) of the zooplankton community that can effectively advance the transition of the Harbour from the present eutrophic to a mesotrophic state. It was shown that a fast growing zooplankton community characterized by grazing rate greater than 0.6 day^{-1} and half saturation constant lower than 100 μg C L^{-1} should minimize the exceedances of the 10 μg chl *a* L^{-1} water quality goal, while the phytoplankton biomass can dramatically increase when the mean summer zooplankton abundance drops below an approximate level of 100 μg C L^{-1} (or 2500 μg wet weight L^{-1}).

Acknowledging the significance of the top-down control in the system, the next critical step is the investigation of the factors that could potentially control the trajectory of the zooplankton community as we gradually shift to a reduced nutrient loading regime. Consistent with our model parameterization which allocates >15% of the daily zooplankton biomass losses to planktivory, the relatively high chlorophyll *a*/total phosphorus ratios (0.41 to 0.62) in the Harbour provide evidence of an odd-link system characterized by strong predation of zooplankton by fish (Gerlofsma et al., 2007). Likewise, the relatively small mean length of cladocerans (320–425 μm) in the Harbour reflects the preferential consumption of the larger zooplankton individuals by the planktivores of the local fish community (Mills et al., 1987; Gerlofsma et al., 2007). The current fish community is mainly dominated by benthivores such as brown bullhead (*Ameiurus nebulosus*), carp (*Cyprinus carpio*), and white perch (*Morone americana*), and planktivores such as alewife (*Alosa pseudoharengus*), and gizzard shad (*Dorosoma cepedianum*), while the channel catfish (*Ictalurus punctatus*) is most likely the dominant piscivore in the system. The predominance of these pollution-tolerant species that tend to thrive under low dissolved oxygen conditions and high suspended solid concentrations has consequently kept many desirable fish species at low levels, such as northern pike (*Esox lucius*), largemouth bass (*Micropterus salmoides*), and walleye (*Sander vitreus*) (Minns et al., 1996). Because the current fish community in the Harbour is out of balance due to impairment of the aquatic habitats and habitat loss, the Hamilton Harbour RAP (1992) identified a number of remedial actions, like the restoration of destroyed or preservation and enhancement of existing habitats in the Harbour and Cootes Paradise. Further, the introduction of indigenous top predators like pike and bass is likely to bring a desirable shift to a more balanced community that will effectively exert control on undesirable species (juvenile carp, white perch and shad) and more quickly establish self-sustaining populations (Bowlby et al., 2009). Importantly, our modeling work suggests that the success of these restoration efforts of the piscivorous populations can conceivably cascade to the primary producer-herbivore interface and should ultimately induce a positive feedback to the pace of restoration and to the stability of the new trophic state in the Harbour.

How much do we know about the role of the microbial food web?

Recent empirical evidence suggests that the microbial food web of Hamilton Harbour may be an indispensable pathway in advancing our understanding of the ecosystem structure and functioning (Munawar and Fitzpatrick, 2007). In conjunction with the planktonic communities, the microbial loop (bacteria, autotrophic picoplankton, heterotrophic nanoflagellates, and ciliates) forms the pelagic component of the lower food web and constitutes an important vector of autochthonous energy transfer to higher trophic levels (e.g., Munawar et al., 2005; Fitzpatrick et al., 2007). The total abundance of the microbial loop is characterized by substantial intra- and interannual variability varying from 500 to 2000 mg m^{-3}, while bacteria account for more than 60% of the total biomass followed by heterotrophic nanoflagellates (10–20%), ciliates (5–10%), and autotrophic picoplankton (<5%) (Munawar and Fitzpatrick, 2007). Further, Munawar et al. (2010) reported high levels of standing biomass of heterotrophic nanoflagellates (500–4000 g m^{-3}) and zooplankton (100–3000 mg m^{-3}) during the occurrence of an extensive algal bloom in the summer of 2006, dominated by the colonial blue green *Coelosphaerium Naeglianum (Woronchinia Naeglianum)*. The relatively large biomass of secondary consumers was somewhat surprising given that the autochthonous carbon pool was dominated by inedible algae (*C. Naeglianum, Microcystis viridus, Ceratium furcoides*). The latter pattern may be evidence that the heterotrophic nanoflagellates provide the primary food resource for zooplankton grazers and can occasionally be an important route of energy transfer that sustains the food web. Yet, the prospect of the microbial loop to emerge as a potentially important supplier of bioavailable nutrients whilst the system gradually shifts to a mesotrophic status has not been examined in the literature, although recent predictions point out that a substantial proportion of the phytoplankton phosphorus demands in the mixed layer can be met by nutrient mineralization (Gudimov et al., 2010).

In our analysis, we found that the subsidies of phosphate originating from the plankton metabolism can significantly modulate the epilimnetic phytoplankton levels. Regardless of the exogenous nutrient loading reductions, the fluxes from the sediments, and/or the control exerted from zooplankton, the exceedance frequency of the chlorophyll *a* target is consistently higher than 90% when high recycling rates are assumed (Fig. 4 and Figs. 3 and 4-ESM). Evidently, the Gudimov et al. (2010) parameterization that assigned approximately 80% of plankton metabolism to replete the epilimnetic phosphate was convenient to simultaneously match the typically high summer chl *a* levels (>15 μg L^{-1}) and low phosphate concentrations (<2–3 μg L^{-1}) in the Harbour epilimnion, but it does disconnect somewhat the summer phytoplankton growth from the exogenous nutrient loading variability. In principle, the rapid nutrient turnover rates postulated by the model can partly explain the relatively small fraction of dissolved inorganic phosphorus relative to the total phosphorus pool as well as the epilimnetic phytoplankton levels (Burley, 2007); an idea that has been amply discussed in the literature over the last three decades (Stone and Berman, 1993). For example, Lehman (1980) and Richey (1979) estimated that nutrient recycling provided 60–90% of the phosphorus supply to the mixed layer in mesotrophic Lake Washington during the summer stratified period. Likewise, earlier work by Goldman (1984) has described the intense microbially mediated recycling as a rapidly turning "spinning wheel", whereby nutrients are returned into the system in short time scales (< 1 day) with minimal losses. The question arising though is how realistic is such ecological parameterization in the present eutrophic state of the system? Further, if our assumption on the importance of the nutrient regeneration mechanisms holds true, should we expect such a consistently moderate phytoplankton response to the anticipated nutrient loading reductions?

Generally, the total amount and the relative importance of the phosphorus recycled depend on the abundance and composition of the zooplankton community as well as on the trophic status of the system and the water temperature (Capblancq, 1990). In particular, several studies have clearly demonstrated that nutrient regeneration by grazers might represent a significant source of inorganic nutrients for phytoplankton, with the smallest organisms (e.g., rotifers, protozoa) being associated with higher rates of phosphorus excretion per unit of biomass relative to the large ones, e.g., cladocerans, copepods (Gulati et al., 1989; Peduzzi and Herndl, 1992; Teubner et al., 2003; Ejsmont-Karabin et al., 2004; Kowalezewska-Madura et al., 2007). Further, it is an established pattern in limnology that plankton dynamics in resource-limited environments mostly depend on internal mechanisms which act to recycle the limiting nutrient many times over within the surface waters, but this dependence on nutrient regeneration decreases as the overall productivity increases (Legendre and Rassoulzadegan, 1995; Biddanda et al., 2001; Cotner and Biddanda, 2002). The idea that the microbial loop exerts its largest relative control in oligo- or mesotrophic pelagic ecosystems seems to contradict our model parameterization or at least to suggest that the slope of the chlorophyll *a*-*TP* loading relationship may not be dramatically steeper as we shift towards *RAP*'s nutrient loading recommendations. While the latter point casts doubt on the anticipated efficacy of the on-going restoration efforts, we believe that it will be more prudent to first consider the relative contribution of other potentially important nutrient sources (i.e., internal loading, episodic events) that may intermittently fuel epilimnetic algal growth and therefore the role of the microbial loop as a nutrient supplier could have been overstated in our earlier work.

Internal nutrient loading: how "innocent" are the sediments?

Sediments act as an important source for a wide variety of chemicals in aquatic ecosystems, where a number of microbiological, geochemical, and physical processes determine the fraction of organic matter, nutrients, and pollutants released into the overlying water (Ramisch et al., 1999). Detailed knowledge of the processes occurring in the top few centimeters of the sediment can be essential for the assessment of water quality and the management of surface waters. In Hamilton Harbour, the regular manifestation of hypolimnetic dissolved oxygen deficit during the stratification period suggests that the internal loading can conceivably be another factor to influence the duration of the transient phase and the recovery resilience (Jeppesen et al., 2005; Dittrich et al., 2009). In this regard, we examined two distinct scenarios of phosphorus sediment release representing (i) the somewhat conservative parameterization presented by Gudimov et al. (2010) (1.2–1.6 mg m^{-2} day^{-1}), and (ii) the extreme case when about one-fourth of the sedimenting particulate phosphorus is instantaneously returned back in the water column (3.2–3.8 mg m^{-2} day^{-1}). Our results show that a nearly twofold increase of the sediment fluxes can dramatically increase the number of violations of the delisting goals (Fig. 4 and Figs. 3 and 4-ESM). In particular, the water quality standard related to the epilimnetic *TP* concentration is quite sensitive to the assumptions made about the internal loading. To examine whether these results constitute a possible threat to the success of the local restoration plans or an unrealistic prediction derived from a theoretical modeling exercise, we need to revisit our knowledge of the pollution history of the sediments and current understanding of the associated diagenetic processes in the Harbour.

Surprisingly, there is an overwhelming absence of studies that have rigorously quantified the release of phosphorus from the sediments of the Harbour, while the relevant fluxes have been assumed to be fairly minimal (Mayer and Manning, 1990). Despite the reportedly substantial release of manganese and iron in the system, one reason proposed to rationalize the hypothesized retention of phosphorus in the sediments has been that the redox potential at the sediment–water interface may be relatively high to allow the release of phosphorus (Kellershohn and Tsanis, 1999). Another possibility may be the frequent interruption of hypoxia by inflows of oxygenated water from Lake Ontario, although it can be counterargued that the interplay with the lake most likely favors the formation of irregular spatiotemporal dissolved oxygen patterns with prolonged patches of hypoxia where phosphorus could still be transferred from the sediments into the overlying waters (Coakley et al., 2002; Rao et al., 2009). Similarly, while Mayer and Manning (1990) reported quite high phosphorus concentrations in solids collected from the sediment–water interface (>3500 mg kg^{-1}) as well as unusually high non-apatite inorganic phosphorus levels in the areas adjacent to the municipal discharges, they concluded that there is sufficient ferric iron in the system to alleviate the impact of the high inputs of P. The same study also speculated that the retention of phosphorus in the sediments may be attributed to the ferric iron reduction, which subsequently leads to the formation of an insoluble "Fe^{+2}-other metal-*P*" complex (Mayer and Manning, 1990). Further, Azcue et al. (1998) reported upward diffusion PO_4 fluxes into the overlying water column at the level of 1.7 mg m^2 day^{-1}, which were very close to the lower value examined herein.

Yet, despite all the arguments historically used to downplay the relative contribution of the sediment fluxes in the system, recent evidence suggests that the phosphate levels in the hypolimnion can easily exceed the level of 30 µg PO_4 L^{-1} for extended period (3–4 weeks) during the late summer/early fall (T. Labencki, unpublished data). This trend poses the critical question of what is the actual cause for this hypolimnetic phosphorus accumulation, but also suggests that the summer epilimnetic environment may also be subjected to intermittent nutrient pulses from the hypolimnion, which in turn can have important ramifications on the abundance, composition or even predictability of the phytoplankton community (Jorgensen and Padisak, 1996; Soranno, 1997. Thus, given also that the hypoxia in the Harbour waters will continue to be an issue (HHTT-WQ, 2007), the likelihood of the internal loading to exert control on the water quality conditions warrants further investigation. Finally, we note that the spatial structure adopted to accommodate the cone-shaped morphology of the Harbour (see Fig. 4 in Gudimov et al., 2010) postulates that sediment fluxes of phosphate occur directly into the epilimnion; a feature that may approximate the contribution of the littoral zone, where the surficial sediments tend to be repositories of both nutrients and contaminants and their resuspension triggered by wind forcing and episodic runoff events can be highly important in predicting offshore water quality (Johengen et al., 2008).

Conclusions

We examined the likelihood of delisting Hamilton Harbour as an Area of Concern if the nutrient loading reductions proposed by the Hamilton Harbour Remedial Action Plan are actually implemented. Generally, our modeling analysis suggests that the target of chlorophyll *a* concentrations in the Harbour lower than 10 μg L^{-1} is achievable, but the water quality setting process must be pragmatic and the natural variability should be explicitly accommodated by permitting a realistic frequency of violations, e.g., exceedences of less than 10–15% of the weekly samples during the stratified period should still be considered as compliance of the system. Likewise, the current epilimnetic total phosphorus goal of 17 μg L^{-1} is probably too stringent and therefore a somewhat higher value (e.g., 20 μg L^{-1}) may provide a more realistic target. We also stress that the accuracy of our projections is conditional upon the credibility of the contemporary nutrient loading estimates in the Harbour, which are uncertain and appear to inadequately account for the contribution of episodic meteorological events (e.g., spring thaw, intense summer storms) and short-term variability at the local wastewater treatment plants. Another source of uncertainty and possibly a compelling reason for shifting towards a probabilistic approach to water quality criteria involves the simplified spatial segmentation of our model and its inability to account for persistent spatial gradients or other hot spots in the system (Rao et al., 2009).

The latter point also offers an opportunity to elaborate on the philosophy underlying the present modeling exercise. First, we strongly believe that the development of a complex model by itself is not the "magic solution" for achieving robust management tools! In fact, the increase of the ecological (expressed as the number of state variables) or the spatial (from zero- to three-dimensional approaches) model complexity does not necessarily improve model performance (e.g., see Table 2 in Arhonditsis and Brett, 2004). Rather, the decisions regarding the complexity of a model should be driven by the system being studied and the questions being asked. In this exercise, our intent was to develop an ecological model to capture the variability of the key components of the lower food web in the Hamilton Harbour and, most importantly, to offer an accurate representation of the key cause–effect relationships pertaining to the environmental management problem at hand. While we do not mean to trivialize the role of the hydrodynamics and the importance of a more sophisticated spatially-explicit approach, our priority herein was to establish a realistic representation of the causal connections among exogenous nutrient loading, ambient nutrient conditions, and phytoplankton biomass, i.e., the factors primarily associated with the manifestation of eutrophication problems in the Harbour. For the purpose of reproducing the broad range of dynamics experienced in the Hamilton Harbour, the uncertainty associated with the exogenous nutrient loading is also accommodated by a high number of Monte Carlo runs. In this endeavor, we opted for a relatively simple spatial structure that offers the flexibility to examine a number of loading scenarios and uncertainty assumptions, while providing assurance that the basic hydrodynamic patterns (e.g., vertical mixing, exchanges with Lake Ontario) are being considered. The same task would have been very difficult with a more cumbersome three-dimensional approach. That being said, both Gudimov et al. (2010) and Ramin et al. (2011) also acknowledged that the simple spatial structure of the current model version is certainly inadequate to elucidate the processes associated with the hypoxia manifestation, to assess the broader impact of suspended solids on the ecosystem functioning, and to evaluate the sensitivity of the water quality patterns in the Harbour to the inflow rates of the water from Lake Ontario.

In the context of model-based water quality management, the elucidation of the major ecological mechanisms that can potentially modulate the response of the system can be as important as the actual deterministic and/or probabilistic predictions (Arhonditsis and Brett, 2005; Arhonditsis et al., 2007; Zhang and Arhonditsis, 2008). In this regard, our analysis suggests the dynamics of phosphorus in the sediment-water column interface need to be revisited, considering that the internal nutrient loading appears to be tightly linked with the epilimnetic *TP* concentrations and therefore can conceivably be a regulatory factor of the duration of the transient phase and the recovery resilience of the Harbour (Fig. 4). We also pinpoint two critical aspects of the system dynamics that invite further investigation and will likely determine our predictive capacity to assess compliance with the chlorophyll *a* goal of 10 μg L^{-1}, i.e., the nutrient recycling mediated by the microbial food web and the structural shifts towards a zooplankton community dominated by large-sized and fast-growing herbivores. The latter prospect reiterates our earlier assertion that the bottom-up (i.e., nutrient loading reduction) approach historically followed in the Harbour was sufficient to bring the system in its present state, but any further improvements should be viewed in the context of a combined bottom-up and top-down (i.e., alleviation of the zooplanktivorous pressure) control. Current modeling efforts are directed towards articulating testable hypotheses and gaining a fundamental understanding of the ecological mechanisms under which erratic outbreaks of noxious and toxin-producing cyanobacteria occur and how hypolimnetic hypoxia evolves during the summer stratified period. We also note that the inability of our model to match the observed hypolimnetic nitrate levels may stem from factors that are tightly intertwined with the previous two vexing water quality problems.

In conclusion, while our modeling analysis does not negate in principle the optimism that the goal of restoring environmental health to Hamilton Harbour is within the community's reach by the year 2015 (Hall et al., 2006), it does highlight that there are many known or unknown "ecological unknowns" warranting deeper investigation. This idea is on par with one of the founding concepts of the Hamilton Harbour remediation; that is, the management strategies and quality goals should heavily rely on continuous research and monitoring and dynamically adapt to the contemporary changes of the ecological conditions. Regarding the priorities of the on-going monitoring efforts, it is important to note that the threshold values of the *TP,* chlorophyll *a*, and Secchi disk standards are merely proxies to characterize the prevailing water quality conditions and therefore other quantitative or even qualitative (e.g., dominance of the zooplankton community by large and fast growing daphnids) features/indices of the ecosystem functioning may be equally insightful to track progress towards the delisting of the system. After all, it is worth to bear in mind that a 10% acceptable frequency of violations implies that if the epilimnetic *TP* concentrations are higher than 20 μg L^{-1} (or if chlolophyll *a* exceeds the 10 μg L^{-1} level) in more than 2 weeks during the summer period, then the system should be deemed as impaired! How realistic is to adhere to such a strict numerical assessment of the water quality conditions in a system like Hamilton Harbour, where numerous anthropogenic activities induce continuous physical, chemical, and biological disturbances?

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.jglr.2011.06.006.

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Predicting the response of Hamilton Harbour to the nutrient loading reductions: A modeling analysis of the “ecological unknowns”

(Electronic Supplementary Material)

Alex Gudimov[1], Maryam Ramin[1], Tanya Labencki[2], Christopher Wellen[1], Milind Shelar[1], Yuko Shimoda[1], Duncan Boyd[2], George B. Arhonditsis[1]*

[1]Ecological Modeling Laboratory
Department of Physical & Environmental Sciences, University of Toronto
Ontario, Canada, M1C 1A4

[2] Water Monitoring & Reporting Section, Environmental Monitoring and Reporting Branch,
Ontario Ministry of Environment, Toronto, Ontario, Canada, M9P 3V6

* Corresponding author
E-mail: georgea@utsc.utoronto.ca, Tel.: +1 416 208 4858; Fax: +1 416 287 7279

1) MODEL DESCRIPTION

The model considers a three-compartment vertical segmentation representing the epilimnion, mesolimnion, and hypolimnion of the Harbour. The depths of the epilimnion and mesolimnion were explicitly specified based on extensive field measurements (1987-2007) and were both set equal to 8 m (Dermott, 2007; Hiriart-Baer *et al.*, 2009). Seasonally-varying mass exchanges among the three compartments were computed using Fick's Law (Klapwijk and Snodgrass, 1985; Hamblin and He, 2003). The exchanges between Hamilton Harbour and the relatively high quality waters of Lake Ontario through the Burlington Ship Canal were based on the Klapwijk and Snodgrass (1985; see their Fig. 1) conceptual model that postulates 20% of the Lake Ontario inflows to be directly discharged into the epi- and mesolimnion, whereas 80% of the fresher oxygenated lake water replaces the hypolimnetic masses in the Harbour.

We used the Canadian Daily Climate Data (1996-2002), the Canadian Daily Climate Normals (1971-2000) and field data to delineate the mean external forcing of the model, such as the solar radiation, day length, precipitation and evaporation, water temperature, and duration of the ice cover period (http://www.climate.weatheroffice.ec.gc.ca/prods_servs/index_e.html). Likewise, the mean hydrological and nutrient loading annual cycle stemming from non-point (Red Hill and Grindstone creeks, combined sewer overflows) and point (Arcelor-Mittal Dofasco and U.S. Steel Canada steel mills, Woodward and Skyway *WWTPs*) sources as well as from the Cootes Paradise Marsh through the Desjardin Canal were based on available data from the Water Survey of Canada (http://www.wsc.ec.gc.ca/) and the *RAP* loading report (Contaminant Loadings and Concentrations to Hamilton Harbour: 2003-2007 Update, 2010).

Our eutrophication model considers the interactions among the following state variables: nitrate, ammonium, organic nitrogen, phosphate, organic phosphorus, three phytoplankton and two zooplankton functional groups (Gudimov *et al.*, 2010). The governing equation for phytoplankton biomass accounts for phytoplankton production and losses due to mortality, settling, dreissenid filtration, and herbivorous zooplankton grazing. The phytoplankton growth is controlled by the water temperature conditions, as well as the nitrogen, phosphorus, and light availability. The ecological submodel simulates three phytoplankton functional groups that differ with respect to their strategies for resource competition (nitrogen, phosphorus, light, and temperature) and metabolic rates as well as their morphological features (settling velocities, self-shading effects) and edibility for zooplankton. The functional group A (*PFG A*) has growth and metabolic attributes of r-selected organisms, superior phosphorus and inferior nitrogen kinetics, lower tolerance to low light availability, low temperature optima, high sinking velocities as well as high palatability as food source for zooplankton. Thus, this functional group primarily aims to reproduce the dynamics of the spring diatom-dominated phytoplankton community, but the high-edibility feature assigned may indirectly reflect the functional role that cryptophytes play in the system (Brett *et al*., 2000). Following the classification scheme presented by Arhonditsis *et al*. (2007), we consider a second functional group (*PFG C*) modeled as K-strategist with regards to its growth and metabolic properties, weak phosphorus and dominant nitrogen competitor, with higher tolerance to low light availability, low settling velocities, high temperature optima, and low edibility. The specification of this group aims to describe the dynamics of the majority Cyanophyta and Dinophyceae species observed in the Harbour. The third assemblage (labelled as *PFG B*) was parameterized, so that the average functional properties assigned resemble those of other major residents of the summer phytoplankton community (chlorophytes, chrysophytes), thereby providing an intermediate competitor that more realistically depicts the continuum between diatom- and cyanobacteria-dominated communities.

Zooplankton grazing and losses due to natural mortality/consumption by higher predators are the main two terms in the zooplankton biomass equation. The present model simulates two zooplankton functional groups aiming to represent the herbivorous and omnivorous zooplankton community in the Harbour. Herbivorous zooplankton has four alternative food sources (the three phytoplankton groups and the biogenic particulate material or detritus) grazed with preference that changes dynamically as a function of their relative contribution to the total food abundance (Fasham *et al*., 1990), although our parameterization also postulates a selective zooplankton preference for the assemblages *PFG A, PFG B,* and detritus over cyanobacteria (see Table 2 in ESM). Omnivorous zooplankton feeds upon herbivorous zooplankton but its diet also depends on the relative abundance of the rest of the food sources in the system. Holling's type II functional response was used to model the temperature-dependent zooplankton grazing and the assimilated fraction of the grazed material that fuels growth. In the absence of information to support more complex forms, we selected a linear closure term that represents the effects of a seasonally invariant predator biomass (see Edwards and Yool, 2000).

The phosphate equation considers the phytoplankton uptake, the proportion of phytoplankton and zooplankton mortality/higher predation that is directly supplied into the system in inorganic form, the bacteria-mediated mineralization of organic phosphorus, and the net diffusive fluxes among the three spatial compartments. The organic phosphorus equation also considers the amount of organic phosphorus that is redistributed through phytoplankton and zooplankton basal metabolism. A fraction of organic phosphorus settles to the sediment and another fraction is mineralized to phosphate through a first-order reaction. The ammonia equation considers the phytoplankton uptake and the proportion of phytoplankton and zooplankton mortality that is returned back to the system as ammonium ions. Ammonia is also oxidized to nitrate through nitrification and the kinetics of this process are modeled as a function of the ammonia, dissolved oxygen, temperature and light availability (Cerco and Cole, 1994; Tian *et al*., 2001). We used Wroblewski's model (1977) to describe ammonia inhibition of nitrate uptake. The nitrate-nitrite equation also takes into account the amount of ammonia oxidized to nitrate through nitrification and the amount of nitrate lost as nitrogen gas through denitrification. The latter process is modeled as a function of dissolved oxygen, temperature and the contemporary nitrate concentrations (Arhonditsis and Brett, 2005). The organic nitrogen equation considers the contribution of phytoplankton and zooplankton mortality to the organic nitrogen pool and the seasonally-forced bacterial mineralization that transforms organic nitrogen to ammonia. Finally, as a first approximation to model the role of the sediments in water column dynamics, we followed a simple dynamic approach that relates the fluxes of nitrogen and phosphorus from the sediment with the algal and particulate matter sedimentation and burial rates while also accounting for the role of temperature (Arhonditsis and Brett, 2005). The relative magnitudes of ammonium and nitrate fluxes were also determined by nitrification and denitrification occurring at the sediment surface.

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2) WHAT IS THE IMPACT OF EPISODIC NUTRIENT LOADING EVENTS?

Both empirical and modeling studies highlight the impact of the phosphorus loading entering the Harbour from the Woodward Wastewater Treatment Plant as a major driver of the epilimnetic plankton dynamics (Charlton and Le Sage, 1996; Charlton, 2001; Gudimov *et al*., 2010; Ramin *et al*., 2011). In this study, we further examined the implications of a recent increasing trend of the dissolved inorganic to total phosphorus ratio of the effluents from the treatment plant (M. Bainbridge, personal communication). Our objective was to evaluate the changes in the phytoplankton abundance and community composition induced by an increase of the PO_4/TP ratio from 27% to 50%, which represents the gradual shift characterizing the loading data from the plant during the 2000s. Our analysis predicts an average increase of the summer epilimnetic chlorophyll *a* levels by 1-2 µg L^{-1} (Fig. 5a, b-ESM), highlighting the ominous prospect of failing to meet the delisting goal of the system by 2015, if we strictly adhere to the current numerical values of the *TP* (20 µg L^{-1}) and chlorophyll *a* (5-10 µg L^{-1}) standards targeted. Interestingly, the phytoplankton functional groups A (e.g., diatoms, cryptophytes) and B (e.g., chlorophytes, chrysophytes), possessing superior growth rates and/or phosphorus kinetics, primarily capitalize on the increase of the bioavailable phosphorus, whereas the third functional group (e.g., cyanobacteria, dinoflagellates) demonstrates a somewhat smaller increase of their relative abundance (Fig. 5c-ESM).

We also examined three scenarios regarding the sensitivity of the chlorophyll *α* and the relative cyanobacteria abundance to changes induced by short-term nutrient loading variability from Cootes Paradise and the Woodward Wastewater Treatment Plant during the summer stratified period. The first scenario is associated with inflows only from Cootes Paradise, while the second and third one also consider flows from the Woodward by-pass associated with a five- and tenfold increase of the incoming nutrient concentrations. Because of the simplified model spatial segmentation, we used an attenuation factor to approximate the impact of the local ecological processes occurring at the point of discharge from Cootes Paradise to the central part of the Harbour, while the magnitude of the pulse events was specified as a proportional increase of the reference loading conditions from the same location. Notably, our analysis predicts dramatic short-term changes in the water quality, such as 5-15% increase of the chlorophyll *a* and up to 50% increase of the relative cyanobacteria biomass, depending on the assumptions made about the intensity of the episodic event, the circulation patterns, and the concurrence of perturbations from the two major exogenous loading sources (Fig. 6-ESM). The Cootes Paradise is a highly productive system with high chlorophyll *a* and *TP* concentrations (Chow-Fraser *et al.* 1998), and therefore the close connection between the related discharges and the offshore water quality is not surprising. Relative to our earlier modeling work though (Gudimov *et al.*, 2010; Ramin *et al.*, 2011), the additional insight offered by the present analysis is that the amount and composition (proportion of cyanobacteria) of the phytoplankton biomass exported from Cootes can potentially stimulate broader changes in the system. Namely, we hypothesize that the qualitative and quantitative features of the phytoplankton inoculum entering the western end of the Harbour coupled with the profound changes on the biogeochemistry and trophic functioning of the littoral zone induced by episodic pulses (summer storms) can significantly alter the contemporary growth and species competition patterns which in turn can be gradually propagated to the offshore sites of the Harbour (Schelske *et al.*, 1995; Eadie *et al.*, 2002; Schallenberg and Burns, 2004; Johengen *et al.*, 2008).

According to our model predictions, the latter conceptual pattern is further accentuated when it coincides with episodic overflow events from the Woodward Waste Water Treatment Plant. Apparently, the substantial amount of bioavailable phosphorus discharged into the Harbour epilimnion can potentially alleviate the competition capacity of the species with inferior phosphorus kinetics (i.e., cyanobacteria) and in conjunction with other prevailing abiotic conditions (e.g., limited light penetration due to high levels of suspended solids) may lead to structural shifts of the phytoplankton community. In view of the potential repercussions of such episodic events on the system dynamics, the question arising is what may cause the occurrence of such by-passes from

Woodward? A significant number (≈30%) of Hamilton residents are connected to combined sewer system which transport both storm water and raw sewage in one pipe to Woodward Waste Water Treatment Plant. When extreme meteorological events occur, combined sewage overflows (CSO) storage tanks typically capture the excessive storm hydraulic loading and slowly release it for further treatment (Contaminant Loadings and Concentrations to Hamilton Harbour: 2003-2007 Update or CLCHH, 2010). Yet, there are rare peak events during which the CSO system as well as the treatment plant may be overloaded and occasional bypasses of these mixed and diluted waste water outfalls directly to Harbour to protect the integrity of treatment facilities and to avoid backflows to basements of local residents. At present, the *WWTP* capacity to handle storm waters is at its limits and around 10% of storm events (or approximately 1-2 events during the summer stratified period) overflow to the Harbour, although future upgrades at the *WWTP* should result in treatment of 95% of waste water from the City of Hamilton.

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3) FIGURES

Figure 1-ESM: Time series plots of the simulated and observed water quality variables for the three spatial compartments of the Hamilton Harbour eutrophication model. Solid lines correspond to monthly mean values, while the dashed lines correspond to the 2.5th and 97.5th percentiles of the model predictions associated with the simulated inter- and intra-annual variability of the loading conditions. The dots represent the observed mean monthly values in the Hamilton Harbour from 2000-2009.

Figure 2-ESM: Map of the Hamilton Harbour watershed: (*a*) locations of exogenous load monitoring stations and (*b*) types of land use.

Figure 3-ESM: Relative frequency (%) of simulated epilimnetic *TP* and chlorophyll *α* concentrations under conditions of higher phosphorus sediment release (3.2-3.8 mg $m^{-2}day^{-1}$).

Figure 4-ESM: Relative frequency (%) of simulated epilimnetic *TP* and chlorophyll *α* concentrations under lower phosphorus sediment release (1.2-1.6 mg $m^{-2}day^{-1}$).

Figure 5-ESM: Sensitivity of the predicted (a) seasonal chlorophyll *a* concentrations, (b) chlorophyll *a* summer epilimnetic values, and (c) seasonal phytoplankton community composition to the PO_4/TP ratios of the phosphorus loading entering the Harbour from the Woodward Wastewater Treatment Plant.

Figure 6-ESM: Sensitivity of the chlorophyll *α* and the relative cyanobacteria abundance predictions associated with extreme pulse flow events from Cootes Paradise and the Woodward Wastewater Treatment Plant during the summer stratified period. The first scenario represents inflows only from Cootes Paradise. The second and third scenarios also consider overflow events from the Woodward

Wastewater Treatment Plant associated with a five- and ten-fold increase of the incoming nutrient concentrations. The attenuation factor is a surrogate parameter of the impact of the discharges from Cootes Paradise to the central part of the Harbour, while the magnitude of the pulse events is expressed as a proportional increase of the reference loading conditions from the same location. [Note that the changes in the phytoplankton abundance and composition relative to the reference water quality conditions refer to 15-day averages following the episodic events.]

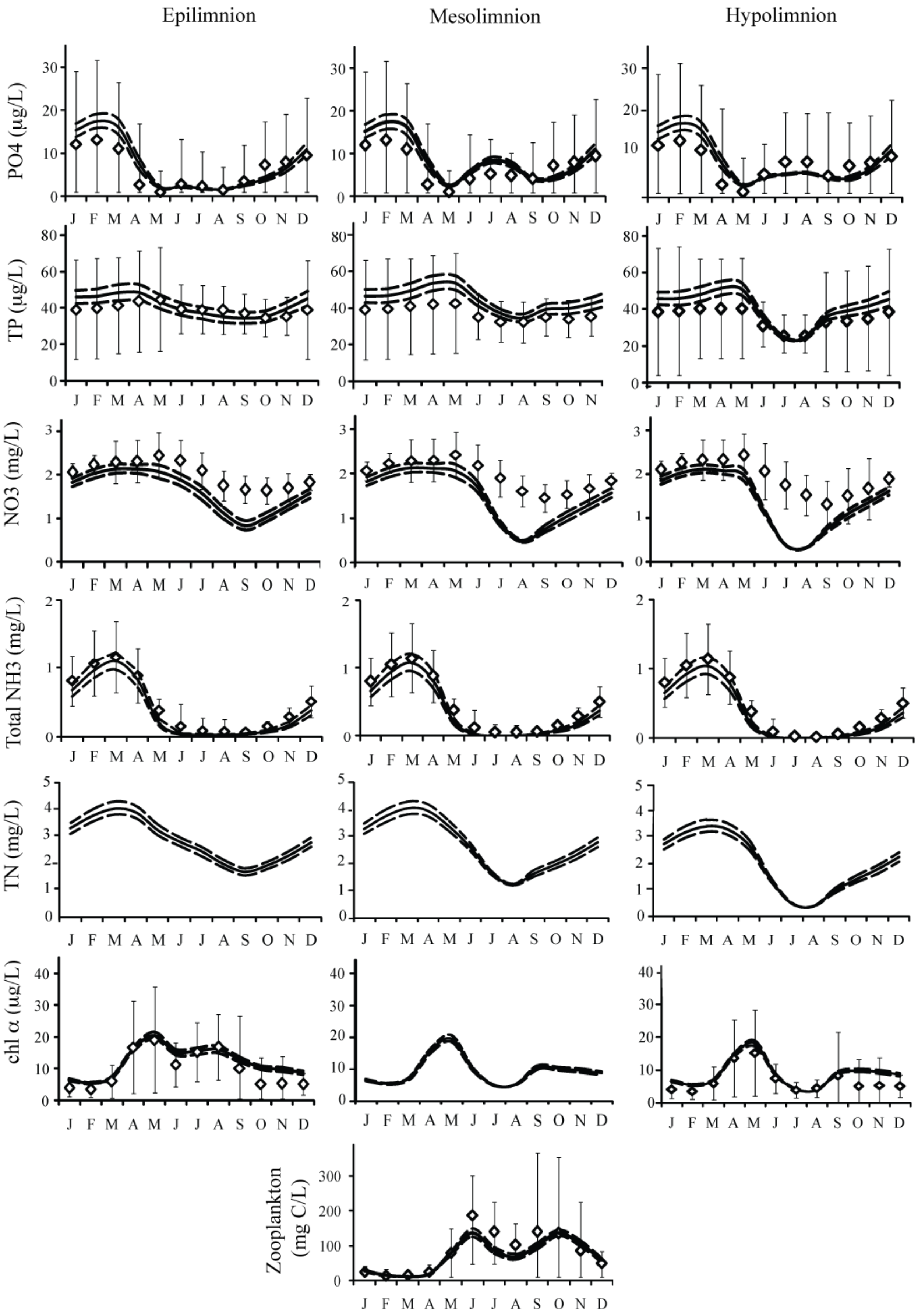
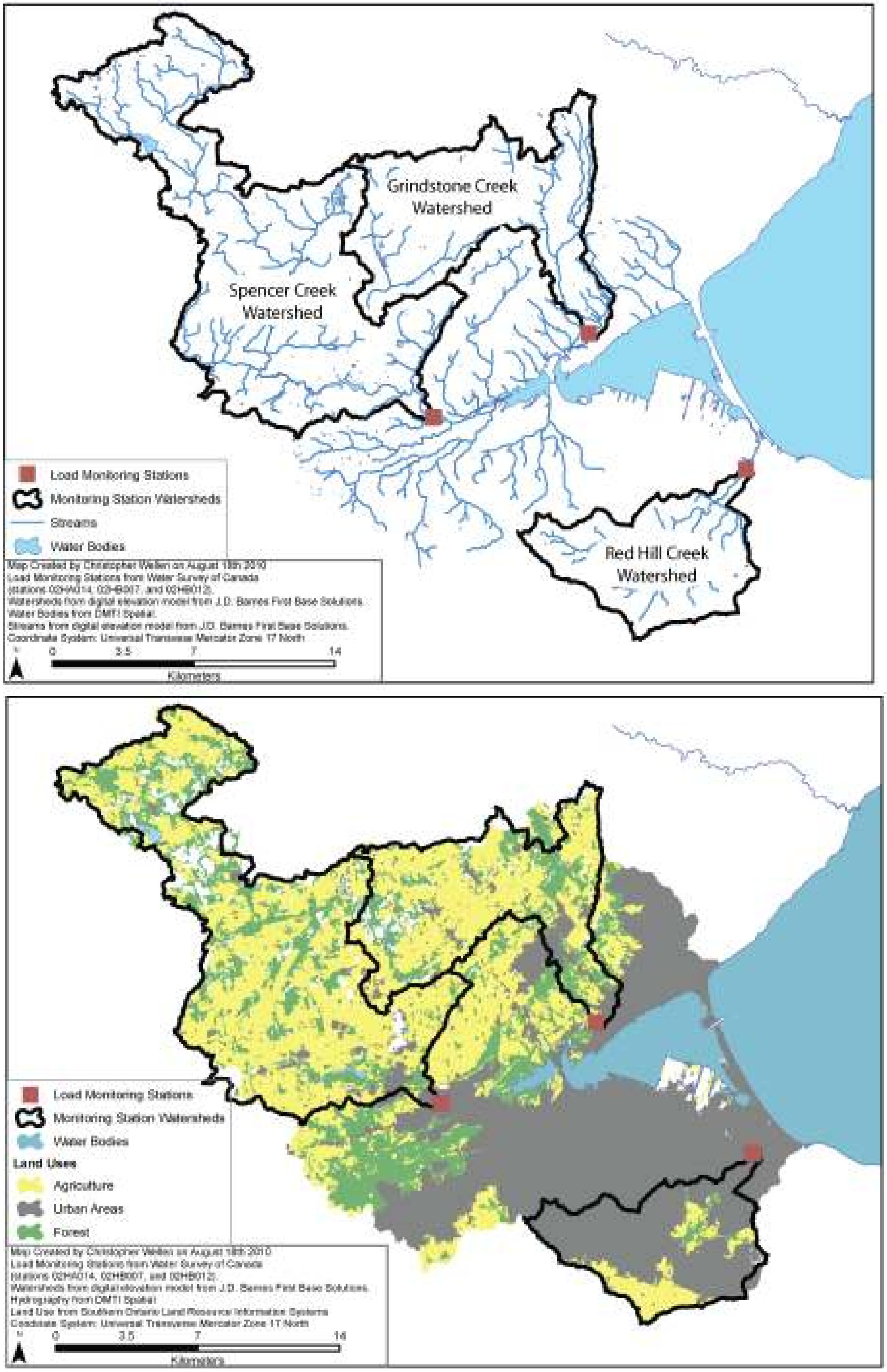

Epilimnion
Mesolimnion
Hypolimnion
PO4 (µg/L)
TP (µg/L)
NO3 (mg/L)
Total NH3 (mg/L)
TN (mg/L)
chl α (µg/L)
Zooplankton (mg C/L)
J F M A M J J A S O N D

Figure 1-ESM



Map Created by Christopher Wellen on August 18th 2010
Load Monitoring Stations from Water Survey of Canada
(stations 02HA014, 02HB007, and 02HB012).
Watersheds from digital elevation model from J.D. Barnes First Base Solutions.
Water Bodies from DMTI Spatial.
Streams from digital elevation model from J.D. Barnes First Base Solutions.
Coordinate System: Universal Transverse Mercator Zone 17 North

Map Created by Christopher Wellen on August 18th 2010
Load Monitoring Stations from Water Survey of Canada
(stations 02HA014, 02HB007, and 02HB012).
Watersheds from digital elevation model from J.D. Barnes First Base Solutions.
Hydrography from DMTI Spatial.
Land Use from Southern Ontario Land Resource Information Systems
Coordinate System: Universal Transverse Mercator Zone 17 North

Figure 2-ESM

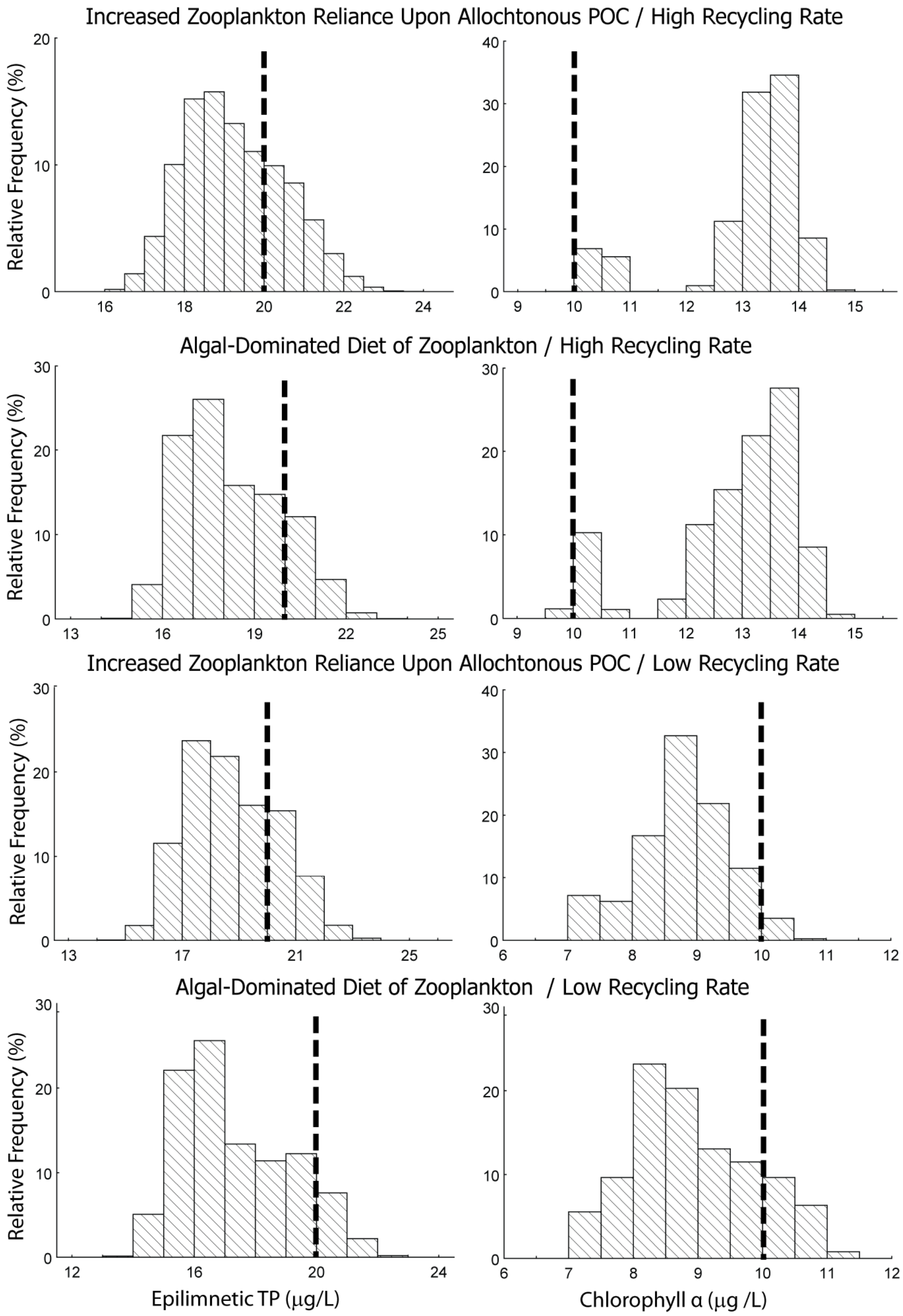
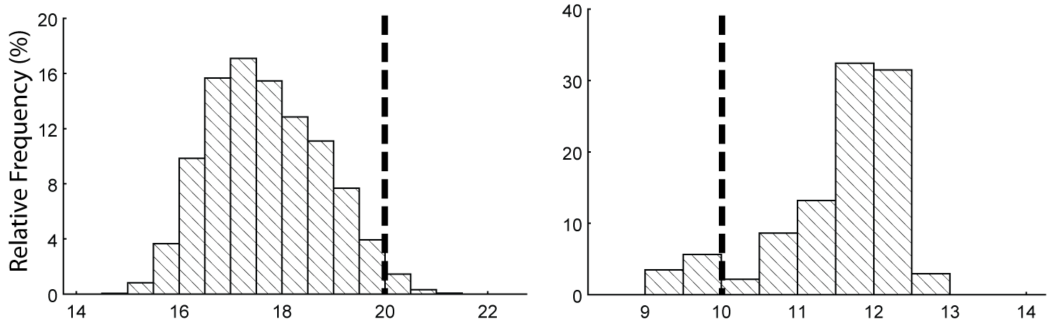
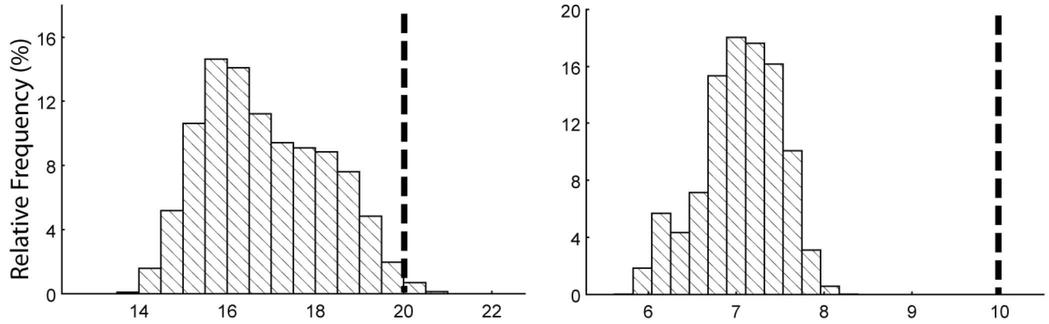

Increased Zooplankton Reliance Upon Allochtonous POC / High Recycling Rate
Algal-Dominated Diet of Zooplankton / High Recycling Rate
Increased Zooplankton Reliance Upon Allochtonous POC / Low Recycling Rate
Algal-Dominated Diet of Zooplankton / Low Recycling Rate
Relative Frequency (%)
Epilimnetic TP (μg/L)
Chlorophyll α (μg /L)
0
10
20
30
40
16
18
20
22
24
9
10
11
12
13
14
15
13
16
19
22
25
13
17
21
25
6
7
8
9
10
11
12

Figure 3-ESM

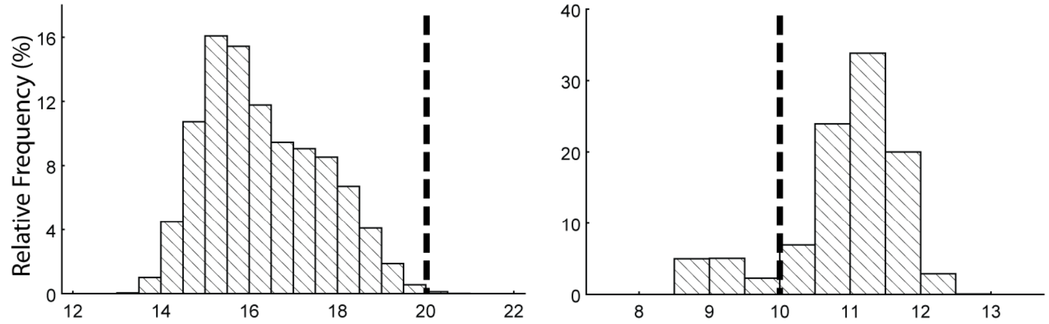
Increased Zooplankton Reliance Upon Allochtonous POC / High Recycling Rate



Increased Zooplankton Reliance Upon Allochtonous POC/ Low Recycling Rate



Algal Dominated Diet of Zooplankton / High Recycling Rate



Algal Dominated Diet of Zooplankton / Low Recycling Rate

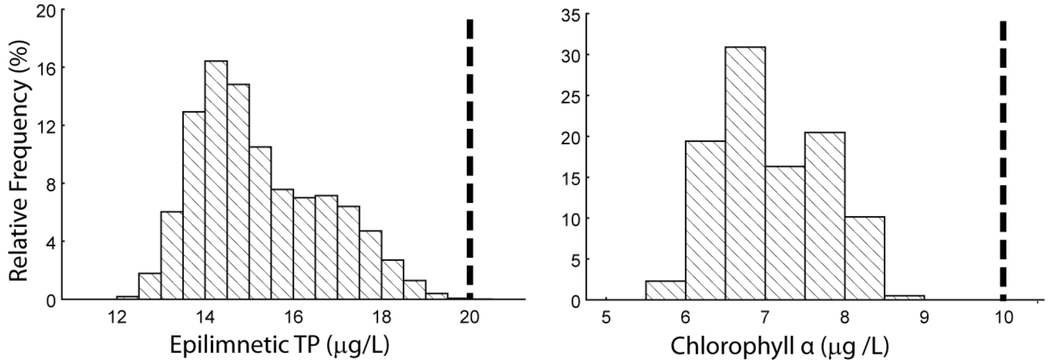


Figure 4-ESM

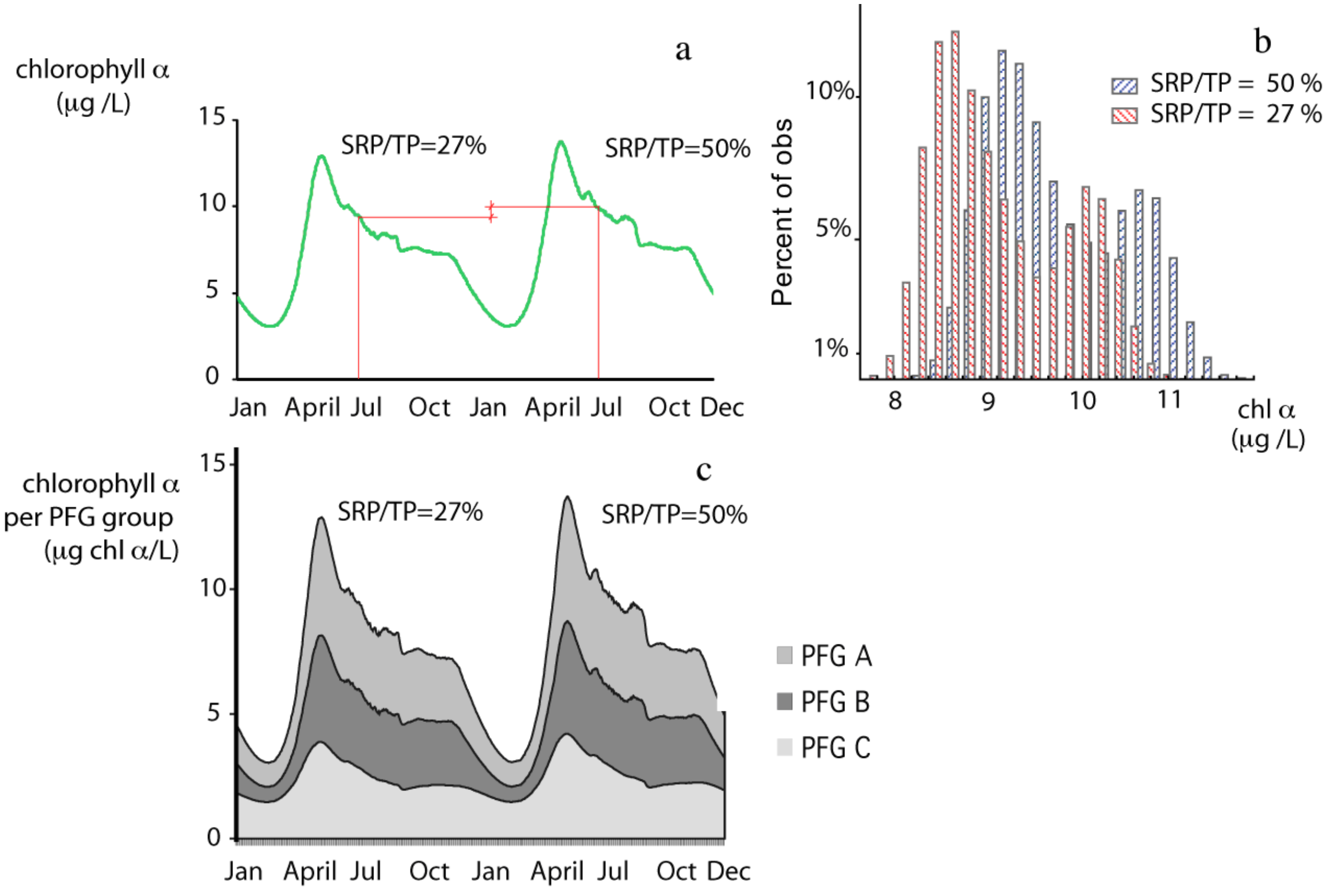

a
chlorophyll α
(μg /L)
15
10
5
0
SRP/TP=27%
SRP/TP=50%
Jan
April
Jul
Oct
Jan
April
Jul
Oct
Dec
b
Percent of obs
10%
5%
1%
SRP/TP = 50 %
SRP/TP = 27 %
8
9
10
11
chl α
(μg /L)
c
chlorophyll α
per PFG group
(μg chl α/L)
15
10
5
0
SRP/TP=27%
SRP/TP=50%
PFG A
PFG B
PFG C
Jan
April
Jul
Oct
Jan
April
Jul
Oct
Dec

Figure 5-ESM

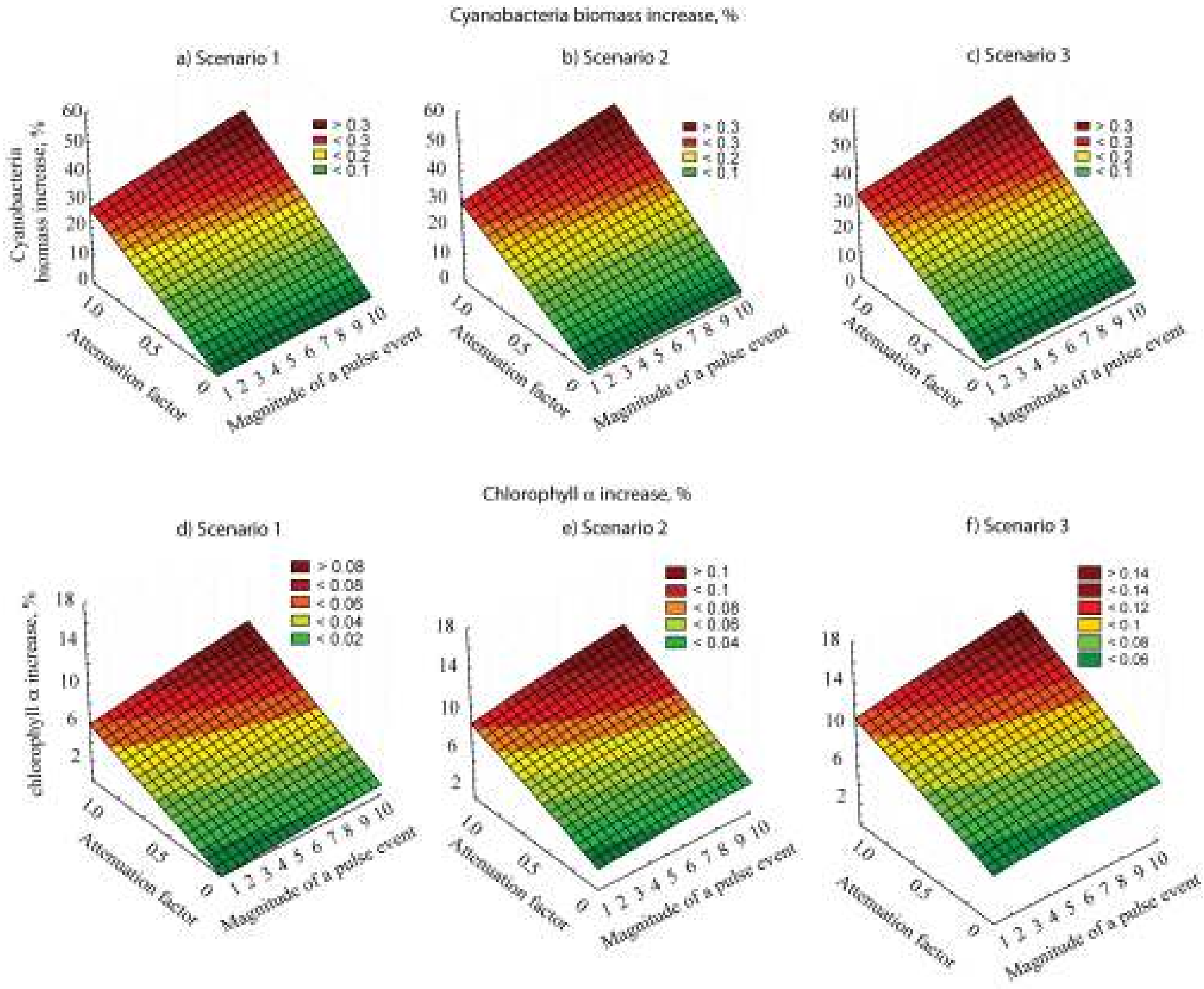

Cyanobacteria biomass increase, %
a) Scenario 1
b) Scenario 2
c) Scenario 3
Cyanobacteria biomass increase, %
> 0.3
< 0.3
< 0.2
< 0.1
0
10
20
30
40
50
60
Attenuation factor
0
0.5
1.0
Magnitude of a pulse event
1 2 3 4 5 6 7 8 9 10
Chlorophyll α increase, %
d) Scenario 1
e) Scenario 2
f) Scenario 3
chlorophyll α increase, %
> 0.08
< 0.08
< 0.06
< 0.04
< 0.02
> 0.1
< 0.1
< 0.08
< 0.06
< 0.04
> 0.14
< 0.14
< 0.12
< 0.1
< 0.08
< 0.06
2
6
10
14
18

Figure 6-ESM

4) TABLES

Table 1: Mathematical description of the model. The *i* subscript refers to the phytoplankton groups *PFG A, PFG B, PFG C;* the *j* subscript refers to herbivorous and omnivorous zooplankton*;* the *x* subscript refers to the spatial segments epilimnion, mesolimnion and hypolimnion.

No.	State Variable	Term	Equation
1	**Phytoplankton biomass**	$\frac{dPHYT_{i,x}}{dt}$	$=growth_{i,x} \times PHYT_{i,x} - mp_i \times e^{kt(Tx-Tempref)} \times PHYT_{i,x} - Vsettling_i \times PHYT_{i,x}/z_x - filter_i \times e^{ktfilt(Tx-Tempref)} \times PHYT_{i,x} - Grazing_{herb\ i,x} \times ftemperature_{herb\ x} \times ZOOP_{herb\ x} - Grazing_{omni\ i,x} \times ftemperature_{omni\ x} \times ZOOP_{omni\ x} \pm Exchanges_{PHYT\ i\ Vertical} \pm Exchanges_{PHYT\ i\ Lake\ Ontario}$, *where*
	Growth rate	$growth_{i,x}$	$=gwthmax_i \times fnutrient_{i,x} \times flight_{i,x} \times ftemperature_{i,x}$
	Nutrient limitation	$fnutrient_{i,x}$	$=min\{\varphi NA_{i,x}, \varphi PO4_{i,x}\}$
	Nitrogen limitation	$\varphi NA_{i,x}$	$=\varphi NO3_{i,x} + \varphi NH4_{i,x}$
	Nitrate limitation	$\varphi NO3_{i,x}$	$= (NO3_x\, e^{(-\psi \cdot NH4_x)})/(NO3_x + NH_i)$
	Ammonium limitation	$\varphi NH4_{i,x}$	$=NH4_x/(NH4_x + AH_i)$
	Phosphate limitation	$\varphi PO4_{i,x}$	$= (Pint_{i,x} - Pmin_i)/(Pmax_i - Pmin_i)$
	Intracellular phosphorus content	$\frac{dPint_{i,x}}{dt}$	$=Pup_{i,x} \times Pfb_{i,x} - growth_{i,x} \times Pint_{i,x}$
	Phosphorus uptake	$Pup_{i,x}$	$=Pmaxuptake_i \times (PO4_x/(PO4_x + PH_i))$
	Feedback control	$Pfb_{i,x}$	$= (Pmax_i - Pint_{i,x})/(Pmax_i - Pmin_i)$
	Light limitation	$flight_{i,x}$	$=2.718 \times (FD/(kext_x \times z_x))(e^{-a1} - e^{-a0})$, *where* $a0_i = (I/Ik_i)e^{-kext_x \times H_x}$, $a1_i = (I/Ik_i)e^{-kext_x (z_x + H_x)}$
	Light attenuation	$kext_x$	$=Kextchla_i \sum_i PHYT_{i,x} \times Chl\alpha C_i + Kextb$
	Temperature limitation	$ftemperature_{i,x}$	$= e^{(-KTgr_i (T_x - Topt_i)^2)}$
		FD	$=$*the fractional day length* $(0 \leq FD \leq 1)$
2	**Herbivorous zooplankton biomass**	$\frac{dZOOP_{herb,x}}{dt}$	$=(\sum_i Grazing_{herb\ i,x} \times ftemperature_{herb,x} \times asfood_{herb,i} + Grazing_{herbdet,x} \times ftemperature_{herb,x} \times asfood_{herb,det}) \times ZOOP_{herb,x} - mz_{herb} \times e^{kt(Tx-Tempref)} \times ZOOP_{herb,x} - Grazing_{omniherb,x} \times ftemperature_{omni,x} \times ZOOP_{omni,x} \pm Exchanges_{herb\ Vertical} \pm Exchanges_{herb\ Lake\ Ontario}$
	Grazing rate for phytoplankton	$Grazing_{herb\ i,x}$	$=maxgrazing_{herb} \times (Pref_{herb\ i,x} \times PHYT_{i,x}) / (KZ_{herb} + Food_{herb,x})$
	Grazing rate for detritus	$Grazing_{herbdet,x}$	$=maxgrazing_{herb} \times (Pref_{herbdet,x} \times Detritus_x) / (KZ_{herb} + Food_{herb,x})$
	Grazing rate by omnivorous zooplankton	$Grazing_{omniherb,x}$	$=maxgrazing_{omni} \times (Pref_{omniherb,x} \times ZOOP_{herb,x}) / (KZ_{omni} + Food_{omni,x})$
	Abundance of food in layer *x*	$Food_{herb,x}$	$=\sum_i Pref_{herb\ i,x} \times PHYT_{i,x} + Pref_{herbdet,x} \times Detritus_x$
	Preference of zooplankton for phytoplankton *i*	$Pref_{herb\ i,x}$	$= (Pref_{herb,i} \times PHYT_{i,x}) / (\sum_i Pref_{herb,i} \times PHYT_{i,x} + Pref_{herbdet} \times Detritus_x)$

No.	State Variable	Term	Equation
	Preference of zooplankton for detritus	$Pref_{herbdet,x}$	$= (Pref_{herbdet} \times Detritus_x) / (\sum_i Pref_{herb,i} \times PHYT_{i,x} + Pref_{herbdet} \times Detritus_x)$
	Temperature limitation for growth	$ftemperature_{herb,x}$	$= e^{(-KTgr_{herb}(T_x - Topt_{herb})^2)}$
3	**Omnivorous zooplankton biomass**	$\frac{dZOOP_{omni,x}}{dt}$	$=(\sum_i Grazing_{omni\ i,x} \times ftemperature_{omni,x} \times asfood_{omni,i} + Grazing_{omnidet,x} \times ftemperature_{omni,x} \times asfood_{omnidet} + Grazing_{omniherb,x} \times ftemperature_{omni,x} \times asfood_{omniherb}) \times ZOOP_{omni,x} - mz_{omni} \times e^{kt(Tx-Tempref)} \times ZOOP_{omni,x} \pm Exchanges_{omni\ Vertical} \pm Exchanges_{omni\ Lake\ Ontario}$
	Grazing rate for phytoplankton	$Grazing_{omni\ i,x}$	$=maxgrazing_{omni} \times (Pref_{omni\ i,x} \times PHYT_{i,x}) / (KZ_{omni} + Food_{omni,x})$
	Grazing rate for herbivorous zooplankton	$Grazing_{omniherb,x}$	$=maxgrazing_{omni} \times (Pref_{omniherb,x)} \times PHYT_{herb,x}) / (KZ_{omni} + Food_{omni,x})$
	Grazing rate for detritus	$Grazing_{omnidet,x}$	$=maxgrazing_{omni} \times (Pref_{omnidet,x} \times Detritus_x) / (KZ_{omni} + Food_{omni,x})$
	Abundance of food in layer *x*	$Food_{omni,x}$	$= \sum_i Pref_{omni\ i,x} \times PHYT_{i,x} + Pref_{omnidet,x} \times Detritus_x$
	Preference of omnivorous zooplankton for phytoplankton *i*	$Pref_{omni\ i,x}$	$= (Pref_{omni,i} \times PHYT_{i,x})/(\sum_i Pref_{omni,i} \times PHYT_{i,x} + Pref_{omnidet} \times Detritus_x)$
	Preference of zooplankton for detritus	$Pref_{omnidet,x}$	$= (Pref_{omnidet} \times Detritus_x)/(\sum_i Pref_{omni\ i} \times PHYT_{i,x} + Pref_{omnidet} \times Detritus_x)$
	Temperature limitation for growth	$ftemperature_{omni,x}$	$= e^{(-KTgr_{omni}(T_x - Topt_{omni})^2)}$
4	**Detritus concentration**	$\frac{dDetritus_x}{dt}$	$= \sum_i [(1-\alpha_{DOC\ i}) \times mp_i \times e^{kt(Tx-Tempref)} \times PHYT_{i,x}] + \sum_{j=omni,herbi} [(1-\alpha_{DOC\ j}) \times mz_j \times e^{kt(Tx-Tempref)} \times ZOOP_{j,x}] - [(maxgrazing_{herb} \times Pref_{herbdet,x} \times Detritus_x) / (KZ_{herb} + Food_{herb,x})] \times ftemperature_{herb,x} \times ZOOP_{herb,x} - [(maxgrazing_{omni} \times Pref_{omnidet,x} \times Detritus_x) / (KZ_{omni} + Food_{omni,x})] \times ftemperature_{omni,x} \times ZOOP_{omni,x} - Vsettling_{(biogenic)} \times Detritus_x/z_x - KCmineral_x \times Detritus_x$
	Carbon mineralization rate	$KCmineral_x$	$= ftemperature\_min_x \times KCrefmineral;$ *where*
	Temperature limitation for mineralization	$ftemperature\_min_x$	$= e^{(-KTFmin(T_x - Toptmin)^2)}$
5	**Phosphate concentration**	$\frac{dPO_{4x}}{dt}$	$= -\sum_i Pup_{i,x} \times Pfb_{i,x} \times PHYT_{i,x} + \sum_i \alpha_{PO4\ i} \times mp_i \times e^{kt(Tx-Tempref)} \times Pint_{i,x} \times PHYT_{i,x} + \sum_{j=herbi,omni} \alpha_{PO4\ j} \times mz_j \times e^{kt(Tx-Tempref)} \times PC_j \times ZOOP_{j,x} + KPmineral_x \times OP_x - FePrecipitation \pm ExchangesPO_{4Vertical} \pm ExchangesPO_{4Lake\ Ontario} + + PO_4EXOG_{EPI} + PO_4ENDOG_x,$ *where*
	Phosphorus mineralization rate	$KPmineral_x$	$= ftemperature\_min_x \times KPrefmineral;$ *where*
	Iron-induced precipitation due to Steel Mills	$FePrecipitation$	$= (1-(9.4 \times [Fe_{Steel\ Mills} + 1400]^{-0.31})) \times PO_{4\ x}$

No.	State Variable	Term	Equation
	discharge		
6	**Organic phosphorus concentration**	$\frac{dOP_x}{dt}$	$=DetritusP_x - \sum_{j=omni,herbi} DetritusGrazingP_{j,x} \times ftemperature_{j,x} \times ZOOP_{j,x} - SettlingP_x \times OP_x / z_x - KPmineral_x \times OP_x \pm ExchangesOP_{Vertical} \pm ExchangesOP_{Lake\ Ontario} + OPEXOG_{EPI} + OPENDOG_x$
	Biogenic organic phosphorus accumulation	$DetritusP_x$	$=\sum_i (1-\alpha_{PO4\,i}) \times mp_i \times e^{kt(T_x - Tempref)} \times Pint_{i,x} \times PHYT_{i,x} + \sum_{j=omni,herbi} (1-\alpha_{PO4\,j}) \times mz_j \times e^{kt(T_x - Tempref)} \times PC_j \times ZOOP_{j,x}$
	Loss due to zooplankton grazing upon detritus	$DetritusGrazingP_{j,x}$	$= (maxgrazing_j \times Pref_{det\,j,x} \times DetritusP_x) / (KZ_j + Food_{j,x})$
	Loss due to particulate phosphorus settling	$SettlingP_x$	$= (DetritusP_x / OP_x) \times Vsettling_{(biogenic)} + (1-(DetritusP_x / OP_x)) \times Vsettling$
7	**Ammonium concentration**	$\frac{dNH4_x}{dt}$	$= -\sum_i \varphi NH4_{i,x} \times gwthmax_i \times flight_{i,x} \times ftemperature_{i,x} \times N/C_{i,x} \times PHYT_{i,x} + \sum_i \alpha NH4_i \times mp_i \times e^{kt(Tx - Tempref)} \times N/C_{i,x} \times PHYT_{i,x} + \sum_{j=omni,herbi} aNH4_j \times mz_j \times e^{kt(Tx - Tempref)} \times N/C_j \times ZOOP_{j,x} + KNmineral_x \times ON_x - Nitrification_x \pm ExchangesNH4_{Vertical} \pm Exchanges\ NH4_{Lake\ Ontario} + NH4EXOG_{EPI} + NH4ENDOG_x$
	Mineralization rate	$KNmineral_x$	$=KN_{refmineral} \times ftemperature\_min_x$
	Nitrification rate	$Nitrification_x$	$=Nitrifmax \times flightnitr_x \times (DO_x / (DO_x + KHdonit)) \times (NH4_x / KHnh4nit + NH4_x) \times ftempnitr_x$
	Light limitation	$flightnitr_x$	$=1$ when $I_x \leq 0.1 \times I$, else $flightnitr_x = 0$
	Temperature limitation	$ftempnitr_x$	$= e^{(-KTFgrnitr(T_x - Toptnitr)^2)}$
	Intensity of light in compartment *x*	I_x	$= I/(kext_x \times z_x)(e^{-kext_x \times H_x} - e^{-kext_x (z_x + H_x)})$
	Nitrogen-to-carbon ratio of the phytoplankton cells	$N/C_{i,x}$	$=16 \times Pint_{i,x}$
8	**Nitrate concentration**	$\frac{dNO3_x}{dt}$	$= -\sum_i \varphi NO3_{i,x} \times gwthmax_i \times flight_{i,x} \times ftemperature_{i,x} \times N/C_{i,x} \times PHYT_{i,x} + Nitrification_x - Denitrification_x \pm ExchangesNO3_{Vertical} \pm ExchangesNO3_{Lake\ Ontario} + NO3EXOG_{EPI} + NO3ENDOG_x;$
	Denitrification rate	$Denitrification_x$	$=Denitrifmax \times (KHdodenit / (DO_x + KHdodenit)) \times (NO3_x / KHno3nit + NO3_x) \times ftempdenitr_x$
	Temperature limitation	$ftempdenitr_x$	$= e^{(-KTgrdenitr(T_x - Toptdenitr)^2)}$
9	**Organic nitrogen concentration**	$\frac{dON_x}{dt}$	$=Detritus\ N_x - \sum_j DetritusGrazing\ N_{j,x} \times ftemperature_{j,x} \times ZOOP_{j,x} - (Detritus\ N_x / ON_x \times Vbiosettling + (1-Detritus\ N_x / ON_x) \times Vsettling) \times ON_x - KNmineral_x \times ON_x \pm ExchangesON_{Vertical} \pm ExchangesON_{Lake\ Ontario} + ONEXOG_{EPI} + ONENDOG_x$
	Biogenic organic nitrogen accumulation	$Detritus\ N_x$	$=\sum_i (1-aNH4_i) \times mp_i \times e^{kt(Tx - Tempref)} \times N/C_{i,x} \times PHYT_{i,x},$

No.	State Variable	Term	Equation
			$+ \sum_j (1- aNH4_j) \times mz_j \times e^{kt(Tx-Tempref)} \times N/C_j \times ZOOP_{j,x}$
	Loss due to zooplankton grazing upon detritus	$DetritusGrazingN_{j,x}$	$=maxgrazing_j \times Pref_{det\,j,x} \times Detritus\ N_x / (KZ_j + Food_{j,x})$
10	**Sediment submodel**		
10.1	**Phosphate sediment release**	$\frac{dPO_{4sed_x}}{dt}$	$= (1 - \beta_P) \times Pdeposition - (\alpha s_{PO4} \times PO4_{sed\,x} \times e^{Ktsed(Tsedx-Tempref_{sed})})$
	Organic phosphorus sedimentation	$Pdeposition$	$= (\sum_i Vsettling_i \times Pint_{i,x} \times PHYT_{i,x} + SettlingP_x \times OP_x)$
10.2	**Ammonium sediment release**	$\frac{dNH_{4sed_x}}{dt}$	$=(1 - \beta_N) \times Ndeposition-(\alpha s_{NH4} \times NH4_{sed} \times e^{Kt}sed^{(Tsed\,x- Tempref_{sed})})$ $- Nitrifmax_{sed} \times (DO_x / (DO_x + KHdonit_{sed})) \times$ $\times (NH_{4\,sed\,x} / (KHnh4nit_{sed} + NH_{4\,sed\,x})) \times ftempnitrsed_x$
	Loss due to particulate nitrogen settling	$Ndeposition$	$= \sum_i Vsettling_i \times N/C_{i,x} \times PHYT_{i,x} + VsettlingN_x \times ON_x$
	Temperature limitation for nitrification in the sediments	$ftempnitrsed_x$	$= e^{(-KTgrnitr_{sed}(T_x-Toptnitr_{sed})^2)}$
10.3	**Nitrate sediment release**	$\frac{dNO_{3sed_x}}{dt}$	$=Nitrifmax_{sed} \times (DO_x/(DO_x+KHdonit)) \times (NH_{4sed\,x}/(KHnh4nit+NH_{4sed\,x})) \times$ $ftempnitr_x - (as_{NO3} \times NO3_{sed\,x} \times e^{Ktsed(Tsed_x-Tempref_{sed})}) - Denitrifmax_{sed} \times$ $(KHdodenit_{sed} /(DO_x+KHdodenit_{sed})) \times (NO_{3sed\,x} /KHno3denit_{sed} + NO_{3\,sed\,x})$ $\times ftempdenitrsed_x$
	Temperature limitation for denitrification in the sediments	$ftempdenitrsed_x$	$= e^{(-KTgrdenitr_{sed}(T_x-Toptdenitr_{sed})^2)}$
	Rate of sediment release of organic nitrogen	$ONSED_x$	$= ONosed \bullet e^{(kt_{sed}(Tsed-Tempref_{sed}))}$, where
		$ONosed$	$= OPosed \times TN/TP,$
	Rate of sediment release of organic phosphorus	$OPSED_x$	$= OPosed \bullet e^{(kt_{sed}(Tsed-Tempref_{sed}))}$, where
		$OPosed$	$= 0.1\ mg\ m^{-2}\ day^{-1}$
	Total nitrogen to total phosphorus ratio	TN/TP	$= 21$

Table 2: Description and calibration values of model parameters.

Symbol	*Description*	*Values*	*Units*	*Sources*
AH_{PFGA}	Half saturation constant for ammonium uptake by PFG A	100	mg N m^{-3}	10
AH_{PFGB}	Half saturation constant for ammonium uptake by PFG B	80	mg N m^{-3}	10
AH_{PFGC}	Half saturation constant for ammonium uptake by PFG C	60	mg N m^{-3}	10
$\alpha_{DOC\ herbi}$	Fraction of herbivorous zooplankton mortality becoming dissolved organic carbon	0.5	-	10
$\alpha_{DOC\ omni}$	Fraction of omnivorous zooplankton mortality becoming dissolved organic carbon	0.5	-	10
$\alpha_{DOC\ PFGA}$	Fraction of PFG A mortality becoming dissolved organic carbon	0.5	-	10
$\alpha_{DOC\ PFGB}$	Fraction of PFG B mortality becoming dissolved organic carbon	0.5	-	10
$\alpha_{DOC\ PFGC}$	Fraction of PFG C mortality becoming dissolved organic carbon	0.5	-	10
$\alpha_{NH4\ herbi}$	Fraction of herbivorous zooplankton mortality becoming ammonium	0.5	-	10
$\alpha_{NH4\ omni}$	Fraction of omnivorous zooplankton mortality becoming ammonium	0.5	-	10
$\alpha_{NH4\ PFGA}$	Fraction of PFG A mortality becoming ammonium	0.5	-	10
$\alpha_{NH4\ PFGB}$	Fraction of PFG B mortality becoming ammonium	0.5	-	10
$\alpha_{NH4\ PFGC}$	Fraction of PFG C mortality becoming ammonium	0.5	-	10
αs_{NO3}	Sediment nitrate release rate	0.5	day^{-1}	
αs_{NH4}	Sediment ammonium release rate	0.5	day^{-1}	
αs_{PO4}	Sediment phosphate release rate	0.5	day^{-1}	
$\alpha_{PO4\ herbi}$	Fraction of herbivorous zooplankton	0.8	-	10

Symbol	***Description***	***Values***	***Units***	***Sources***
	mortality becoming phosphate			
$\alpha_{PO4\ omni}$	Fraction of omnivorous zooplankton mortality becoming phosphate	0.8	-	10
$\alpha_{PO4\ PFGA}$	Fraction of PFG A mortality becoming phosphate	0.8	-	10
$\alpha_{PO4\ PFGB}$	Fraction of PFG B mortality becoming phosphate	0.8	-	10
$\alpha_{PO4\ PFGC}$	Fraction of PFG C mortality becoming phosphate	0.8	-	10
$asfood_{herbi\ det}$	Herbivorous zooplankton assimilation efficiency for detritus	0.45	-	
$asfood_{herbi\ PFGA}$	Herbivorous zooplankton assimilation efficiency for PFG A	0.5	-	
$asfood_{herbi\ PFGB}$	Herbivorous zooplankton assimilation efficiency for PFG B	0.5	-	
$asfood_{herbi\ PFGC}$	Herbivorous zooplankton assimilation efficiency for PFG C	0.15	-	
$asfood_{omni\ det}$	Omnivorous zooplankton assimilation efficiency for detritus	0.45	-	
$asfood_{omni\ herb}$	Omnivorous zooplankton assimilation efficiency for herbivorous zooplankton	0.55	-	
$asfood_{omni\ PFGA}$	Omnivorous zooplankton assimilation efficiency for PFG A	0.5	-	
$asfood_{omni\ PFGB}$	Omnivorous zooplankton assimilation efficiency for PFG B	0.5	-	
$asfood_{omni\ PFGC}$	Omnivorous zooplankton assimilation efficiency for PFG C	0.15	-	
$ChlaC_{PFGA}$	Chlorophyll to carbon ratio in PFG A	0.02	-	8,9,11,15
$ChlaC_{PFGB}$	Chlorophyll to carbon ratio in PFG B	0.02	-	8,9,11,15
$ChlaC_{PFGC}$	Chlorophyll to carbon ratio in PFG C	0.02	-	8,9,11,15
$Denitrifmax$	Maximum denitrification rate	5	mg N m^{-2} day^{-1}	
$Denitrifmax_{sed}$	Maximum sediment denitrification rate	25	mg N m^{-2} day^{-1}	

Symbol	*Description*	*Values*	*Units*	*Sources*
$filter_{PFGA}$	PFG A filtering rate from dreissenids	0.02	day^{-1}	
$filter_{PFGB}$	PFG B filtering rate from dreissenids	0.015	day^{-1}	
$filter_{PFGC}$	PFG C filtering rate from dreissenids	0.01	day^{-1}	
$gwthmax_{PFGA}$	Maximum growth for PFG A	2.3	day^{-1}	13,14
$gwthmax_{PFGB}$	Maximum growth for PFG B	2	day^{-1}	13,14
$gwthmax_{PFGC}$	Maximum growth for PFG C	1.7	day^{-1}	13,14
$H_{epilimnion}$	Distance from water surface to top of the epilimnion segment layer	0	m	
$H_{metalimnion}$	Distance from water surface to top of the metalimnion segment	8	m	
$H_{hypolimnion}$	Distance from water surface to top of the hypolimnion segment	16	m	
Ik_{PFGA}	Half saturation light intensity for PFG A	150	$MJ\ m^{-2}\ day^{-1}$	
Ik_{PFGB}	Half saturation light intensity for PFG B	150	$MJ\ m^{-2}\ day^{-1}$	
Ik_{PFGC}	Half saturation light intensity for PFG C	150	$MJ\ m^{-2}\ day^{-1}$	
KCrefmineral	Particulate carbon mineralization rate at reference temperature	0.01	day^{-1}	
Kextb	Background light attenuation	0.15	m^{-1}	15
$Kextchla_{PFGA}$	Light attenuation coefficient for PFG A	0.04	$m^2\ mg^{-1}$	13,15
$Kextchla_{PFGB}$	Light attenuation coefficient for PFG B	0.04	$m^2\ mg^{-1}$	13,15
$Kextchla_{PFGC}$	Light attenuation coefficient for PFG C	0.05	$m^2\ mg^{-1}$	13,15
KHdodenit	Half saturation concentration of DO deficit required for nitrification	0.5	$mg\ O_2\ m^{-3}$	10
$KHdodenit_{sed}$	Half saturation concentration of DO deficit required for denitrification in the sediments	1	$mg\ O_2\ m^{-3}$	
KHdonit	Half saturation concentration of DO required for nitrification	1	$mg\ O_2\ m^{-3}$	10
$KHdonit_{sed}$	Half saturation concentration of DO required for nitrification in the sediments	2	$mg\ O_2\ m^{-3}$	
KHnh4nit	Half saturation concentration of	1	$mg\ N\ m^{-3}$	10

Symbol	***Description***	***Values***	***Units***	***Sources***
	ammonium required for nitrification			
KHnh4nit$_{sed}$	Half saturation concentration of ammonium required for nitrification in the sediments	75	mg N m^{-3}	
KHno3denit	Half saturation concentration of nitrate required for denitrification	15	mg N m^{-3}	10
KHno3denit$_{sed}$	Half saturation concentration of DO deficit required for denitrification in the sediments	15	mg O_2 m^{-3}	
KNrefmineral	Nitrogen mineralization rate at reference temperature	0.01	day^{-1}	10,15
KPrefmineral	Phosphorus mineralization rate at reference temperature	0.005	day^{-1}	3,15,10
kt	Effects of temperature on phytoplankton mortality	0.069	$^{o}C^{-1}$	3, 7,10,11
ktfilt	Effects of temperature on phytoplankton filtration	0.069	$^{o}C^{-1}$	
KTFmin	Effects of temperature on mineralization	0.004	$^{o}C^{-2}$	
KTgrdenitr	Effect of temperature on denitrification	0.004	$^{o}C^{-2}$	
KTgrdenitr$_{sed}$	Effect of temperature on sediment denitrification	0.004	$^{o}C^{-2}$	
KTgr$_{herbi}$	Effect of temperature on herbivorous zooplankton	0.005	$^{o}C^{-2}$	1-2-3-4-5
KTgrnitr	Effect of temperature on nitrification	0.004	$^{o}C^{-2}$	10,16
KTgrnitr$_{sed}$	Effect of temperature on sediment nitrification	0.004	$^{o}C^{-2}$	
KTgr$_{omni}$	Effect of temperature on omnivorous zooplankton	0.005	$^{o}C^{-2}$	
KTgr$_{omni}$	Effect of temperature on omnivorous zooplankton	0.005	$^{o}C^{-2}$	2,3
KTgr$_{PFGA}$	Effect of temperature on PFG A	0.005	$^{o}C^{-2}$	3,10,13,14

Symbol	***Description***	***Values***	***Units***	***Sources***
$KTgr_{PFGB}$	Effect of temperature on PFG B	0.005	$^{o}C^{-2}$	3,10,13,14
$KTgr_{PFGC}$	Effect of temperature on PFG C	0.005	$^{o}C^{-2}$	3,10,13,14
kt_{sed}	Effects of temperature on sedimentation	0.004	-	
KZ_{herb}	Half saturation constant for grazing by herbivorous zooplankton	105	mg C m^{-3}	6-7
KZ_{omni}	Half saturation constant for grazing by omnivorous zooplankton	105	mg C m^{-3}	6,7
$maxgrazing_{herb}$	Maximum grazing rate for herbivorous zooplankton	0.5	day^{-1}	6-7
$maxgrazing_{omni}$	Maximum grazing rate for omnivorous zooplankton	0.5	day^{-1}	6,9
mp_{PFGA}	Mortality rate for PFG A	0.045	day^{-1}	3,7,10,11,15
mp_{PFGB}	Mortality rate for PFG B	0.025	day^{-1}	3,7,10,11,15
mp_{PFGC}	Mortality rate for PFG C	0.015	day^{-1}	3,7,10,11
mz_{herb}	Mortality rate for herbivorous zooplankton	0.15	day^{-1}	1,3, 6,7, 8,9
mz_{omni}	Mortality rate for omnivorous zooplankton	0.17	day^{-1}	1-3, 6,7,9
N/C_{herbi}	Nitrogen to carbon ratio for omnivorous zooplankton	0.2	mgN mg C^{-1}	17,18
N/C_{omni}	Nitrogen to carbon ratio for herbivorous zooplankton	0.2	mgN mg C^{-1}	17,18
NH_{PFGA}	Half saturation constant for nitrate uptake by PFG A	100	mg N m^{-3}	13-15
NH_{PFGB}	Half saturation constant for nitrate uptake by PFG B	80	mg N m^{-3}	13-15
NH_{PFGC}	Half saturation constant for nitrate uptake by PFG C	60	mg N m^{-3}	13-15
$Nitrifmax$	Maximum nitrification rate at optimal temperature	20	mg N m^{-3} day^{-1}	10,15,16
$Nitrifmax_{sed}$	Maximum sediment nitrification rate	50	mg N m^{-2} day^{-1}	

Symbol	***Description***	***Values***	***Units***	***Sources***
P/C_{herbi}	Phosphorus to carbon ratio for herbivorous zooplankton	0.025	mg P mg C^{-1}	17,18
P/C_{omni}	Phosphorus to carbon ratio for omnivorous zooplankton	0.025	mg P mg C^{-1}	17,18
PH_{PFGA}	Half saturation constant for phosphorus uptake by PFG A	10	mg P m^{-3}	9,13,14
PH_{PFGB}	Half saturation constant for phosphorus uptake by PFG B	12	mg P m^{-3}	9,13,14
PH_{PFGC}	Half saturation constant for phosphorus uptake by PFG C	20	mg P m^{-3}	9,13,14
$Pmax_{PFGA}$	Maximum PFG A internal phosphate	0.025	mg P mg C^{-1}	7,13,15
$Pmax_{PFGB}$	Maximum PFG B internal phosphate	0.025	mg P mg C^{-1}	7,13,15
$Pmax_{PFGC}$	Maximum PFG C internal phosphate	0.025	mg P mg C^{-1}	7,13,15
$Pmaxuptake_{PFGA}$	Maximum phosphorus uptake rate for PFG A	0.02	mg P mg C^{-1} day^{-1}	7,13,15
$Pmaxuptake_{PFGB}$	Maximum phosphorus uptake rate for PFG B	0.015	mg P mg C^{-1} day^{-1}	7,13,15
$Pmaxuptake_{PFGC}$	Maximum phosphorus uptake rate for PFG C	0.01	mg P mg C^{-1} day^{-1}	7,13,15
$Pmin_{PFGA}$	Minimum PFG A internal phosphorus	0.008	mg P mg C^{-1}	7,13,15
$Pmin_{PFGB}$	Minimum PFG B internal phosphorus	0.008	mg P mg C^{-1}	7,13,15
$Pmin_{PFGC}$	Minimum PFG C internal phosphorus	0.008	mg P mg C^{-1}	7,13,15
$Pref_{herb\ det}$	Preference of herbivorous zooplankton for detritus	1	-	
$Pref_{herb\ PFGA}$	Preference of herbivorous zooplankton for PFG A	1.5	-	
$Pref_{herb\ PFGB}$	Preference of herbivorous zooplankton for PFG B	1	-	
$Pref_{herb\ PFGC}$	Preference of herbivorous zooplankton for PFG C	0.5	-	
$Pref_{omnidet}$	Preference of omnivorous zooplankton for detritus	1	-	

Symbol	***Description***	***Values***	***Units***	***Sources***
$Pref_{omniherb}$	Preference of omnivorous zooplankton for herbivorous zooplankton	1.5	-	
$Pref_{omniPFGA}$	Preference of omnivorous zooplankton for PFG A	1	-	
$Pref_{omniPFGB}$	Preference of omnivorous zooplankton for PFG B	1	-	
$Pref_{omniPFGC}$	Preference of omnivorous zooplankton for PFG C	0.5	-	
$Tempref$	Water reference temperature	20	^oC	3,7,10,11
$Tempref_{sed}$	Sediment reference temperature	20	^oC	
$Toptdenitr$	Optimal temperature for denitrification	20	^oC	
$Toptdenitr_{sed}$	Optimal temperature for denitrification in sediment	20	^oC	
$Topt_{herbi}$	Reference temperature for herbivorous zooplankton	20	^oC	1-5
$Toptmin$	Optimal temperature for mineralization	20	^oC	
$Toptnitr$	Optimal temperature for nitrification	20	^oC	10,16
$Toptnitr_{sed}$	Optimal temperature for denitrification in sediment	20	^oC	
$Topt_{omni}$	Reference temperature for omnivorous zooplankton	20	^oC	1-5
$Topt_{PFGA}$	Reference temperature for PFG A metabolism	20	^oC	3,7,10,11
$Topt_{PFGB}$	Reference temperature for PFG B metabolism	22	^oC	3,7,10,11
$Topt_{PFGC}$	Reference temperature for PFG C metabolism	24	^oC	3,7,10,11
$Vsettling_{(biogenic)}$	Biogenic particle settling velocity	0.15	m day^{-1}	
$Vsettling$	Allochthonous particle settling velocity	0.65	m day^{-1}	8,10,13,14
$Vsettling_{PFGA}$	PFG A settling velocity	0.15	m day^{-1}	2,10-12
$Vsettling_{PFGB}$	PFG B settling velocity	0.1	m day^{-1}	2,10-12

Symbol	*Description*	*Values*	*Units*	*Sources*
$Vsettling_{PFGC}$	PFG C settling velocity	0.02	m day^{-1}	2,10-12
β_N	Fraction of inert nitrogen buried into deeper sediment	0.4	-	
β_P	Fraction of inert phosphorus buried into deeper sediment	0.9	-	
ψ	Strength of the ammonium inhibition for nitrate uptake	0.05	(µg N/L)$^{-1}$	
$z_{epilimnion}$	Depth of epilimnion department	8	m	
$z_{mesolimnion}$	Depth of mesolimnion department	8	m	
$z_{hypolimnion}$	Depth hypolimnion department	8	m	

1) Lampert and Sommer, 1997; 2) Wetzel, 2001; 3) Omlin *et al*., 2001; 4) Orcutt and Porter, 1983; 5) Downing and Rigler, 1984; 6) Sommer, 1989; 7) Jorgensen *et al*., 1991; 8) Wetzel, 2001; 9) Chen *et al*., 2002(and references therein); 10) Cerco and Cole, 1994(and references therein); 11) Reynolds, 1984; 12) Sandgren, 1991; 13) Arhonditsis and Brett, 2005; 14) Reynolds, 2006; 15) Hamilton and Schladow, 1997 (and references therein); 16) Berounsky and Nixon, 1990; 17) Hessen and Lyche, 1991; 18) Sterner *et al*., 1992.

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