EFFECTS OF ZEBRA MUSSELS
ON CHLOROPHYLL, NITROGEN,
PHOSPHORUS AND SILICA
IN NORTH SHORE WATERS OF LAKE ERIE

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Ontario

Ministry of
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SUMMARY

Chlorophyll a and nutrient concentrations have been measured weekly and year-round at five municipal water supply intakes in Lake Erie since 1976. The establishment of zebra mussels (*Dreissena polymorpha*) in Lake Erie in the late 1980's-early 1990's resulted in dramatic reductions in chlorophyll levels at all five locations in all seasons of the year. The greatest change was in the western basin (Union intake), where summer concentrations averaging 6.3 μg/L during a 4-year pre-zebra mussel period declined to 1 μg/L during a 4-year post mussel time period. Declines in total phosphorus (TP) were less dramatic; the chlorophyll-to-TP ratio was three times higher before the establishment of zebra mussels than after. TP values during summer in the western and west-central basins of the lake were less than the -95% confidence band for Box-Jenkins ARIMA (autoregressive integrated moving average) forecast values based on the pre-zebra mussel data, and provide supporting evidence for the net removal of phosphorus from the water column by zebra mussels. The reduction in phosphorus was greater than the reduction in nitrogen and resulted in a doubling of summer total N-to-total P ratios after the arrival of zebra mussels. The reduction in summer TP of 20 μg/L at the north shore, central basin sampling location (Elgin intake) was used to conservatively estimate a near shore (0-12m depth contour) summertime removal of about 6000 metric tons for the whole lake. Observed increases in fall dissolved reactive silica and dissolved reactive phosphorus were attributed to reduced phytoplankton biomass by zebra mussel filtration of the water, and consequently, a lowered rate of uptake of dissolved phosphorus and silica from the water column. Summer ammonium-N concentrations were reduced 45-77% at the five locations apparently in response to reduced biomass and decomposition of phytoplankton contributing to a reduction in availability of organic-N for ammonification, especially in the west-central basin, where summer ammonium-N concentrations were well below the lower 95% confidence values of the ARIMA prediction. Eastern basin ammonium-N data were cyclic (with a period of about seven years) coinciding with flow rates of major southern Ontario rivers. The dramatic reduction in ammonium-N detected in the short term "before and after" comparisons at the two eastern basin sampling locations (Dunnville and Rosehill) may therefore have had less to do with the arrival of zebra mussels than with the cyclic supply of ammonium-N from the watershed.

INTRODUCTION

The arrival of zebra mussels (*Dreissena polymorpha*) in parts of the Laurentian Great Lakes in the late 1980's and early 1990's was accompanied by declines in chlorophyll a concentrations and phytoplankton biomass and increased water clarity (Leach, 1993; Nicholls and Hopkins, 1993; Holland 1993; Fahnenstiel et al. 1995). With the establishment of the zebra mussel in Lake Erie, there was also the potential for changes in dissolved and particulate forms of nitrogen and phosphorus and other nutrients as a result of the feeding and waste elimination habits of the zebra mussel. To date, little information is available on these effects in the Great Lakes (Holland et al., 1995; Johengen et al., 1995; Effler et al., 1996). An understanding of this potential impact is critical because it could influence the interpretation of the effectiveness of sewage treatment and phosphorus pollution control programmes on which several $ Billions have been spent in Canada and the United States during the past two decades (International Joint Commission, 1988).

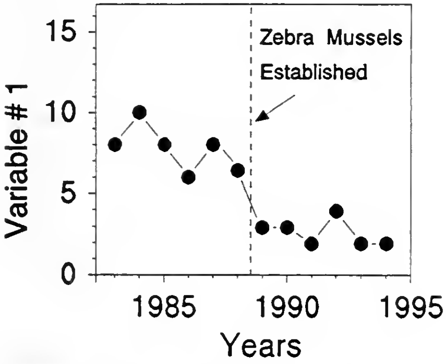

Figure 1. Hypothetical data set showing a significant decline in "variable #1" after the establishment of zebra mussels.

The measurement of zebra mussel effects on water quality depends on an ability to separate a zebra mussel effect from other factors with similar or counter-acting influences. In the absence of a long time series of pre-zebra mussel water quality data, the options for answering the question are limited to simple statistical comparisons of relatively short term "before and after" data sets (Fig. 1). In this example, an analysis of the difference between the measures of central tendency of the six-year pre- and post zebra mussel time periods would show a significant difference and therefore an inferred zebra mussel impact. However, a longer term pre-zebra mussel data series appended to this original hypothetical example (Fig. 2) could yield a very different conclusion. The "scenario a" data of Figure 2 can be fitted to an exponential function, to which the post-zebra mussel data fit very well. So, although the six-year post zebra mussel data are significantly lower than the six-year pre-zebra mussel data, a strong case could be made for no zebra mussel impact simply because the six-year post zebra mussel data are in agreement with the prediction derived from the longer term pre-zebra mussel dataset. Similarly, it can be argued that there is strong evidence of a zebra mussel impact in the "scenario b" data which includes a six-year post-zebra mussel dataset which is not significantly different from the six-year pre-zebra mussel dataset immediately preceding it (1983-1988). This is because the more realistic comparison of the 1989-1994 ("scenario b") data is not with the 1983-1988 pre-zebra mussel data, but rather with the predicted values for the post zebra mussel period when that prediction is based on the entire pre-zebra mussel record.

Clearly, real-life scenarios are not likely to be so simplistic. The challenge in identifying environmental effects of the zebra mussel invasion reduces to one of employing appropriate statistical analyses to detect trends or break points in the presence of data "noise". Because the power of any test of environmental change is determined to a large extent by the frequency and number of samples (Osenberg et al., 1994), the water intake monitoring programme with its weekly collection of samples since 1976, is an excellent database for evaluation of trends in near shore Great Lakes waters and of the effects of the zebra mussel invasion in particular. A major purpose of this report was therefore to generate statistical characterizations of the pre-zebra mussel nutrient concentrations that would serve as the basis for forecasts of post zebra mussel nutrient concentrations. The predicted concentrations were then compared with the measured post zebra mussel nutrient concentrations as the basis for inferring a zebra mussel impact. This approach was used successfully by Nicholls and Hopkins (1993) to infer a zebra mussel impact on Lake Erie phytoplankton after predicting post zebra mussel phytoplankton biomass from a pre-zebra mussel phosphorus loading-phytoplankton relationship.

This report utilizes data we have collected at five municipal water supply intakes in Lake Erie over the period 1976 through 1994. Samples have been collected weekly and analyzed at the Ministry of Environment and Energy Laboratories in London and Toronto. We will emphasize the apparent zebra mussel effects on silica, nitrogen and phosphorus in this report. Chlorophyll a data are also presented to provide a context for discussion of changes in nutrient concentrations because it is our contention that one mechanism of zebra mussel impact on nutrients involves the consumption of phytoplankton and the consequent reduction of nutrient uptake resulting from decreased phytoplankton biomass.

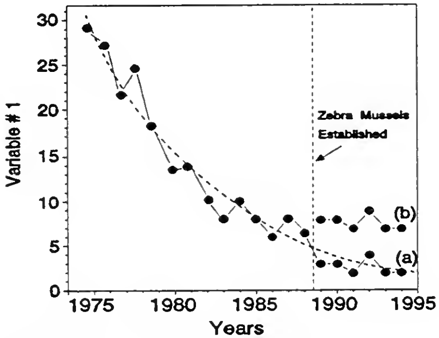

Figure 2. Longer term hypothetical data set (scenario a) fitted to an exponential function.

EFFECTS OF ZEBRA MUSSELS ON CHLOROPHYLL, NITROGEN, PHOSPHORUS AND SILICA IN NORTH SHORE WATERS OF LAKE ERIE

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METHODS

Samples of raw untreated Lake Erie water were collected weekly beginning in 1976 from five municipal water supply intakes (but 1978 at the Rosehill location) on the north shore of Lake Erie (Fig. 3). Chemical analyses were automated and spectrophotometric (based on "Standard Methods"; Ontario Ministry of the Environment, 1981). The method for chlorophyll was described previously by Nicholls and Hopkins (1993). For the summer periods beginning in 1992, while water temperatures >12°C, chlorine injection (continuous feed) has been used to control zebra mussel infestation on the inside walls of the intake pipes and in the infrastructure of each of the five water treatment plants. At all locations except Dunnville, water samples were collected after interruption of the chlorine feed and flushing of the intake pipe to insure a chlorine-free sample. At both the Dunnville and the Rosehill water treatment plants, many samples have apparently been chlorinated, but is not evident that this has had a measurable effect on nutrient concentrations, so results from analyses of all samples have been included here, irrespective of their chlorination status.

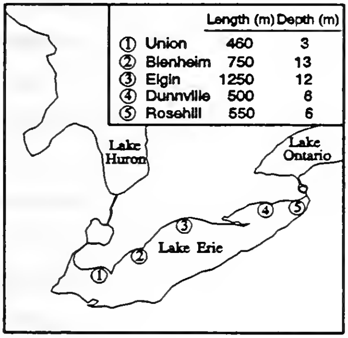

Figure 3. Locations, lengths and depths of the five Lake Erie municipal water supply intakes from which samples have been obtained weekly since 1976.

Far-right outliers were removed from the original weekly data if they exceeded the [median + 5 * St. Dev.]. This highly conservative approach to outlier detection resulted in the replacement (by near neighbour interpolation) of <1% of the dataset. Monthly means were calculated in a spreadsheet and missing means similarly accounted for <1% of the calculated data except for chlorophyll a data from Dunnville, where seven months of data were not obtained in 1977 (3% of the data set). Missing monthly means were interpolated from near neighbours of the same months [adjacent years, within the same treatment (pre- or post zebra mussels)]. For ARIMA forecasting (see below), monthly data were organized into four seasons as follows: winter = December of the previous year + January and February; spring = March, April and May; summer = June, July and August; fall = September, October and November.

We have analyzed the data in two different ways. The first way allowed a comparison with the recently published findings of Holland et al. (1995) who determined changes in a number of nutrient variables after the arrival of zebra mussels in Hatchery Bay (Gibraltar Island area) of western Lake Erie. We selected the same pre- and post zebra mussel years (1984-87 and 1990-93, respectively) as Holland et al. (1995) and determined significant differences by Mann-Whitney *U*-tests between the two time periods after reducing the data to monthly means and grouping by seasons. The various measures of central tendency, descriptive statistics and tests of significant difference were computed with commonly available spreadsheet and statistical analysis software. The key nutrient variables (total phosphorus, dissolved reactive phosphorus, reactive silicate, nitrate, nitrite, ammonium and organic nitrogen) for all four seasons of the pre- and post zebra mussel periods were also ordinated by detrended correspondence analysis using a reciprocal averaging algorithm applied to 26 segments in the primary ordination field through four rescaling cycles with software supplied by Kovach Computing Services, Wales, UK.

The second approach to data analysis was the application of Box-Jenkins ARIMA (autoregressive, integrated moving average) techniques (Box and Jenkins, 1970; Jenkins, 1979) whereby the pre-zebra mussel data set (1976-1987) was used to forecast the expected nutrient concentrations during the post zebra mussel time period. The ARIMA models were generated by PC software supplied by Human Edge Software Corp., San Kateo, CA. and were used to predict nutrient concentrations for the post zebra mussel period. The modelling procedures identified any existing seasonal and trend components of the data series and determined the best values for the model parameters using the "method-of-moments" technique to make the initial estimates and then iteratively refined those estimates with a numerical analysis based on a modified Marquadt algorithm. It also determined (on the basis of a preliminary analysis of the data) whether or not an appropriate Box-Cox transformation enhanced the model's accuracy. Only those variables showing >95% of measured post zebra mussel values outside the 95% confidence bands of the prediction were deemed to demonstrate a significant departure from concentrations expected in the absence of zebra mussels. Because the apparent zebra mussel effects on eastern basin Lake Erie phytoplankton lagged about a year behind those in the western basin (Nicholls and Hopkins, 1993), and because the data collection at our Rosehill location did not begin until late 1978, the dataset used to build the forecasts for the Rosehill location was from 1978-88 (in contrast to 1976-1987 at the other sites).

RESULTS

"Before and After"

At all five sites and during all four seasons, chlorophyll a concentrations were lower in the four-year period following the establishment of zebra mussels than during the four-year pre-zebra mussel period. The greatest change was in the Union samples during August and September (Fig. 4) when concentrations dropped from an average of 9.9 μg/L to 1.6 μg/L.

Several nutrient variables demonstrated marked seasonality, before and/or after the establishment of zebra mussels. Some examples include 1) a late fall-early winter maximum of both total phosphorus and filtered reactive phosphorus, 2) a spring maximum and a summer minimum of nitrate, 3) an early summer minimum and either a late summer or a winter maximum of silicate, depending on the sampling location, and 4) summer peaks in ammonium-N (Figs 4-8). Nitrate-N concentrations were about an order of magnitude higher than ammonium-N concentrations and nitrite-N levels averaged only about 5% of nitrate-N concentrations. As a consequence, the seasonal distribution of total inorganic nitrogen closely approximated the nitrate concentrations before and after the arrival of zebra mussels.

The seasonal distribution of ammonium-N was dramatically changed after the arrival of zebra mussels. The pre-zebra mussel summer peaks characterizing the 1984-1987 period never developed in 1990-1993 when concentrations remained relatively uniform at about 0.01-0.02 mg N/L at all locations except at the Elgin intake site, where summer concentrations were about 0.03 mg N/L and winter, spring and fall concentrations were <0.01 mg N/L (Figs 4-8). The largest differences in silica concentrations before and after zebra mussels were in spring and fall at all locations except Union (Figs 4-8). Owing to a proportionately greater decline in total phosphorus relative to nitrogen, summer total N-to-total P ratios about doubled after the establishment of zebra mussels in the lake (Fig. 9).

Those variables and seasons showing large changes include filtered reactive phosphorus during fall at Union (+135%) and at Rosehill (+98%), reactive silicate at Blenheim during spring (+122%) and fall (+88%) and at Rosehill during winter (+94%) and fall (+86%), ammonium-N concentrations during spring (-83%) and summer (-74%) at Dunnville and at Rosehill (spring, -67%; summer, -75%) and total N-to-total P ratios during summer at Union (+129%), at Elgin (+150%) and at Rosehill (+93%). Of the 260 changes measured (all variables, all locations and all seasons, 33 were statistically significant increases and 67 were statistically significant decreases (Figs 10-14). Only fall silica concentrations and summer N-to-P ratios showed a consistent increases after the arrival of zebra mussels at all five sampling locations, while summer total phosphorus and ammonium-N, fall ammonium-N, and the summer

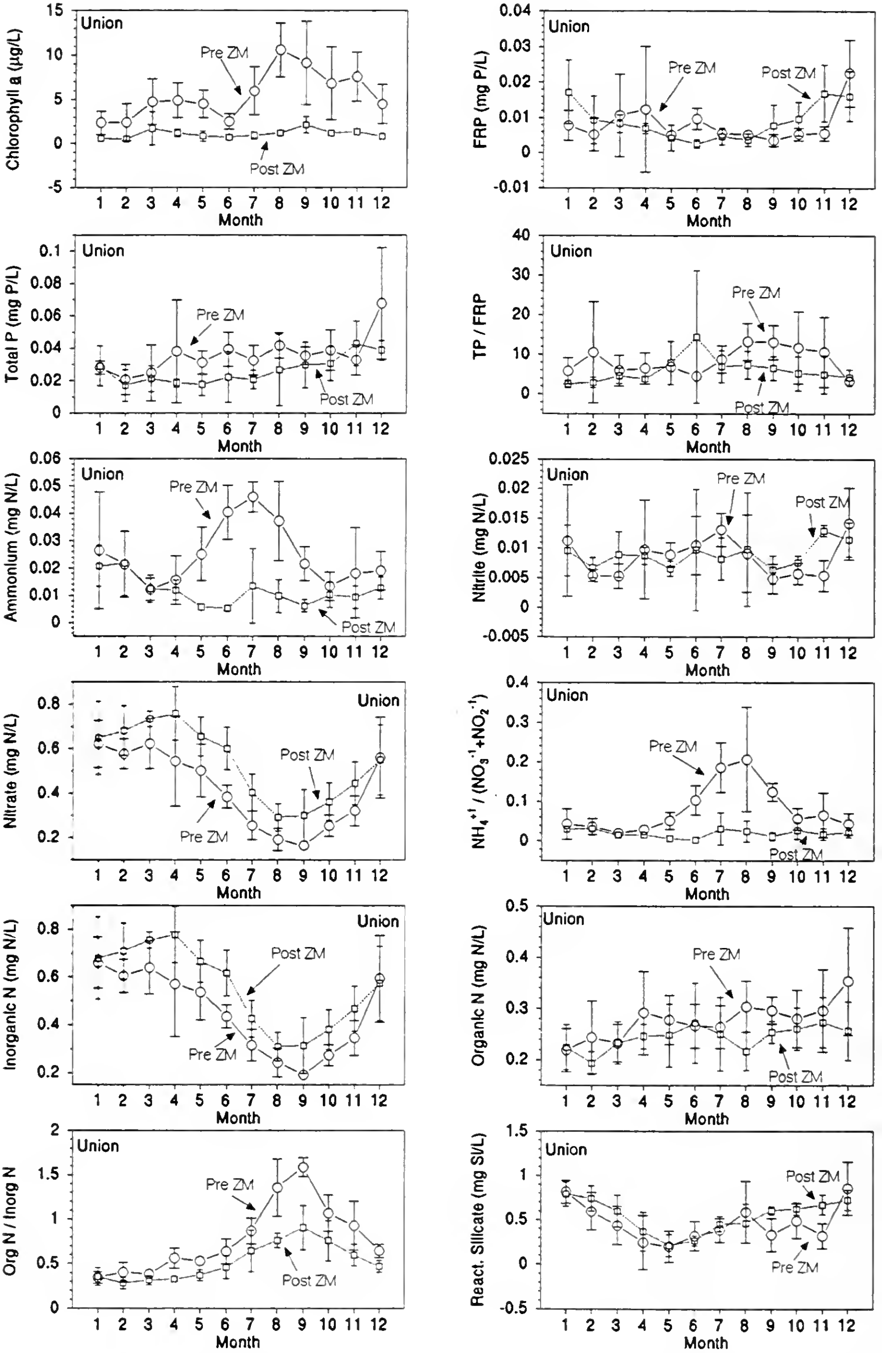

Figure. 4. Monthly means ± 1 St. Dev. of chlorophyll and nutrient concentrations during pre- (1984-87) and post (1990-94) zebra mussel time periods in samples from the Union water intake.

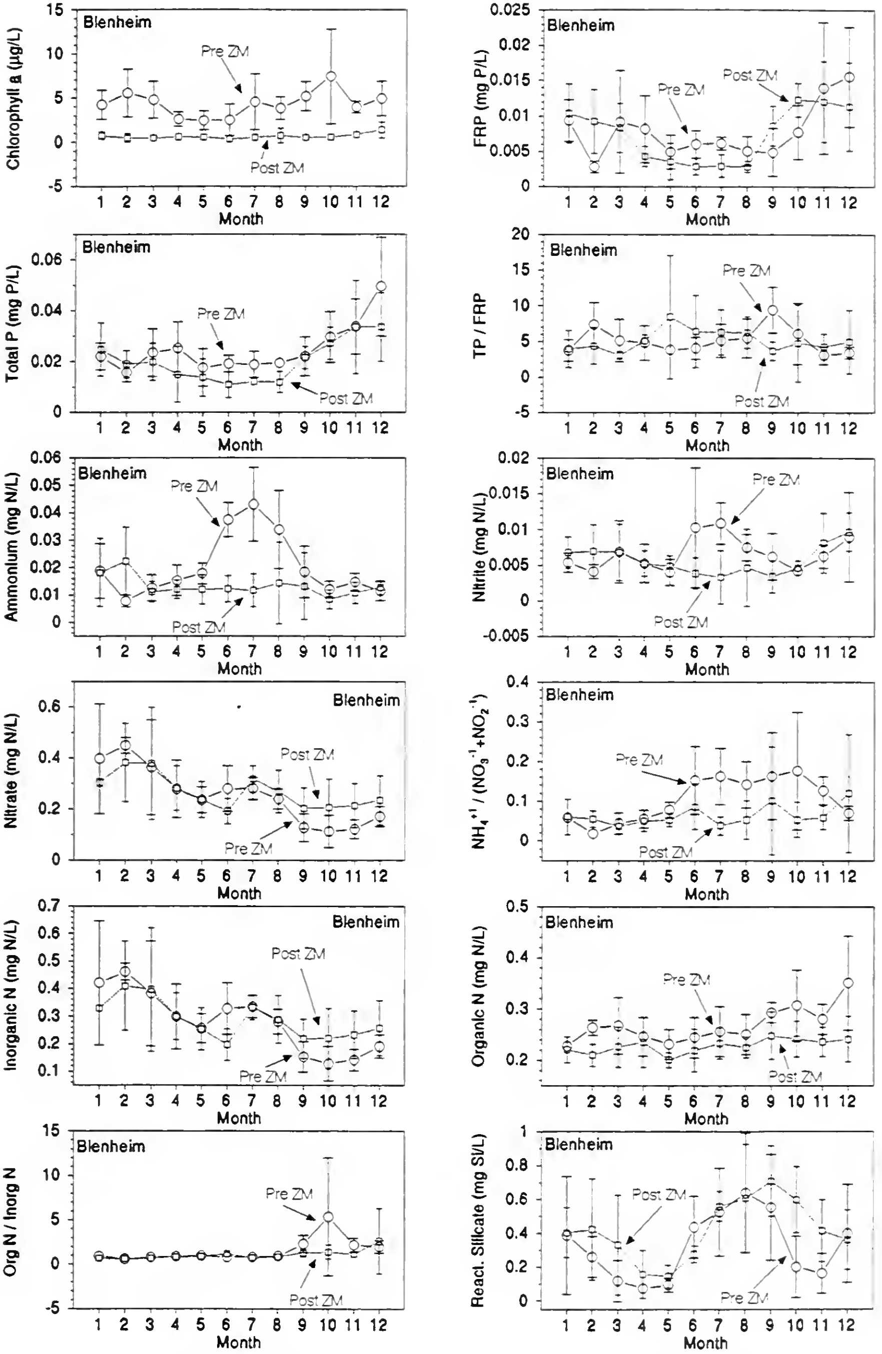

Figure. 5. Monthly means ± 1 St. Dev. of chlorophyll and nutrient concentrations during pre- (1984-87) and post (1990-94) zebra mussel time periods in samples from the Blenheim water intake.

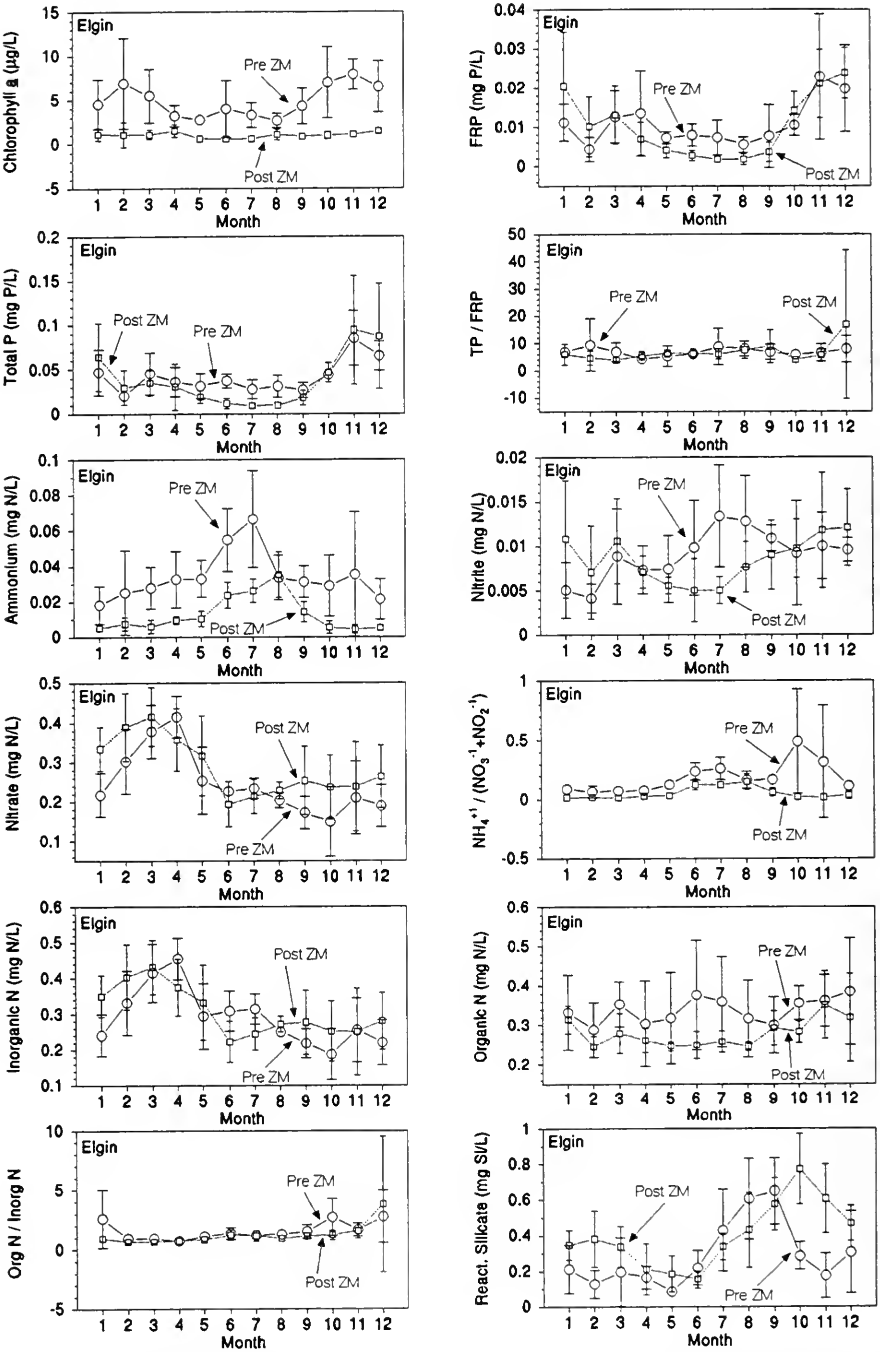

Figure. 6. Monthly means ± 1 St. Dev. of chlorophyll and nutrient concentrations during pre- (1984-87) and post (1990-94) zebra mussel time periods in samples from the Elgin water intake.

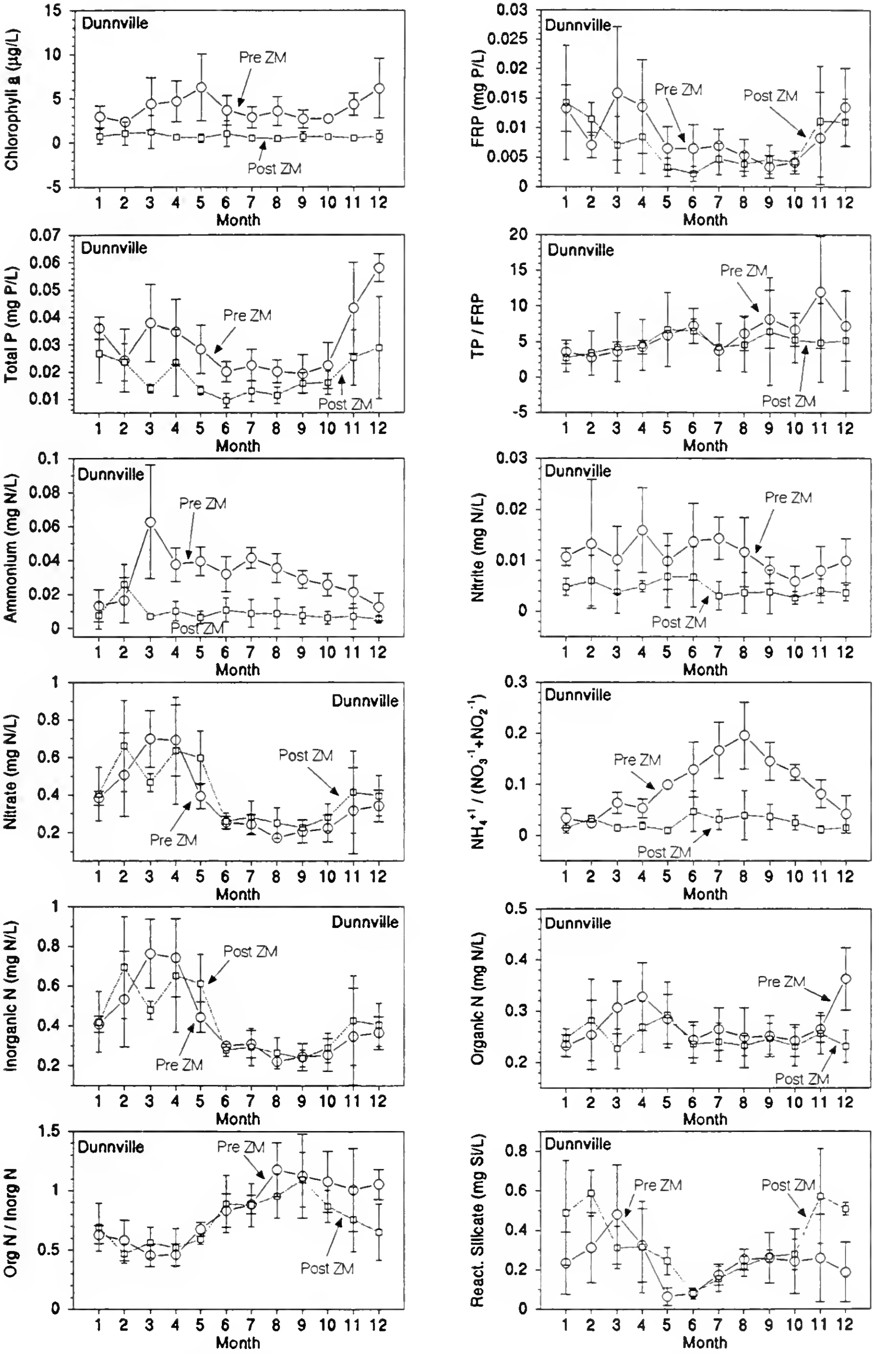

Figure. 7. Monthly means ± 1 St. Dev. of chlorophyll and nutrient concentrations during pre- (1984-87) and post (1990-94) zebra mussel time periods in samples from the Dunnville water intake.

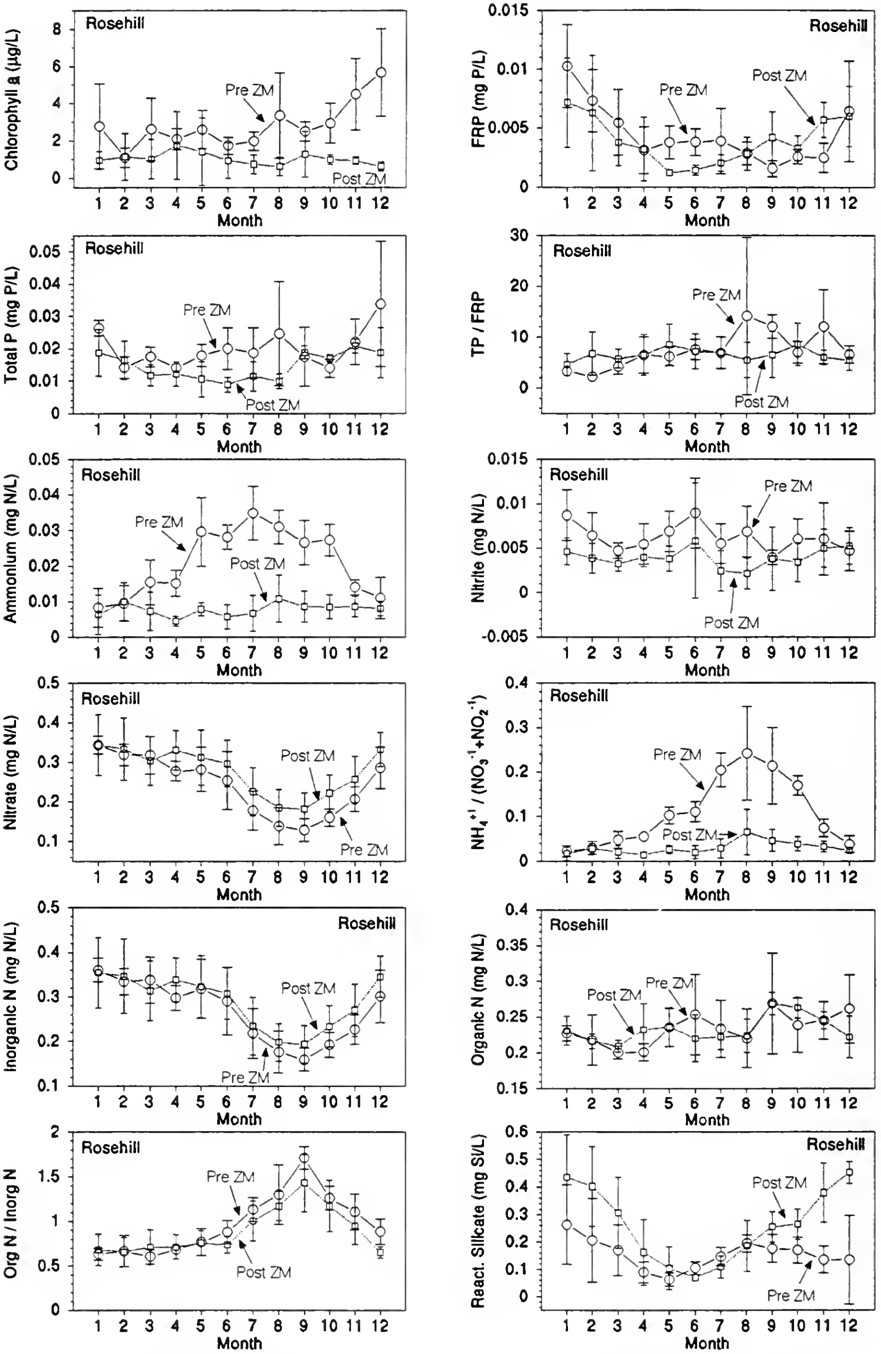

Figure. 8. Monthly means ± 1 St. Dev. of chlorophyll and nutrient concentrations during pre- (1984-87) and post (1990-94) zebra mussel time periods in samples from the Rosehill water intake.

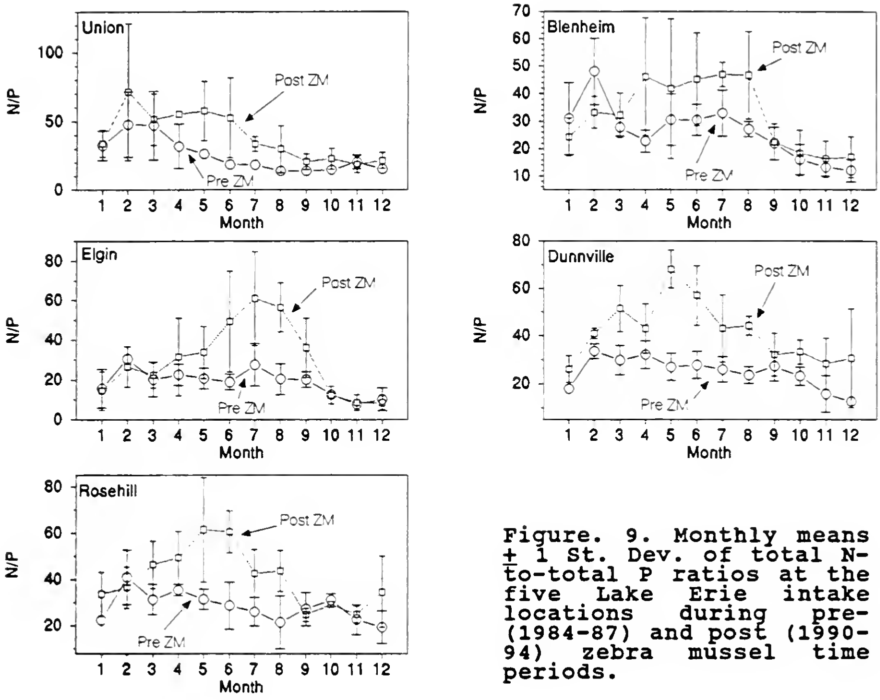

Figure. 9. Monthly means ± 1 St. Dev. of total N-to-total P ratios at the five Lake Erie intake locations during pre- (1984-87) and post (1990-94) zebra mussel time periods.

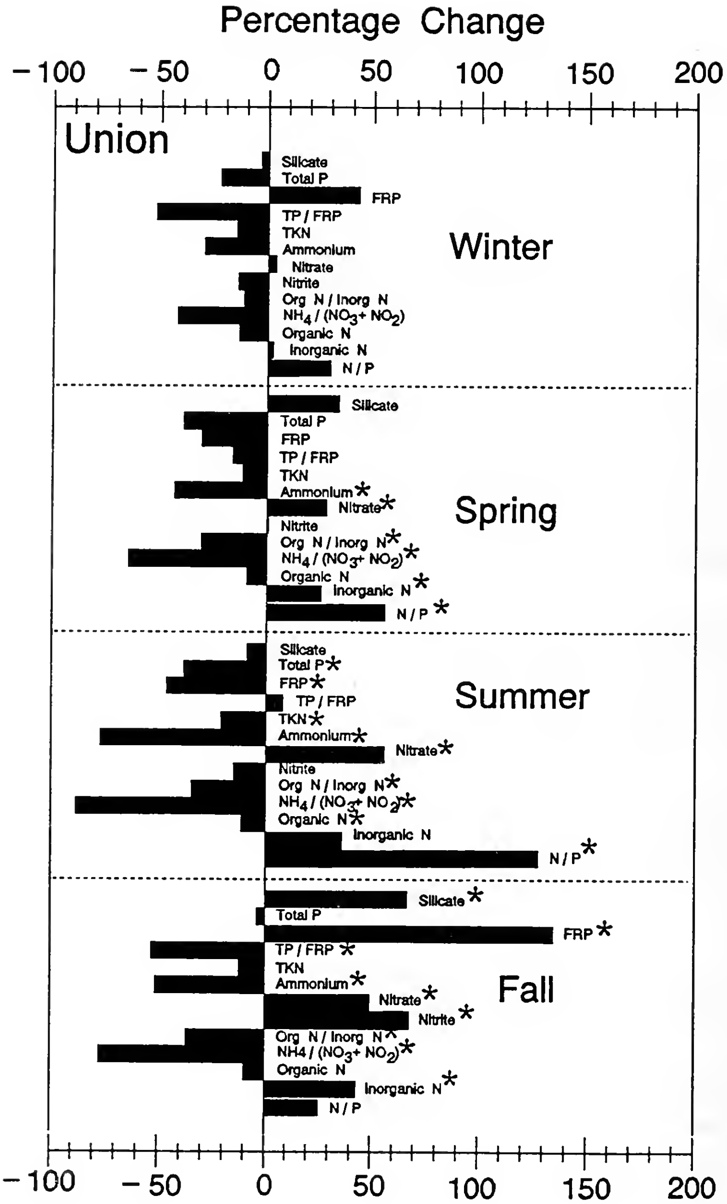

Figure 10. Percentage change in selected nutrient variables and ratios pre- (1984-87) and post (1990-93) zebra mussels at the Union intake sampling location. Those marked with an asterisk are statistically significant (Mann-Whitney U-test; P<0.05).

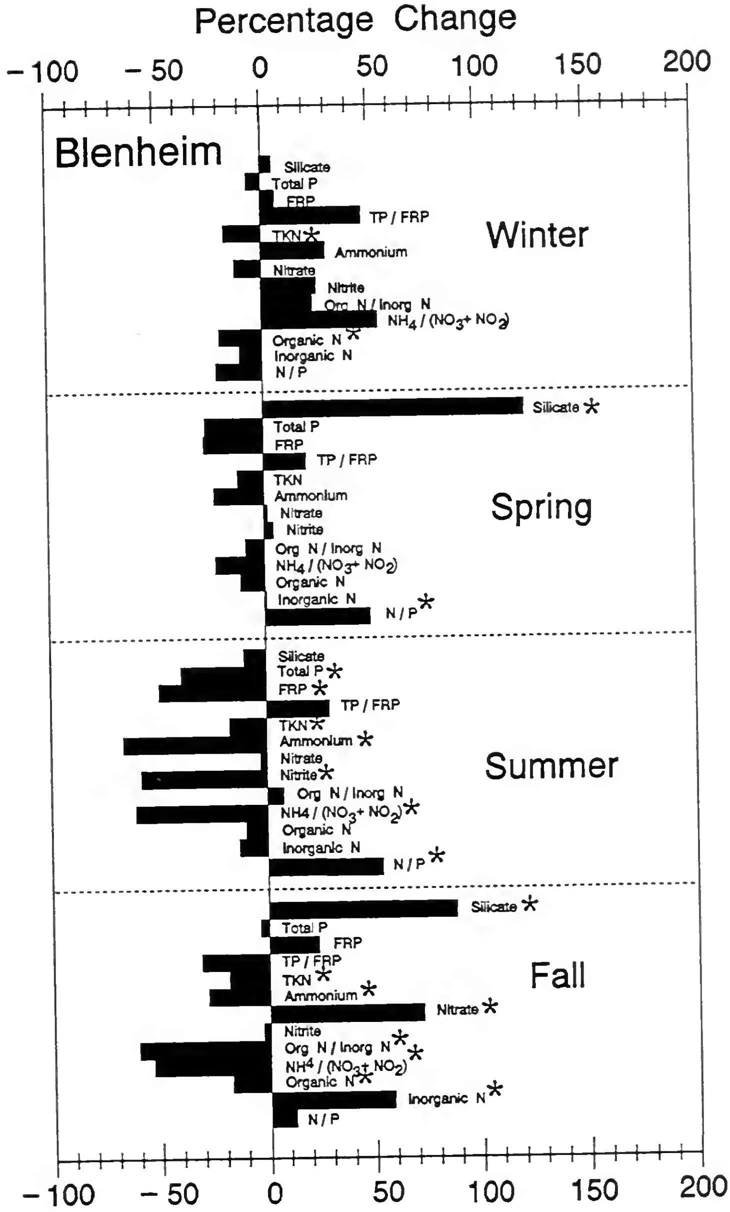

Figure 11. Percentage change in selected nutrient variables and ratios pre- (1984-87) and post (1990-93) zebra mussels at the Blenheim intake sampling location. Those marked with an asterisk are statistically significant (Mann-Whitney U-test; P<0.05).

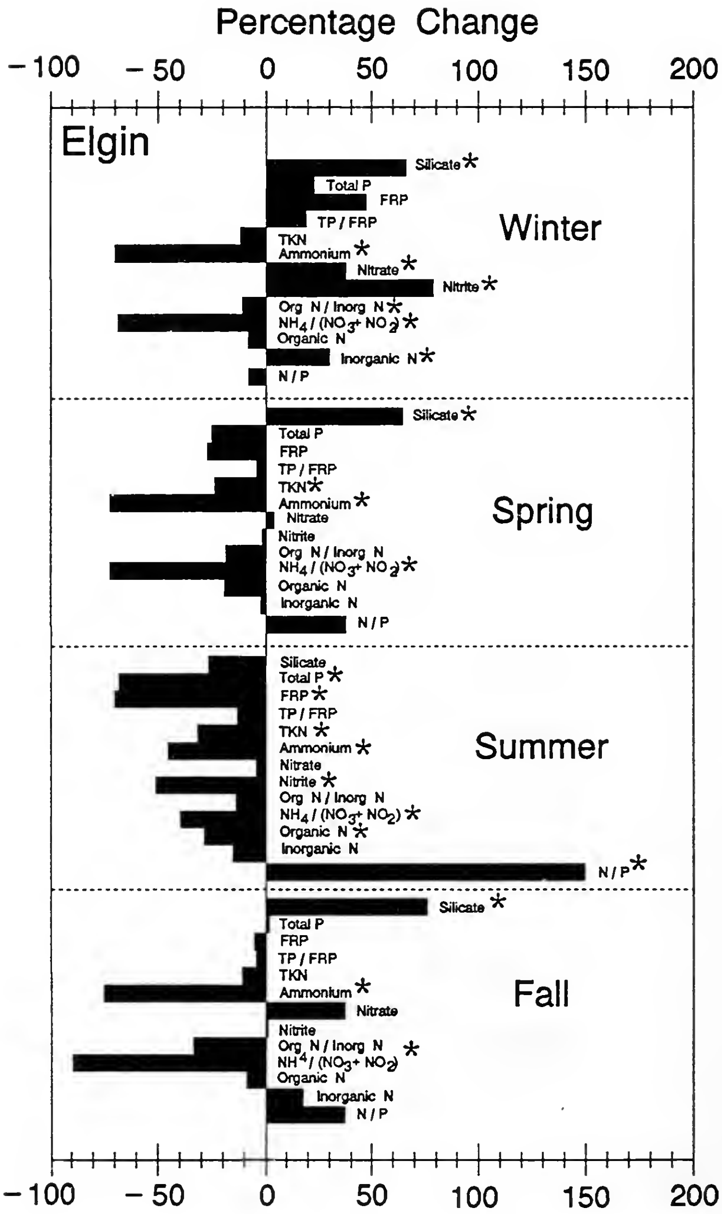

Figure 12. Percentage change in selected nutrient variables and ratios pre- (1984-87) and post (1990-93) zebra mussels at the Elgin intake sampling location. Those marked with an asterisk are statistically significant (Mann-Whitney U-test; P<0.05).

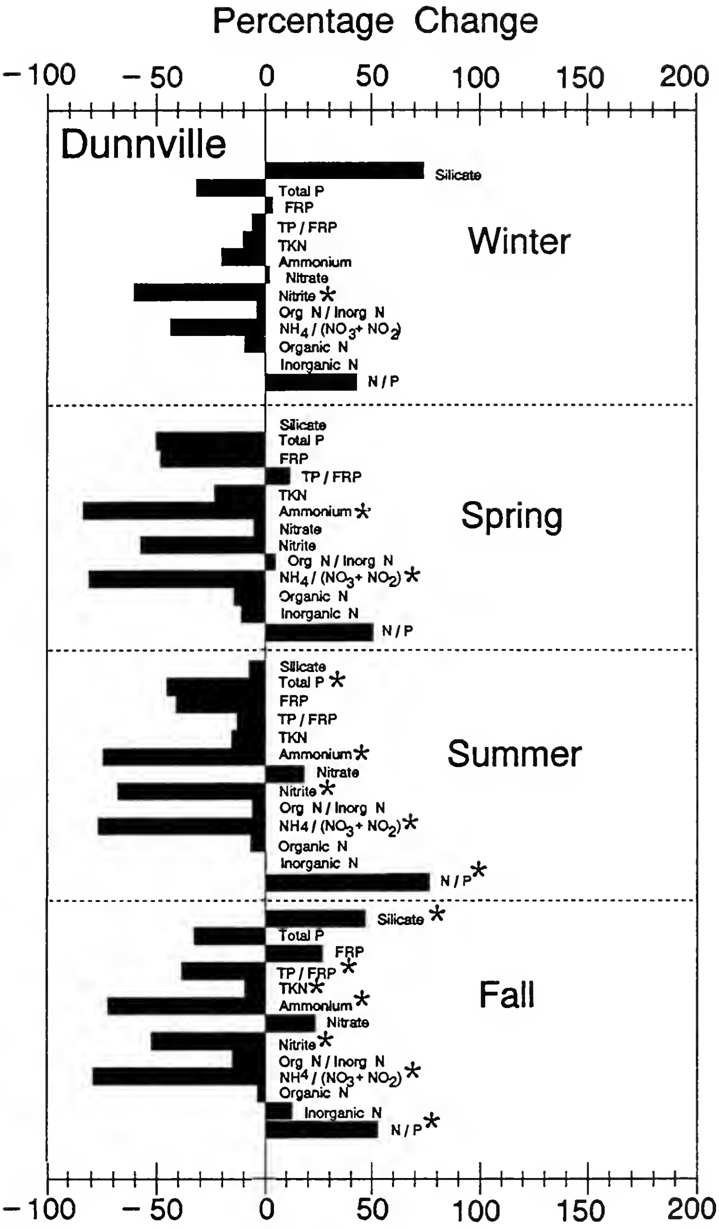

Figure 13. Percentage change in selected nutrient variables and ratios pre- (1984-87) and post (1990-93) zebra mussels at the Dunnville intake sampling location. Those marked with an asterisk are statistically significant (Mann-Whitney U-test; $P<0.05$).

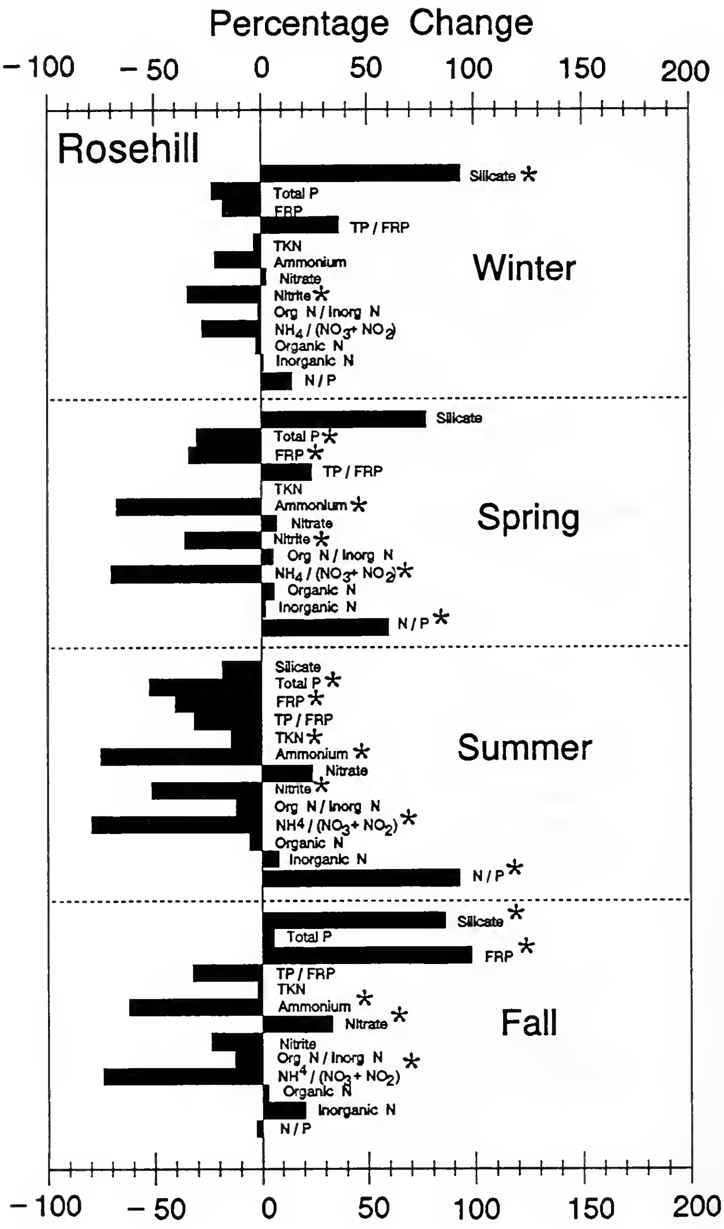

Figure 14. Percentage change in selected nutrient variables and ratios pre- (1984-87) and post (1990-93) zebra mussels at the Rosehill intake sampling location. Those marked with an asterisk are statistically significant (Mann-Whitney U-test; $P<0.05$).

Table 1 . Summary of statistically significant changes in nutrients (comparing four-year pre-zebra mussel with four-year post zebra mussel treatments). Double asterisks indicate significance (95% confidence level, Mann-Whitney U-tests) at all five sampling locations; a single asterisk indicates significance at four of the five sampling locations.

	INCREASE	DECREASE
fall SiO_2	**	
summer N-to-P ratio	**	
summer TP		**
summer FRP		*
spring NH_4^{+1}		*
summer NH_4^{+1}		**
fall NH_4^{+1}		**
spring $NH_4^{+1}/(NO_3^{-1}+NO_2^{-1})$		*
summer $NH_4^{+1}/(NO_3^{-1}+NO_2^{-1})$		**
fall $NH_4^{+1}/(NO_3^{-1}+NO_2^{-1})$		**

TP = total phosphorus; FRP = filtered, reactive phosphorus ("phosphate"-P)

Other notable changes (but not necessarily statistically significant in all cases) include higher spring and fall FRP (4 of 5 locations, decreased silica during summer (all 5 locations), a consistent reduction in organic N (all sites, all seasons, except spring and fall at Rosehill), and a spring increase in total N-to-total P ratios.

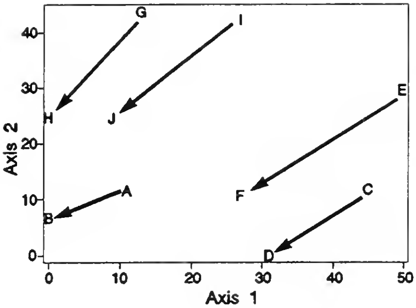

Figure 15. Ordination (detrended correspondence analysis) of the five Lake Erie sampling locations based on seasonal concentrations of seven nutrient variables. The arrows indicate the pre- and post zebra mussel positions in the ordination field (first two axes) for Union (A→B), Blenheim (C→D), Elgin (E→F), Dunnville (G→H), and Rosehill (I→J).

and fall ratios of ammonium-N-to-(nitrate + nitrite) decreased significantly at all five sites (Table 1).

Detrended correspondence analysis (DCA) of the five sampling sites using seasonal concentrations of seven nutrient variables (silica, TP, FRP, NH_4^{+1}, $NO_3^{-1,}$, $NO_2^{-1,}$ and org-N) yielded a well defined shift in the relative positions of all five stations in the ordination field (Fig. 15). This confirms that the directional changes in the nutrient variables after the establishment of zebra mussels were consistent among all five sites. The combined effect of nutrient change was greatest at the Elgin location and least at the Union site. 15).

ARIMA Forecasts

Chlorophyll a concentrations declined at all five sampling locations in all seasons coincidentally with the establishment of zebra mussels in Lake Erie (Appendix Figs 1 and 2). The largest declines relative to the 95% confidence boundaries of the ARIMA forecasts were during the fall at all locations and during the summer at the Union and Dunnville locations (Fig. 16). The decline in chlorophyll a was greater than the decline in total phosphorus following the zebra mussel invasion. The yield of chlorophyll per unit total P was nearly three times higher during the pre-zebra mussel period (Fig. 17).

Summer total phosphorus at Blenheim and Elgin and summer ammonium-N at Blenheim were the only nutrient variables consistently showing measured values during the post zebra mussel period lying outside the -95% confidence bands of the forecasts (Fig. 17). Several fall silica measurements during the post zebra mussel period at the Blenheim, Elgin, Dunnville and Rosehill locations exceeded the +95% confidence band for forecast values, but most were distributed between the mean prediction line and the upper confidence limit (Fig. 18).

Several other insights are provided by the longer term data set used for the ARIMA

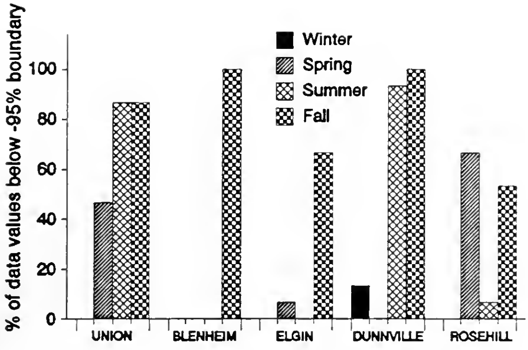

Figure 16. The percentage of measured chlorophyll a data values located below the -95% confidence boundary of the ARIMA forecasts for the five Lake Erie sites.

forecasts over that offered by a short-term "before and after" comparison. For example, the "before and after" analysis showed an 83% reduction in spring ammonium-N levels associated with the establishment of zebra mussels at Dunnville. The ARIMA forecasting analysis showed that these lower post zebra mussel ammonium concentrations were within the 95% confidence limits of the forecast concentrations (Fig. 19). Data used to generate this forecast included apparently two cyclic periods of about seven years duration having minima during the mid 1970's and early 1980's that were similar to the low values recorded during the post zebra mussel time period. Similar cyclic patterns were found in the summer ammonium-N data at Dunnville and Rosehill (Fig. 20).

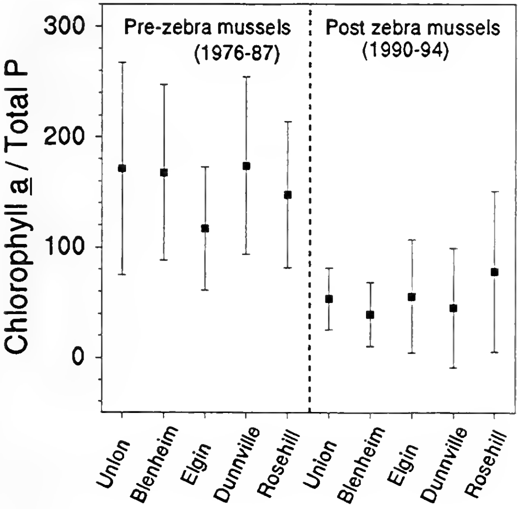

Figure 17. Means ± 1 St. Dev. of April to November chlorophyll a-to-total phosphorus ratios at the five Lake Erie intake sampling locations during pre- and post zebra mussel time periods.

The ARIMA analysis showed all of the Blenheim fall ammonium-N measured values during 1991-94 were above the forecast mean which was characterized by both seasonality and a downward trend (Fig. 20). Although the ARIMA analysis showed measured values were higher than expected (but not significantly), the "before and after" analysis identified a significant ($\underline{P}<0.05$) 28% decrease when only the short-term pre-zebra mussel data were used.

The upward trend in summer nitrate-N concentrations at the Blenheim and Elgin locations between 1976 and 1988, was abruptly broken with the establishment of zebra mussels in 1988-89. Again, the conservative output from the ARIMA modelling did not capture the continuation of this trend in its forecast as anticipated (Fig. 21). Consequently, the measured values were lower (but not significantly) than the ARIMA prediction, but they would have been much lower had the ARIMA analysis projected a positive slope for the post zebra mussel forecast, consistent with a subjective view of the pre-zebra mussel nitrate data.

Of the nine site-season "before and after" comparisons with significantly higher post zebra mussel total N-to-total P ratios, all showed post zebra mussel measured N/P values that were well above the ARIMA forecasts; Blenheim, Elgin and Dunnville summer and Rosehill spring measured N/P values were consistently outside the +95% boundary of the forecasts for the post zebra mussel years (Fig. 23).

DISCUSSION

Univariate forecasting models that include confidence intervals around their forecasts can be used as screening tools to identify behaviour in a data series which is atypical of past behaviour (Jenkins, 1979). Univariate stochastic models use only the past history of the variable in question to generate forecasts. In many cases, these models cannot be expected to generate very accurate forecasts over the long term (Jenkins, 1979; Prankratz, 1983). However, for relatively short term forecasting (i.e. 20-30% of the background modelled time period), univariate forecasting models are a logical first step for predicting nutrient concentrations independent of zebra mussel effects during the post zebra mussel years. The procedure was useful here for identifying deviations in the predicted nutrient concentration data from the measured data for the post zebra mussel years. Thus, ARIMA analysis has provided some statistical basis for interpretation of changes in nutrient concentrations in Lake Erie occurring about the time of the establishment of the zebra mussels.

One difficulty in interpreting some of these changes in an overall context is that some changes have been shown to be statistically significant at one or two sampling locations, but not at the others, thus not permitting all-inclusive statements about change. Conclusions about

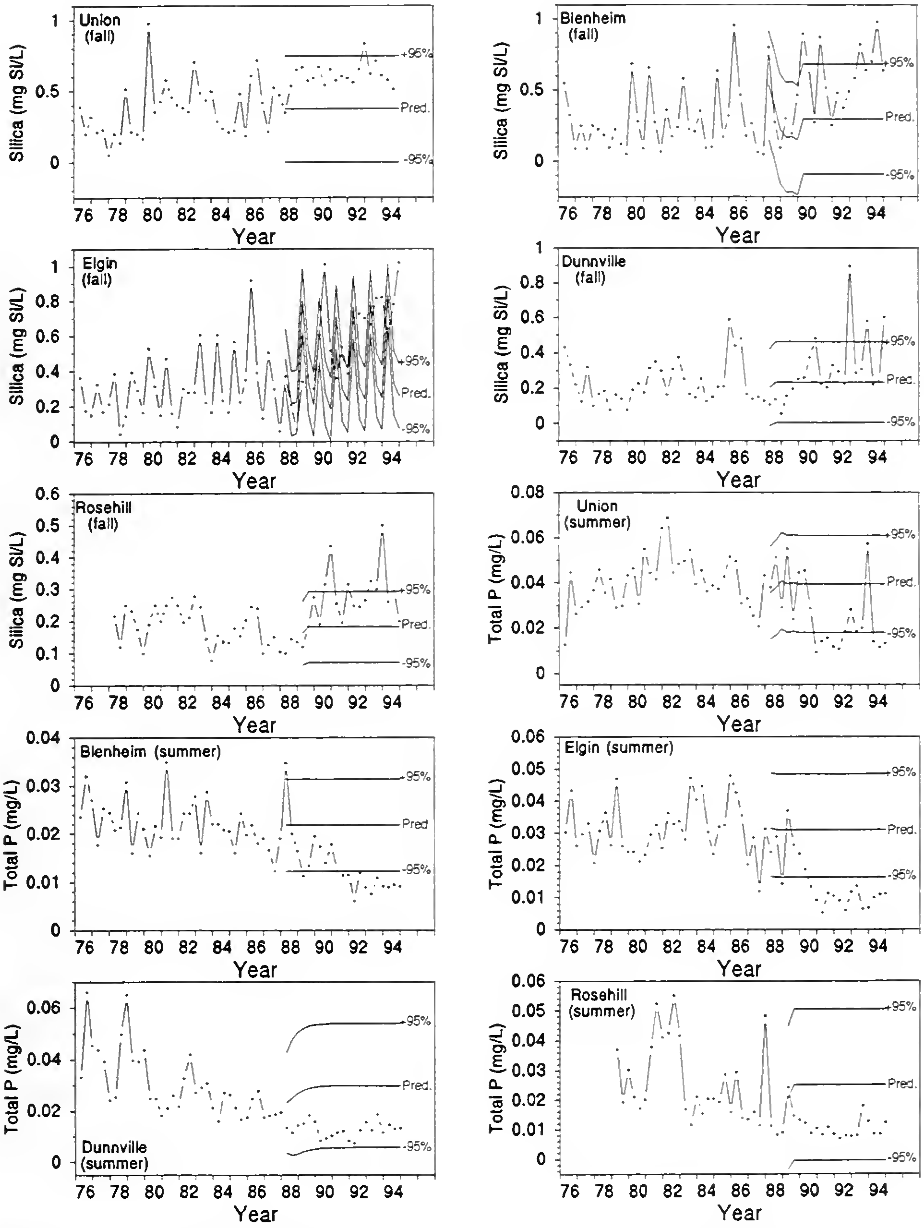

Figure 18. ARIMA forecasts of fall silica and summer total phosphorus concentrations for the post zebra mussel period at the five Lake Erie sampling locations. Measured data points lying outside the ±95% confidence envelope of a forecast imply a significant deviation from those expected on the basis of the pre-zebra mussel data.

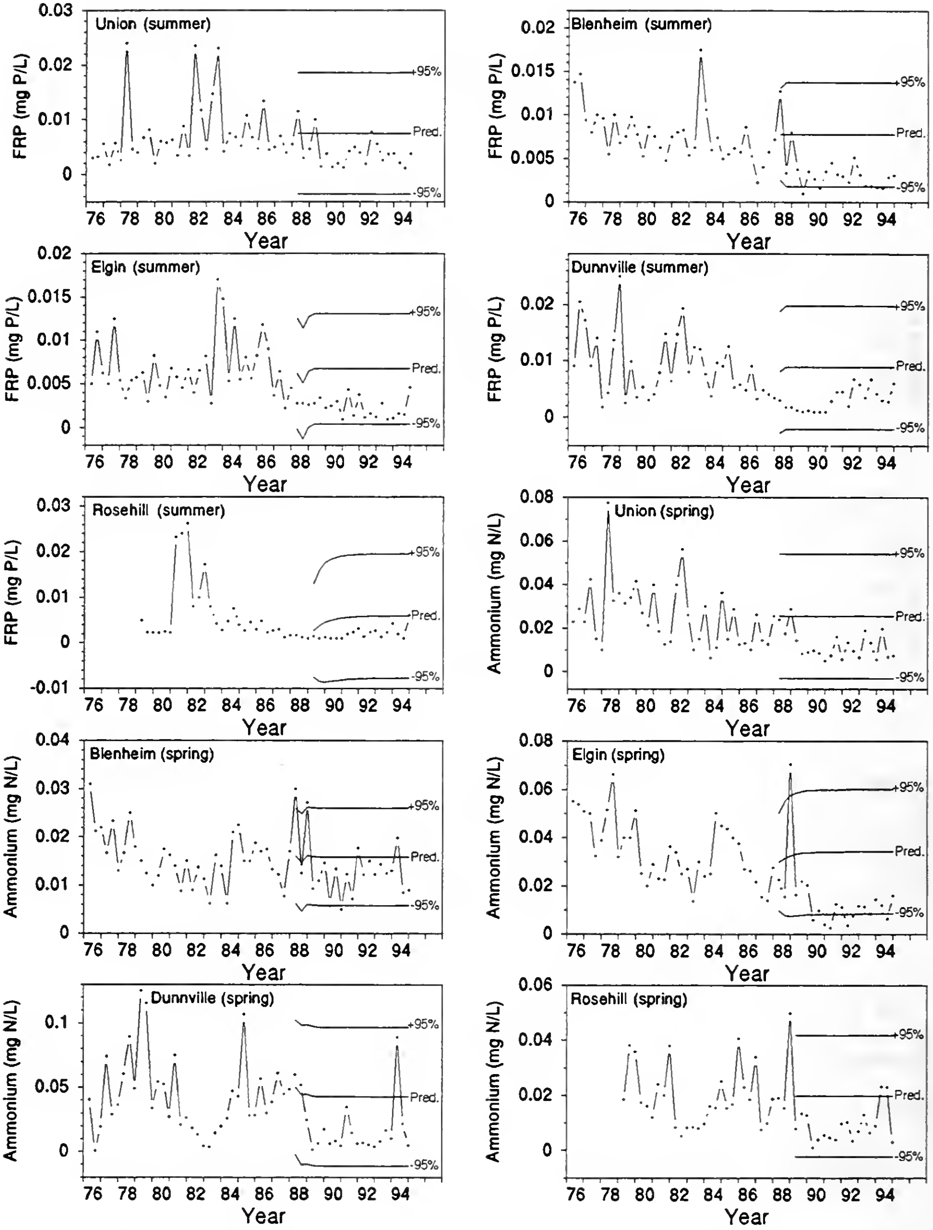

Figure 18. ARIMA forecasts of summer filtered reactive phosphorus (FRP) and spring ammonium-N concentrations for the post zebra mussel period at the five Lake Erie sampling locations. Measured data points lying outside the ±95% confidence envelope of a forecast imply a significant deviation from those expected on the basis of the pre-zebra mussel data.

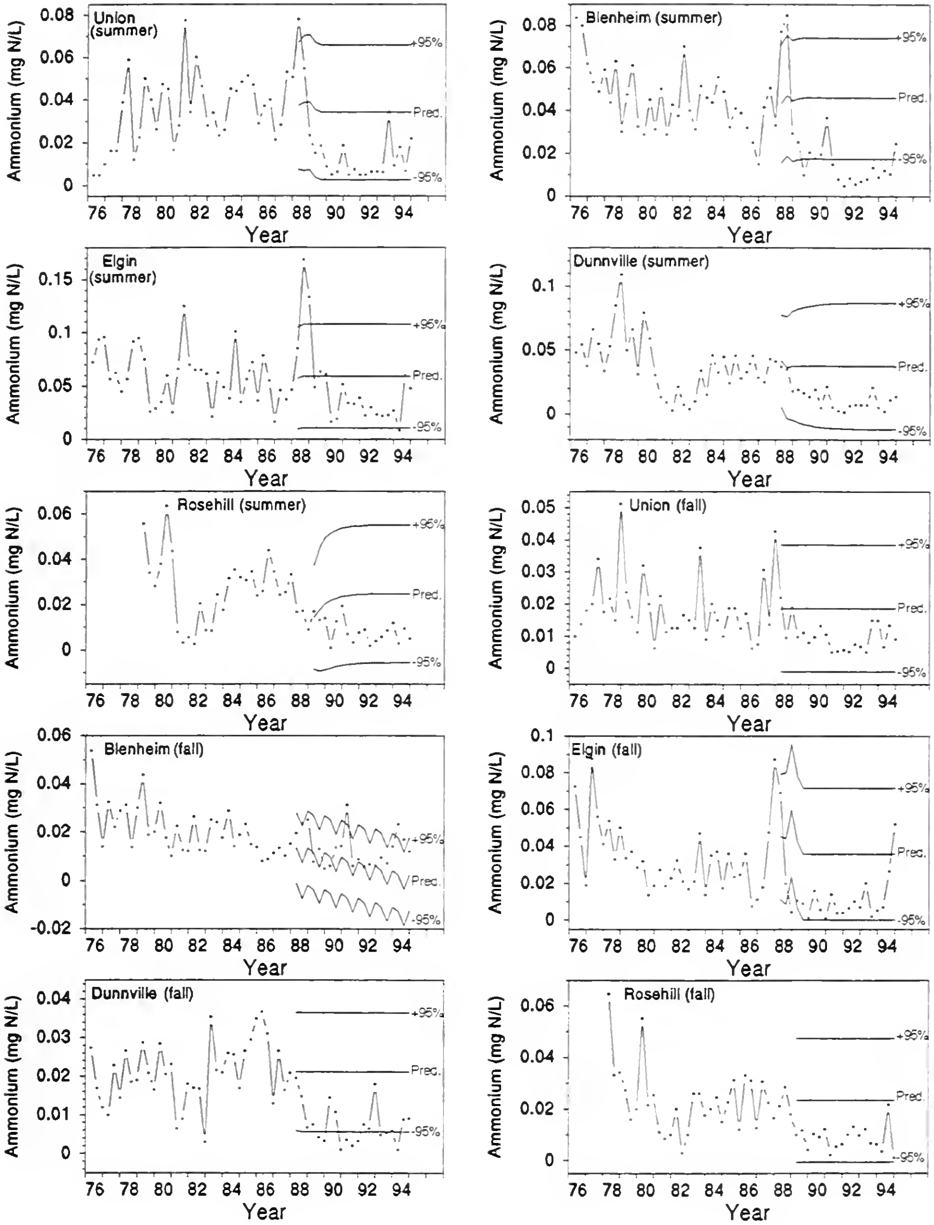

Figure 20. ARIMA forecasts of summer and fall ammonium-N concentrations for the post zebra mussel period at the five Lake Erie sampling locations. Measured data points lying outside the ±95% confidence envelope of a forecast imply a significant deviation from those expected on the basis of the pre-zebra mussel data.

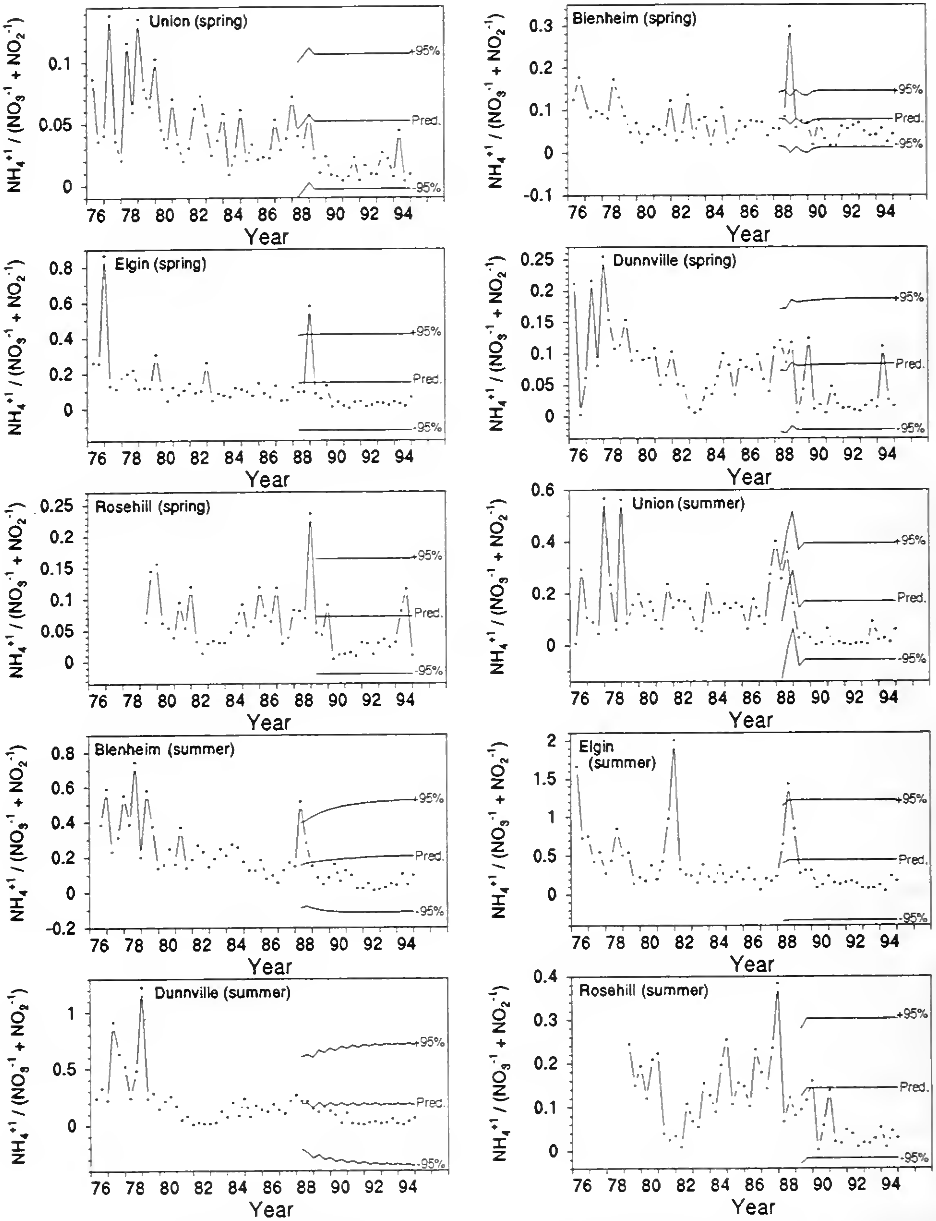

Figure 21. ARIMA forecasts of spring and summer ammonium-to-(nitrate + nitrite) ratios for the post zebra mussel period at the five Lake Erie sampling locations. Measured data points lying outside the ±95% confidence envelope of a forecast imply a significant deviation from those expected on the basis of the pre-zebra mussel data.

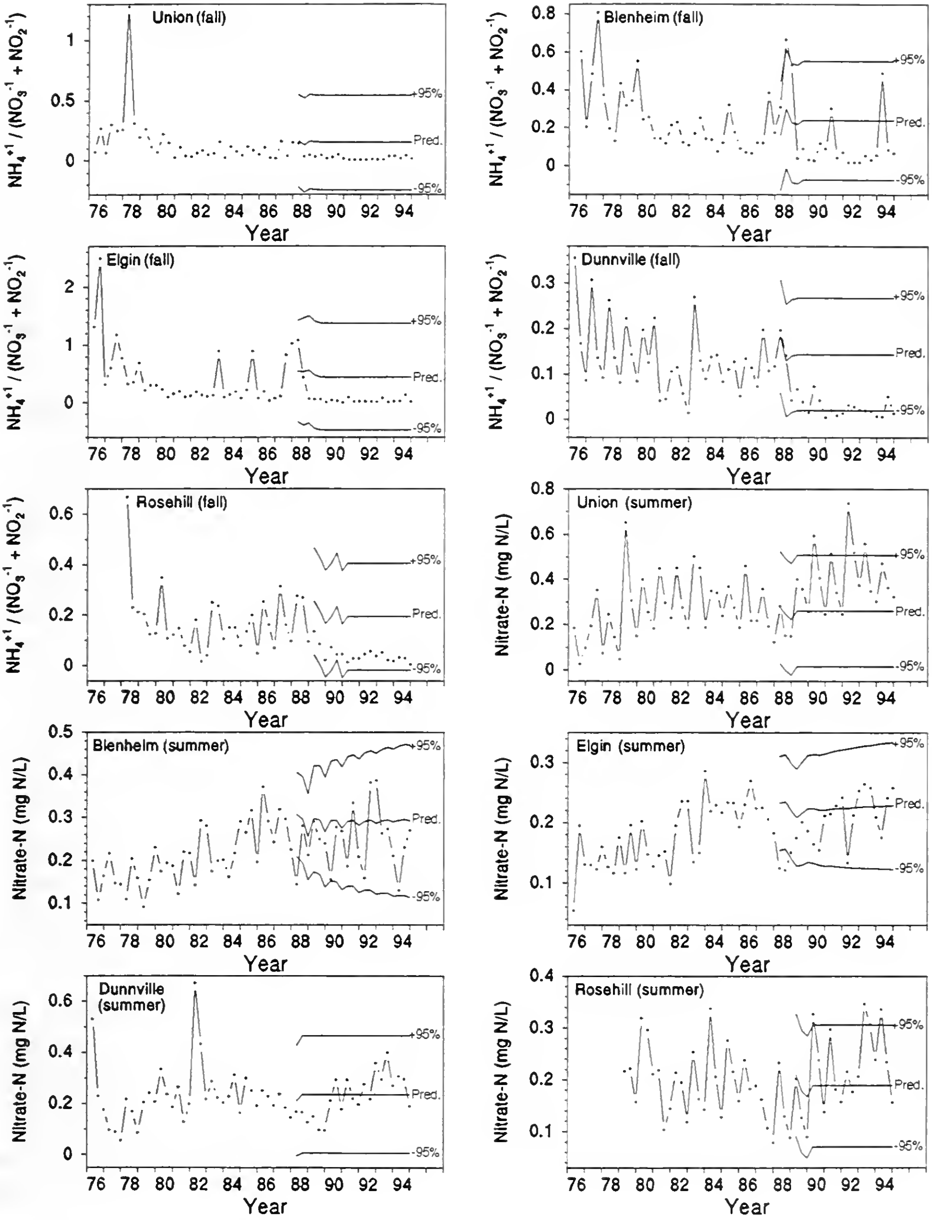

Figure 22. ARIMA forecasts of fall ammonium-to-(nitrate + nitrite) ratios and summer nitrate-N concentrations for the post zebra mussel period at the five Lake Erie sampling locations. Measured data points lying outside the ±95% confidence envelope of a forecast imply a significant deviation from those expected on the basis of the pre-zebra mussel data.

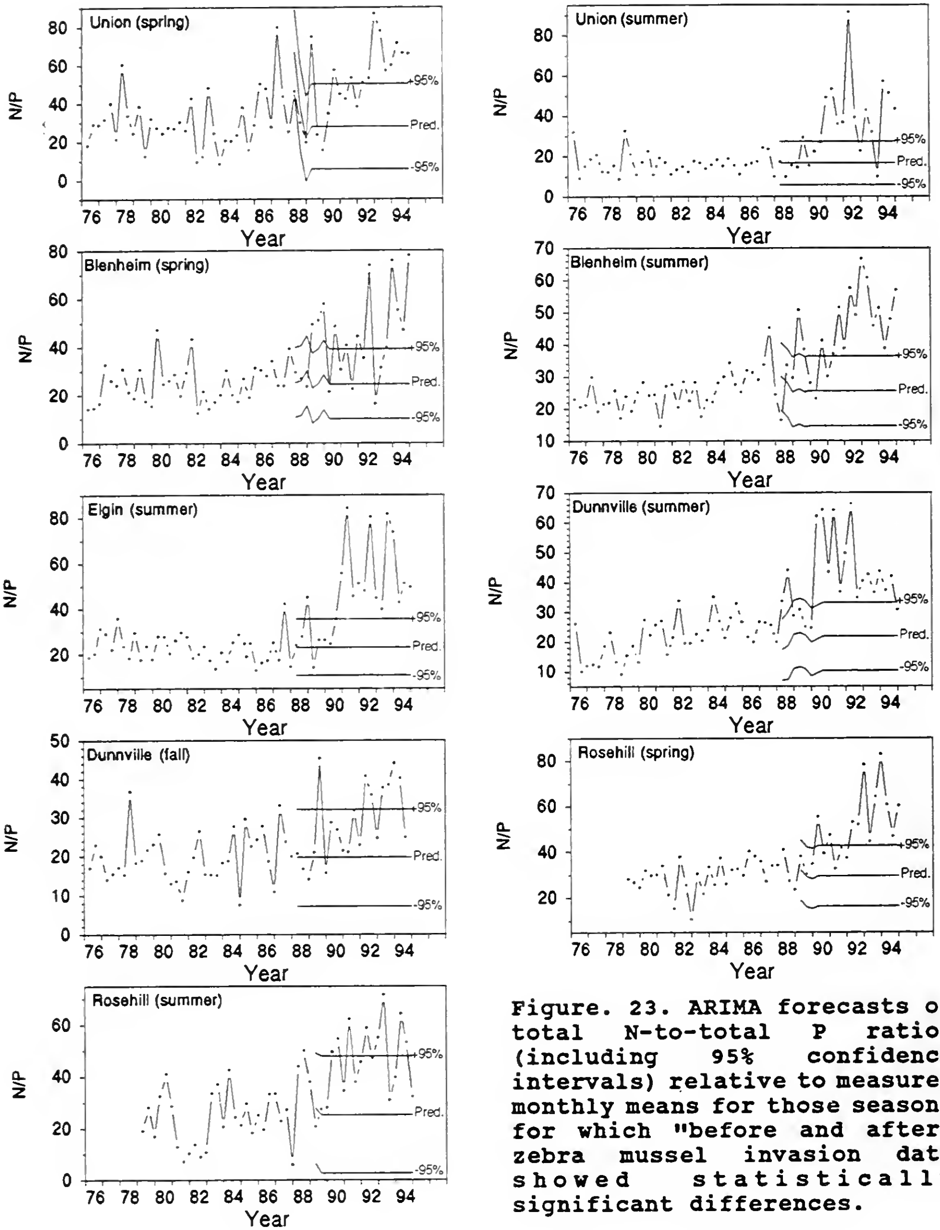

Figure. 23. ARIMA forecasts of total N-to-total P ratios (including 95% confidence intervals) relative to measured monthly means for those seasons for which "before and after" zebra mussel invasion data showed statistically significant differences.

change are difficult to make for other reasons too. For example, measured nitrate concentrations during the post zebra mussel period were lower than expected on the basis of the pre-zebra mussel data, but still within the bounds of the 95% confidence intervals of the ARIMA forecasts. Had the forecasts been upward-trending as anticipated (at least at the Blenheim and Elgin locations where a subjective view of the long term data indicates a positive slope), the resulting larger residuals would have implied a greater zebra mussel-related impact on summer nitrate. With the analysis in hand however, it cannot be said that the downturn in nitrate concentrations which coincided with the establishment of zebra mussels was any greater than that anticipated through chance alone. The lower than expected post zebra mussel nitrate levels were probably in response to a much reduced availability of ammonium-N for nitrification.

Some of the observed changes in nutrient concentrations coinciding with the establishment of zebra mussels can be related to concurrent declines in phytoplankton (Nicholls and Hopkins, 1993). Lower densities of algae have apparently resulted in lowered uptake rates of dissolved nutrients and their subsequent accumulation in the water column. This would explain the increased concentrations of dissolved reactive phosphorus in spring and fall and higher silica concentrations, especially in the fall, reflecting reduced uptake by diatoms.

The decline in total phosphorus has apparently resulted from the removal of particulate phosphorus from the water column by direct zebra mussel filtration, of which chlorophyll-bearing particles have historically been an important component (Leach, 1975). Ingested particles not used as food by zebra mussels are expelled in the form of "pseudofeces" consisting of a matrix of particles and mucus (McNaught, 1994). Although there is some potential for nutrients in this pseudofecal material to re-enter the water column in dissolved forms after "processing" by other organisms, we suggest that the establishment of zebra mussels in Lake Erie has facilitated a direct transfer of particles from the water column to the lake sediments concurrent with an overall reduction in the opportunity for mineralization of nutrients. A large proportion of the total phosphorus pool which existed in pre-zebra mussel plankton is now (post zebra mussels) apparently directed into zebra mussel biomass and pseudofeces.

The disproportionately greater decline in chlorophyll relative to total phosphorus would indicate that there was a larger proportion of non-algal particles (containing phosphorus or to which phosphorus was adsorbed) in the water column after zebra mussel colonization. The ratio of chlorophyll-to-phosphorus in water samples from all five locations greatly decreased after the zebra mussel invasion. This likely reflects a higher relative contribution to the total phosphorus pool by P in resuspended sediments and in dissolved forms. An explanation for this might be that during pre-zebra mussel times, the total P pool was comprised mainly of both wind-induced resuspended sediment particles and phytoplankton cells. Zebra mussel filtration removes P from both compartments but sediment resuspension can occur quickly in near shore zones in response to winds and currents. In the shallow areas of Lake Erie, zebra mussels can filter particles at a rate sufficient to control algal biomass accrual (MacIsaac et al., 1992), but would not likely be able to control the densities of resuspended particles (resulting from wind-driven turbulence) so rapidly that remnants of a resuspension event would not be measured as a phosphorus "spike" in water samples sometime after the event. The net effect of the arrival of the zebra mussels was therefore lower total phosphorus concentration and a lower relative contribution to the total particulate P pool by algae, and hence a lower chlorophyll-to-total P ratio.

Mazumder (1994a) used data from experimental enclosures and lakes to show that reductions in chlorophyll a below expected levels are characteristic of north temperate lakes dominated by large *Daphnia* which are generally believed to be more efficient grazers of algae than small zooplankton species. In subsequent work (Mazumder, 1994b) he found that one of the important causes of the reduction of chlorophyll yield per unit of total phosphorus was that a greater proportion of the total phosphorus pool was contributed by total dissolved phosphorus and zooplankton phosphorus (where zooplankton phosphorus was that fraction >200μm). In lakes dominated by large *Daphnia*, both high grazing and reduced phosphate demand resulted in a shift from phosphorus in algae to phosphorus in zooplankton and in dissolved forms. Mellina et al. (1995) used laboratory experiments (mesocosms) to determine effects of zebra mussel densities on phosphorus and chlorophyll a concentrations and phosphorus excretion rates. At zebra mussel densities >0.25 L^{-1}, the resulting phosphorus and chlorophyll trends in mesocosms were erratic. They also used mass balance models to predict the changes in phosphorus and chlorophyll in Lake Erie resulting from establishment of zebra mussels. Their modelled Lake Erie phosphorus decline was 29%, but they predicted an increase in chlorophyll of about 2%.

Our measured decrease in total phosphorus concentrations at the north shore intake sampling sites is consistent with observations by Johengen et al. (1995) for Saginaw Bay of Lake Huron but was not supported by Holland et al. (1995) for the southern portion of western Lake Erie (Gibraltar Island area) where lower total P concentrations were not found after the establishment of zebra mussels. It is possible that total P concentrations at that location have been dominated by river and sewage treatment plant inputs of phosphorus, the daily supply of which must have exceeded the removal by zebra mussel filtration of phosphorus associated with particles. Holland et al. (1995) did, however, speculate that much of the total phosphorus filtered from the water column was being returned to the water by sediment reflux.

Other similarities and differences between our N shore results compared with the Gibraltar Island findings include: i) remarkably similar seasonal distributions of total P and filtered reactive P (highest concentrations in late fall and winter), and nitrate (lowest in late summer and highest in winter-early spring and fall), ii) the N shore locations showed a dramatic pre-zebra mussel ammonium-N peak which was not found in the Gibraltar Island area. Although based on only one year of pre-zebra mussel data, increases in nitrate and ammonia (but not in dissolved reactive phosphorus) were found in two post zebra mussel years in inner Saginaw Bay of Lake Huron. Significant increases in these dissolved nutrients were not found in a "control" group of sampling sites where zebra mussels were rare (Johengen et al., 1995). Effler et al. (1996) studied the changes in a number of physical and chemical variables between 1990 and 1993 resulting from the zebra mussel invasion of the Seneca River in New York. They reported a marked reduction in chlorophyll (but not in total phosphorus) along with increases in water clarity, dissolved reactive phosphorus and ammonium concentrations after the arrival of zebra mussels.

The post zebra mussel summer decline in ammonium-N in our data appear to be unique. The "before and after" comparisons showed statistically significant reductions of 45%, 67%, 74%, and 77% at the five locations. We hypothesize that pre-zebra mussel decomposition of sedimented organic matter (mainly of spring and early summer algal origin) was enhanced at summer water temperatures, and, during the pre-zebra mussel period, ammonium-N from the ammonification of organic-N accumulated in the water column in excess of phytoplankton uptake requirements (under conditions of phosphorus limitation). During the post zebra mussel period, the spring-early summer crop of phytoplankton was rerouted into zebra mussel biomass and pseudofeces such that ammonification of organic-N was much less significant. Except perhaps at the Rosehill location, organic-N concentrations at all locations were consistently higher during the pre-zebra mussel period and provides some support for this hypothesis. The ARIMA forecasts showed that only at the Blenheim location were measured values consistently lower than predicted. Undoubtedly this relates to the cyclic nature of the ammonium-N data during the 1970's and 1980's, which the "before and after" analyses did not utilize. Unfortunately, there were not enough of these pre-zebra mussel cycles to be reflected in the forecast, so the forecast was conservatively described as a near-horizontal line about which the forecast data had an equal probability of falling above or below. The cyclic patterns in ammonium-N at these locations appear to be related to flow from major rivers; both the Grand River and the Thames River (the two largest rivers in southern Ontario) showed peaks in their hydrographs in the mid-1970's and mid-1980's with low flows in 1980-81 and again in 1989-90

(Environment Canada, unpublished). Nicholls *et al.* (1983) have demonstrated an impact of the Grand River on north shore nutrients and phytoplankton, so it is also possible that higher pre-zebra mussel ammonium-N concentrations may have been contributed by the high river discharges of the late 1980's.

The measured declines in total phosphorus are of great significance in light of the several $ Billions spent on phosphorus loading control. At the Elgin sampling location, summer concentrations declined about 20 μg/L on average. It is instructive to express this concentration change in terms of a mass removal of phosphorus. For the purposes of simplifying and imparting conservatism to the calculation, it is assumed that the zone of impact extends from the lake shore only to the 12m depth contour (the depth of the Elgin intake). The approximate volume of Lake Erie water contained in this zone is 2.8×10^{11} m^3 (Robertson and Jordan, 1978). The measured decline in total phosphorus concentration associated with the establishment of zebra mussels therefore equates to a removal of approximately 6000 metric tons from the water column of Lake Erie's near-shore zone during summer. This is approximately 3X higher than the total annual phosphorus loading from U.S. and Canadian municipal sources during the late 1980's (Dolan, 1993). More sophisticated modelling that might be able to relate this zebra mussel removal of phosphorus to an equivalent reduction in the total external loading rate and effects on the whole lake is beyond the scope of this report; still, the simple conversion from concentration to mass for the near shore zone adds some perspective to the magnitude of the apparent water quality impact of the zebra mussels in Lake Erie.

The phosphorus reductions associated with the arrival of zebra mussel in Lake Erie should not be grounds for relaxing phosphorus loading controls now in place. Were loading rates to increase and the zebra mussel population collapse (the most likely cause being disease), reversion to historical relationships between P loading rate and algal biomass would likely be reestablished, including an associated deterioration of water quality. Experience and history has shown that it is much more costly to reduce loading rates after the fact than it is to put in place preventative programmes now or to uphold existing protocols for phosphorus load management.

The "before and after" and ARIMA analyses have provided objective statistical tools for assessing change at each of the five Lake Erie locations. Lacking in this approach, is a more integrated summary of overall change which might include variables for which the degree of change did not meet the stringent requirements for statistical significance. If included in a more subjective assessment of change, the inclusion of these variables in some measure of combined response should reinforce the evidence for overall biologically (if not statistically) significant change. In our view, a quasi-subjective overview of a comprehensive dataset like that presented here is appropriate when interpreting changes that might be caused by the arrival of zebra mussels. The chlorophyll data from the Blenheim location serve to illustrate this point. The ARIMA forecast of the post zebra mussel chlorophyll concentrations revealed that the measured values fell within the 95% bounds of the forecast and therefore were to be expected in the absence of a zebra mussel impact. A totally subjective view of these data however would suggest that there is a clear discontinuity in the dataset at about the time of the arrival of the zebra mussels. After the establishment of zebra mussels in the central basin, the measured chlorophyll concentrations were consistently lower than any recorded previously. In the absence of any other viable hypothesis to explain this, "intuition" says that despite the ARIMA output, there was apparently a direct zebra mussel effect on chlorophyll concentrations at the Blenheim location. At face value, the ARIMA analysis provided an answer to whether or not a change in a single variable was statistically significant at a single location. But it is equally (or perhaps more) important that any overall consistency in the direction of change be identified, and for this, the DCA ordination of sites using several before and after nutrient variables was helpful. It is important to note that the input to the correspondence analysis included nutrient concentration data for all seasons, and the output demonstrated that at all five Lake Erie locations the direction of change was consistent. These changes can be rationalized limnologically in terms of changes in algal biomass accrual and nutrient uptake, sedimentation, decomposition and transformation of organic matter.

We conclude that the individual "before and after" statistical analyses and the individual ARIMA analyses are important for a site by site evaluation of change, but a more subjective overview of several supportive long-term data sets is equally important in deciphering the significance of overall change. So, as a summary of important changes resulting from the establishment of zebra mussels along the Canadian shore of Lake Erie, we have identified the following effects based on a combination of the statistical tests and more subjective assessments of the spatial consistency and the magnitude and direction of change as follows:

- dramatic reductions in chlorophyll during all seasons,
- dramatic increases in silica, especially in the fall,
- dramatic decreases in summer total phosphorus concentrations,
- declines in summer dissolved reactive P and ammonium-N concentrations,
- increased spring and fall concentrations of dissolved reactive P,
- decreased summer silica concentrations,
- lower organic-N levels during all seasons, except at the Rosehill location in spring and fall,
- increased total N-to-total P ratios, especially in summer.

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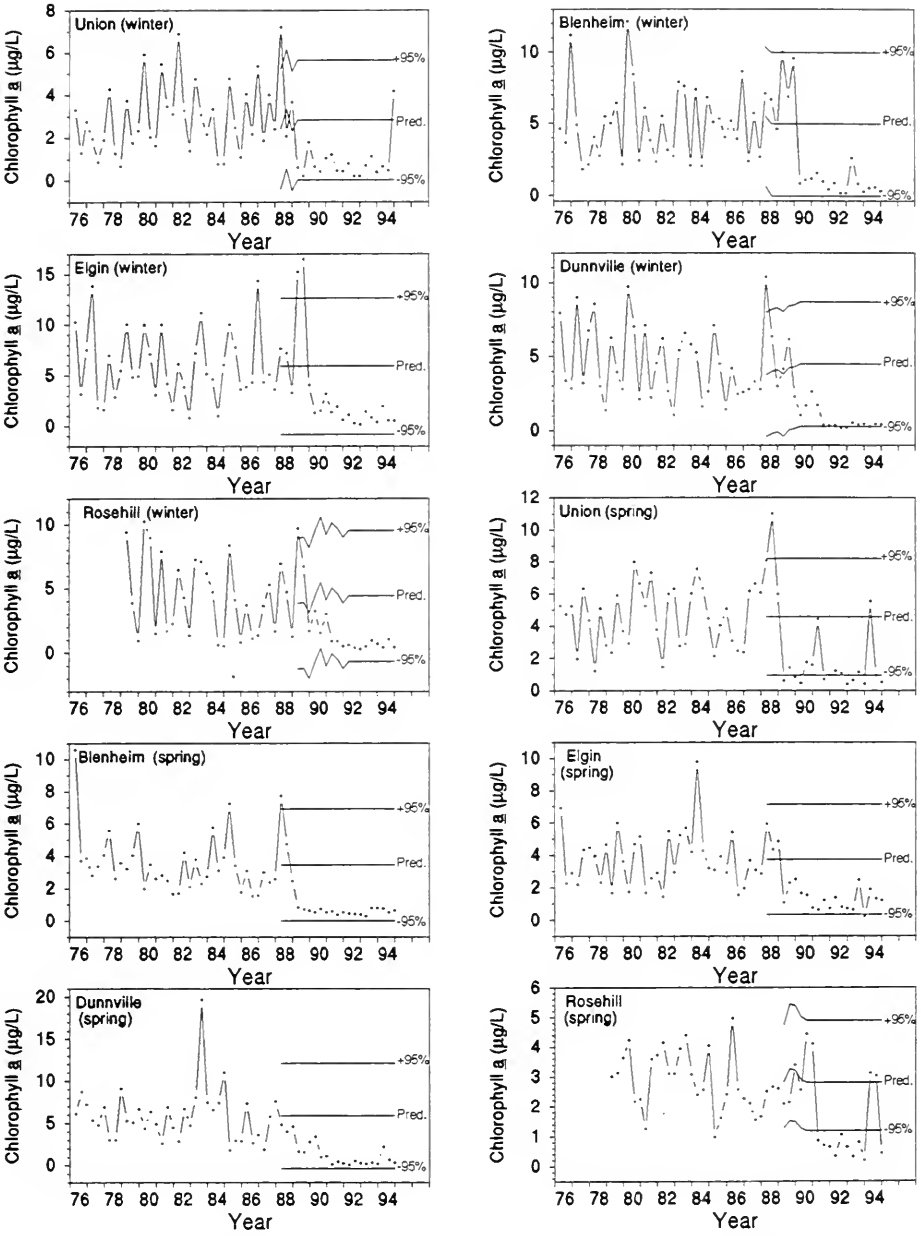
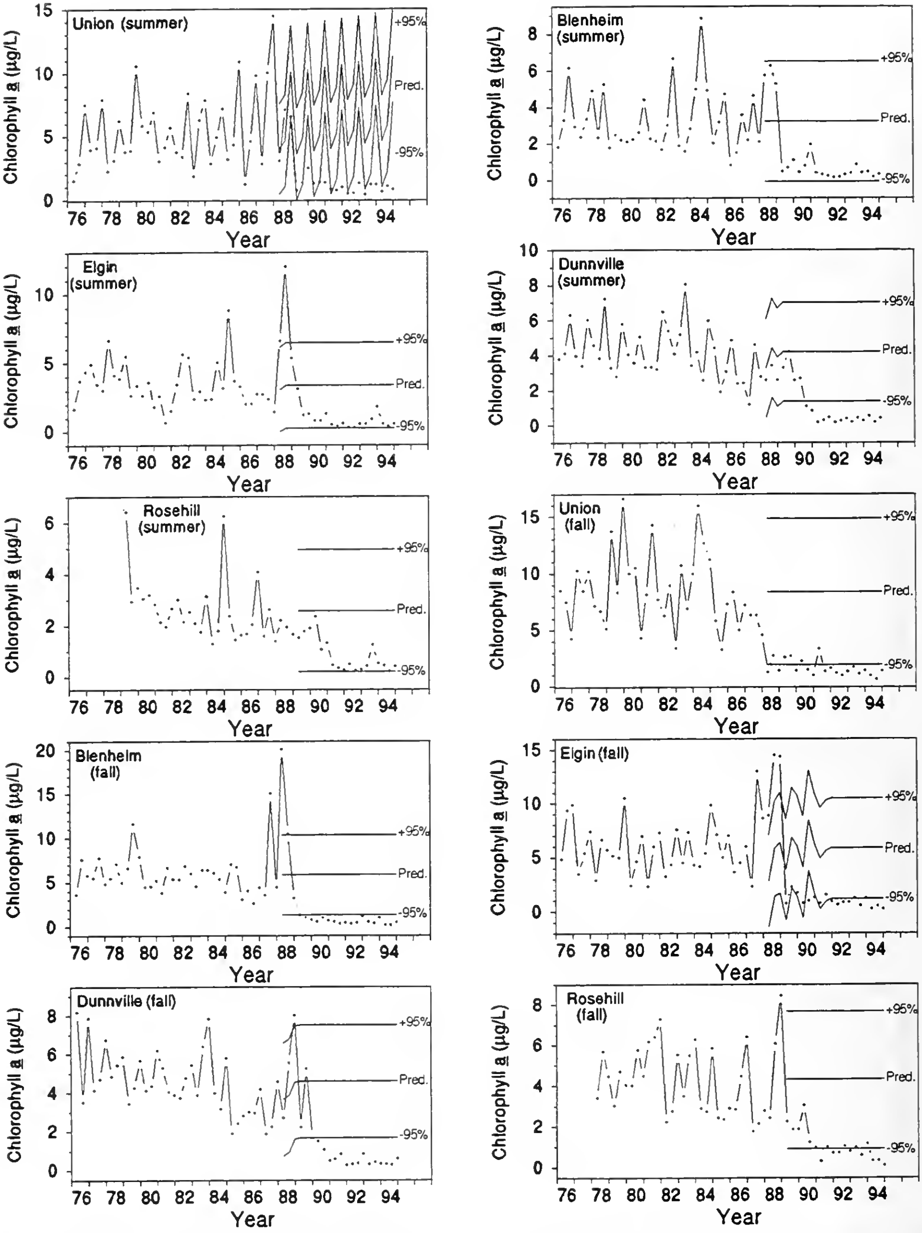
Appendix

(Figs 1 and 2, and Table 1)



Appendix Figure 1. Monthly mean chlorophyll a concentrations during winter (December, January and February) and spring (March, April and May) with ARIMA forecasts for the post zebra mussel period at the five Lake Erie sampling locations. Measured data points lying outside the ±95% confidence envelope of a forecast imply a significant deviation from those expected on the basis of the pre-zebra mussel data.



Appendix Figure 2. Monthly mean chlorophyll a concentrations during summer (June, July and August) and fall (September, October and November) with ARIMA forecasts for the post zebra mussel period at the five Lake Erie sampling locations. Measured data points lying outside the ±95% confidence envelope of a forecast imply a significant deviation from those expected on the basis of the pre-zebra mussel data.