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CHESAPEAKE BAY
WATER QUALITY MONITORING PROGRAM
ECOSYSTEM PROCESSES COMPONENT (EPC)

LEVEL ONE REPORT #23 (INTERPRETIVE)

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MARYLAND CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

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INTERPRETIVE REPORT

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Executive Summary

Background: *Objectives of the Water Quality Monitoring Program*

The EPC has undergone program modification since its inception in 1984 but its overall objectives have remained consistent with those of other Monitoring Program Components. The objectives of the 2005 EPC program were as follows:

1. Characterize the present status of the Patuxent River estuary (including spatial and seasonal variation) relative to ***near-shore habitat and water quality conditions***. This portion of the program (DATAFLOW) involved high-resolution water quality mapping in the Patuxent River estuary.

2. Evaluate the variation in spatial and temporal scales of water quality in both near-shore and off-shore areas of the Patuxent River estuary using the same DATAFLOW mapping system.

3. Measure ***epiphyte accumulation rates*** on SAV mimics and associated water quality conditions at several sites in the Patuxent River estuary, extending the developing time series of this important SAV habitat indicator process.

4. ***Integrate the information*** collected in this program with other elements of the monitoring program to gain a better understanding of the processes affecting water quality of the Chesapeake Bay and its tributaries and the maintenance and restoration of living resources. In this reporting period we have constructed an N and P budget for the Patuxent River Basin. This involved integration of data from many aspects of the Water Quality Monitoring Program, the larger Chesapeake Bay Program and University Research Programs.

Patuxent River Flows and Total Nitrogen Loads

One of the central features of the Chesapeake Bay Program and Maryland's component of this program is an emphasis on reduction of nutrient loading rates to the mainstem Bay and tributary rivers. It has become clear that the Bay ecosystem is nutrient over-enriched and that this leads to a variety of water quality, habitat and living resource problems. It has also become clear that a large fraction of the nutrient load to the Bay and tributaries comes from diffuse sources. Hence, consideration of river flow, the vehicle of diffuse source nutrient transport, is of central interest to those tasked with understanding the performance of these systems and deciding on appropriate management actions. Finally, it also appears that these ecosystems, such as the Patuxent River estuary, respond to changes in river flow and associated nutrient loads on relatively short time-scales (year) and examination of multi-decade records of these parameters (flow and nutrient loads) is appropriate and useful. We summarize here the main management-related points derived from this effort.

1. Multiple aspects of the monitoring program were synthesized with a box-model for the Patuxent River Estuary. The end result of this box modeling effort was a set of TN loading

estimates for the head of the mesohaline estuary. The importance of this is that all sources of inputs upstream of Benedict are included in this estimate and there is no longer the need to use just the fall line load as an index of nutrient load magnitude or temporal pattern.

2. Monthly load estimates from 1985 to 2005 averaged about 2700 kg TN day^{-1} and ranged from several hundred to more than 10,000 kg TN day^{-1}. Despite this very considerable variability, seasonal-scale patterns were distinct with lower input rates during summer and fall and much higher rates during winter and spring. Very high inputs (>8000 kg TN day^{-1}) occurred during 1989, 1993, 1994, 1996 and 2003, all associated with particularly wet periods indicating the importance of diffuse sources of nutrients in this system.
3. It should be noted that BNR technologies at the major sewage treatment plants were operational by about 1992. These plants operated (and with one exception; Western Branch Sewage Treatment Plant) BNR technology on a seasonal basis (April – October). Combined, these plants remove about 1100 kg N/day when they are operating BNR technologies. However, TN loads to the mesohaline portion of the Patuxent River estuary do not show a marked decline during the post-BNR period. In fact, 8 of the 9 highest load years in the data record occurred after BNR became operational. This observation points to two factors, one of which is quite certain and the other more speculative. The post-BNR period was wetter than the pre-BNR period and hence diffuse sources of N were larger during the more recent post-BNR period. Certainly the magnitude of loads indicates the importance of diffuse sources in this system. The second factor is changing land use. During the period 1960 – 1980 much of the development in the Patuxent was located in the upper portion of the basin. The fact that 8 of the 9 major sewage treatment plants are located in the upper basin supports this observation. However, since the 1990's development (e.g., loss of forested and pasture lands) has rapidly increased in the lower basin and could also have contributed to the very large loads estimated to have occurred during the wetter, post-BNR period.
4. TN fluxes at comparable river flows were lower during the post-BNR period than during the pre-BNR period. Said another way, per unit of river flow less TN entered the mesohaline estuary during the post-BNR period. At average river flows (~17.5 m^{3} sec $^{-1}$) about 500 kg TN day $^{-1}$ less TN is delivered to the mesohaline estuary. We have argued earlier that there may well have been increased TN loads coming from the middle basin due to several decades of land-use changes (e.g., conversion of forests to residential/urban uses) and we have shown that the post-BNR period was wetter, leading to generally higher diffuse source loads. In spite of these processes, at a given level of river flow, TN loads were still lower during the post-BNR period. The most reasonable explanation for this is that nitrogen removal at sewage treatment plants have contributed to measurable TN load reductions to the mesohaline estuary. While loads remain moderate to high compared to other estuarine ecosystems (Boynton and Kemp 2006), BNR has apparently caused modest load reductions. BNR reductions have helped, but are partially off-set by diffuse source loads coming from the basin between Bowie and Benedict.

Community Metabolism

Rates of primary production and community respiration are fundamental characteristics of aquatic ecosystems. However, the production and respiration characteristics of estuarine systems have been far less well studied or monitored than is the case with portions of coastal waters and certainly of lakes. Since it is well-established that these rates are sensitive to nutrient loading rates reliable estimates of these rates would serve both as an index of system performance as well as an indicator of system response to nutrient load reductions. During the last several decades several things have changed in the monitoring/research world that have made it far more feasible and affordable to consider using open water community metabolism measurements as components of monitoring or research programs in estuarine systems. First, several generations of in-situ devices have come into common use, each providing more reliable measurements of DO, temperature, salinity, pH and more recently chlorophyll-a and turbidity. These devices now have the capability of making these measurements in a reasonably reliable fashion for periods of one to two weeks in nutrient-enriched estuarine ecosystems. The addition of wiper blades and other self-cleaning devises have further enhanced the reliability of these devices. Finally, these in-situ sondes are capable of making rapid (~ 20 measurements/minute; more frequently measurements are made at a frequency of 4/hour), repeated measurements thus ensuring that a fine-scale record of diel changes in concentrations is captured. Second, computational capacity and associated software have improved greatly. It is now possible to readily store and manipulate the large data files associated with a group of continuously recording sondes. It is also possible to develop programs to compute metabolism variables, thus largely removing the time consuming nature of these analyses. Thus, reliable data sets collected at frequencies amenable for metabolism calculations and computer hardware and software more than capable of conveniently storing and making calculations have combined to make these community-scale processes very attractive. We summarize here the main management-related points derived from the metabolism commutations made for this report.

1. One of the central issues related to Chesapeake Bay restoration is the reduction of nutrient loading rates. This goal results from the fact that algal production of organic matter is often related to loading rates of both nitrogen and phosphorus. Further, this organic matter often sinks to deeper waters, decomposes via respiratory processes and oxygen is depleted in the process. Having in-situ measurements of these two processes (e.g., production and respiration) provides a strong empirical link to Bay Program goals, namely, the reduction of nutrient loading rates.
2. There are at present a very large number of sites for which metabolism computations might be applied. ConMon-like measurements began about 1998 at three sites in the Pocomoke River. During 2005 there were 39 sites being monitored in Maryland tributary rivers of Chesapeake Bay and the Maryland Coastal Bays. At most of these sites measurements are collected from April through October and sites remain active for three consecutive years; in a few cases more years of data are available. Thus, at a specific site there is the potential for about 210 measurements of production and respiration per year and a total of about 630 measurements during a three year deployment cycle. Such a relatively large set of rate process measurements would certainly help us better understand the status and trends of these systems as nutrient and sediment loads are modified by management actions.
3. The longest time-series record of data suited for metabolism calculations that we are aware of in Chesapeake Bay was initially collected by Cory working for the USGS at a bridge site in the Patuxent River estuary (MD Rt. 231 Bridge at Benedict, MD). This data set was then used by Sweeney (1995) to compute metabolism for the 1963-1969 period and he also deployed a more modern instrument at the same location during 1992. We later deployed

instruments during the late-1990's, again at the same location. Metabolism results suggest that this site in the Patuxent is sensitive to changes in nutrient loading rate and that the response is quite large. Metabolism rates were considerably lower in recent years following the institution of Biological Nitrogen Removal (BNR) at sewage treatment plants in the upper basin (after 1992). There is a clear indication of increasing metabolism through that decade as sewage treatment plants began discharging and land-use changes became large-scale.

4. For purposes of this preliminary exercise we selected ConMon and other sites that would provide some indications of the utility of making these computations as a routine part of shallow water monitoring. We have been working with this method of computing important estuarine rate processes for a relatively short time. Our initial impressions are that we have data collection platforms that produce a large amount of data suitable for these analyses. Furthermore, ConMon sites are situated in a broad array of Bay habitats so the potential for comparative ecology is very great. Finally, there is strong support in the literature for the linkage between the magnitude, seasonal pattern and variance of metabolic rates and nutrient loading rates, thus making these measurements a useful index of system performance and a gauge of management action effectiveness. However, we have a number of steps to take before we would recommend adding this approach to the arsenal of analyses currently being used. To date we have accomplished the following and plan to continue additional analyses as listed below:

    1) We have confirmed the internal reliability of the metabolism algorithym using very simple data sets and compared results to traditional hand-based graphical analyses.

    2) We have considered several pre-testing schemes to help eliminate inappropriate data.

    3) We have considered several other computational schemes and will continue to investigate these in the coming months.

    4) We have initiated an effort to model these rates using ConMon and other data and at this early stage are optimistic about results. We may consider selecting a range of stations and attempt modeling efforts in a comparative context.

    5) We have concluded at this stage that there are important ecosystem changes captured with this approach and that these will serve as indices of change in these shallow water ecosystems.

    6) Finally, if we can develop a reliable and operational computation system we would like to move these measurements to the Eyes on the Bay web site along with readily understood graphics and text explaining the significance of these measurements.

Temporal Adjustments of DATAFLOW Observations

The use of a relatively new technology, DATAFLOW, in the Chesapeake Bay Biomonitoring program has led to advances in describing spatial pattern in many Chesapeake Bay tributaries, especially in shallow water areas not previously directly monitored in the traditional monitoring program. While limited to surface water quality measurements, use of DATAFLOW has increased observations of important water quality variables, such as water clarity, dissolved oxygen and algal biomass (as indexed by chlorophyll-a) by several orders of magnitude. However, as with any measurement technology, there are technical and other issues that must be addressed. In the case of DATAFLOW, calibration of sensor-derived values with traditional laboratory-based values is critical and is the focus of on-going analyses. In addition, there are temporal issues to be resolved with DATAFLOW measurements. Specifically, DATAFLOW cruises generally start in early morning and conclude by late afternoon. While relatively synoptic, there are some variables collected with DATAFLOW that change considerably during a cruise period. Thus, we can obtain a somewhat distorted view of spatial distribution of these variables. The focus of this Chapter is to present an analysis of data collected from three different measurement platforms in the Patuxent River estuary towards the goal of adjusting DATAFLOW observations to a single base time during each cruise and thereby obtain an unbiased set of observations. We summarize here the main management-related points derived from the above analyses.

1. This assessment studies the efficacy of using ConMon data from a single site to adjust for the short term temporal signal that influences DATAFLOW measurements during a synoptic cruise. The case studied here uses the diel trend of DO at the shallow ConMon location to adjust surface DO observations made by a continuous Buoy monitor in the mid-channel nearby. By comparing the day by day overlay plots of the buoy and ConMon data, it is readily apparent that DO in these two locations is responding differently to the local habitat. Both have a diel signal of high DO during the day and low DO at night. However, DO at the ConMon location tends to go lower at night presumably in response to the more proximate benthic community. At the buoy location, daytime DO can be highly variable and often exceeds saturation by considerable amounts.
2. This assessment shows that the adjustment process shows promise in that the adjusted data are improved relative to unadjusted data. However, a prediction error of 1.0 to 2.0 mg/l of DO is large compared to criteria of 3.0 to 5.0 mg/l. Research to improve on this should be pursued. As noted above, this test case might be classed as a fairly difficult one. One line of research would be to investigate test cases where the data serving as a model for diel trend and the data being adjusted come from more similar habitats.
3. Future research should attempt to address all three dimensions that might affect the accuracy of adjustment: time, space, and changes of habitat. A simple experiment that would provide information on these three dimensions could be conducted by using the DATAFLOW boat to repeatedly run a cruise track near a ConMon monitor. For example, start near the monitor and run a cruise track along shore, move to mid-channel, and return to the monitor. The cruise track should be designed to be repeated every hour. Data from the first run would serve as the base-time data. Data from subsequent runs could be adjusted using the diel trend from the monitor and compared to the base-time run.
4. It is clear that these new technologies that allow the collection of temporally and spatially dense data offer many opportunities for improving the resolution of assessing the shallow water environment. With this opportunity comes the discovery of problems that have been ignored in the past. Adjusting for the diel trend in a synoptic survey is one such problem that remains to solved. It is shown by this assessment that the problem is significant and that it is possible to some extent to use the ConMon data to adjust for the diel trend in the synoptic data.

Spatially Intensive Shallow Water Quality Monitoring of the Patuxent River: A Multi-Year Analysis

This chapter includes analyses, based mainly on Patuxent River DATAFLOW data collected between 2003 and 2005, a period that included extremely wet as well as more normal weather conditions. We have emphasized analyses focusing on chlorophyll-*a* both because it is a central water quality variable with relevance to both SAV and hypoxia and because chlorophyll, as a proxy for algal biomass, is known to be responsive to nutrient loading rates. Furthermore, we have focused these analyses on the mesohaline region of the Patuxent because this is the region thought to be most sensitive to changes in nutrient supply rates. During 2005 we evaluated patterns in surface water quality using the DATAFLOW VI mapping system in the Patuxent River. The monitoring effort of 2005 marked the third year of a three year shallow water monitoring sampling cycle for the Patuxent River estuary. DATAFLOW VI was deployed from a small research vessel and provided high-resolution spatial mapping of surface water quality variables. Our cruise tracks included both shallow (<2.0m) and deeper waters, and sampling was weighted towards the littoral zone that represented habitat critical to Submerged Aquatic Vegetation (SAV) and associated organisms. We summarize here the main management-related points derived from this analysis.

1. **Inter-Annual Variations**
    a. ***There is a clear and dramatic response to nutrient loading rates***. Chlorophyll concentrations in surface waters were very large during spring 2003 throughout most of the mesohaline estuary with much of the estuary having concentrations above 60 µg/l and about 20% of the mesohaline estuary with concentrations in excess of 120 µg/l. During 2004 and 2005 concentrations were much lower in general, especially during 2004 when, even during the period of maximum chlorophyll concentration, much of the mesohaline region was below that required for SAV (chlorophyll < 15 µg/l). In addition, the position of the chlorophyll maximums appear related to river flow. During the very high flow year relatively high chlorophyll was present throughout the mesohaline estuary. During average or lower flow conditions high chlorophyll values were observed towards the up-stream end of the mesohaline region rather than throughout the system.
    b. ***In all three years maximum chlorophyll concentrations occurred during mid to late spring as has been observed in the mainstem Chesapeake Bay.*** Our interpretation of this is that this chlorophyll mass is supported by "new nitrogen" inputs, mainly coming from the Patuxent watershed. This emphasizes the need for reductions in later winter and spring nutrient inputs from the land.
    c. ***There does not seem to be any strong and consistent signal regarding chlorophyll accumulation in channel versus shoal areas.*** For example, during the high chlorophyll year (2003) very high concentrations were seen in both shoal and channel areas. In contrast, during the average flow year (2004) highest concentrations were restricted to the upper mesohaline area and were largely associated with the southern shore. During the drier year (2005) high chlorophyll concentrations were relatively rare but were associated with the channel in the upper half of the mesohaline region. We had anticipated observing highest chlorophyll concentrations in shallower areas because of both less likelihood of algal cells sinking beneath the pycnocline and hence out of the euphotic zone and because of better linkage between sediment nutrient sources and euphotic waters. However, at

least in this analysis of maximum chlorophyll concentrations, a clear shoal versus channel pattern did not emerge.

    d. ***There does not appear to be much in the way of "nutrient memory" in this ecosystem.*** We have commented on this issue in previous reports and papers. In this case chlorophyll values in spring 2003 were very high and we have argued this was in response to elevated winter-spring nutrient loading rates during the winter – spring of 2003.

2. **Comparisons of DATAFLOW and Traditional Monitoring Data**
    a. Area weighted chlorophyll concentrations ranged from 2.1 µg/l (May 2004) to 107.2 µg/l (May 2003) during the measurement period. In all years highest concentrations occurred in May or June. The general pattern of area weighted chlorophyll concentration for the mesohaline estuary was similar based on LTBM data. Chlorophyll concentrations ranged from 5.5 µg/l (April 2004) to 127.0 µg/l (May 2003).
    b. There was a noticeable bias towards higher LTBM compared to DATAFLOW measurements. For example, at annual time scales (April-October) LTBM concentrations were higher than DATAFLOW values for the same year. Month-based comparisons showed a similar pattern.. These consistent differences could have arisen for several reasons including the fact that two different measurement systems were employed in making measurements (LTBM uses lab-based chlorophyll extraction while DATAFLOW uses in-situ fluorometry) and two different interpolation schemes were used. It appears to us unlikely that the bias is based mainly on differences in chlorophyll measurements.
3. **DATAFLOW Chlorophyll-*a* Distribution in Deep versus Shallow Water Environments**
    a. Surface water chlorophyll concentrations throughout the mesohaline portion of the Patuxent River estuary ranged from 3.7 to 135 µg/l in shallow waters and between 2.3 and 80 µg/l in deep waters. While the highest concentrations occurred in shallow waters, during most cruises there were small differences between deep and shallow concentrations.
    b. There was considerable variability concerning the months during which highest chlorophyll concentrations occurred. For example, during the wet year of 2003 highest concentrations occurred during April-June in both deep and shallow portions of the estuary with highest concentrations favoring shallow areas. During 2004, a year of near-average river flow, peak concentrations were much reduced in all mesohaline areas and peak concentrations occurred in June-July in shoal areas but not until August-September in deeper zones of the estuary. During 2005, a dry year, highest concentrations occurred during June-August at both deep and shallow sites.
    c. From the point of view of enhancing SAV survival, water quality conditions were more favorable for growth during both spring and fall and less favorable during summer periods.
    d. There was close correspondence in inter-annual chlorophyll patterns in shallow and deep waters and these patterns reflect the general pattern of nutrient loading rates.
4. **SAV Habitat Criteria and Shoreline Length**
    a. In years of especially strong river flow (and nutrient loading rates) much of the estuary, at least during some portions of the SAV growing period, have chlorophyll concentrations in excess of SAV criteria. In 2003, for example, both shallow and

deep waters throughout the mesohaline estuary had chlorophyll concentrations at generally high levels during June. Exceptions to this include small portions of the river shoreline in the vicinity of St. Leonards Creek. However, the clear message here is one wherein chlorophyll concentrations were well beyond SAV habitat criteria during a wet year. In lower flow years (2004 and 2005) quite a different pattern emerged wherein chlorophyll concentrations in portions of the mesohaline estuary are below SAV criteria values and the portions in compliance tend to be in the high-mesohaline and on the northern shore of the estuary. This suggests that upland sources of nutrients supporting chlorophyll accumulation are a dominant driver in this system.

   b. We have also made numerical estimates of the length of shoreline (total shoreline of mesohaline estimated to be 75.2 km) exceeding SAV chlorophyll criteria. The range in shoreline length exceeding criteria ranged from zero or near-zero (5 of 20 cruises) to very considerable (>25% of shoreline during 7 of 20 cruises). During the high flow year of 2003 about 85% of mesohaline shoreline had chlorophyll concentrations above criteria values during May and during April – June, 2003 at least 68% of mesohaline shoreline did not meet criteria. During this high flow year the early spring SAV growing period was likely very compromised by high chlorophyll concentrations. However, during this year the percent of shoreline not meeting criteria rapidly dropped for the rest of the growing season. This “high flow” pattern was not evident in 2004 and 2005, both years with normal or below average flow. In these years there were no prolonged periods when substantial shoreline did not meet criteria and the period when criteria were least achieved was during summer, a period when some SAV species (e.g. eelgrass) do not grow a great deal or lose much of their above-ground biomass. Thus, there appear to be a range of conditions related to river flow that change both the magnitude and seasonal pattern of shoreline habitat quality relative to SAV growth and survival.

5. **Relationships Between N Loading Rate and Mesohaline Chlorophyll Concentrations**
   a. In a system like the Patuxent there is ample evidence that nitrogen is a key variable regulating rates of primary production and algal biomass accumulation. However, we could ask “Is this normal for estuarine ecosystems or is the Patuxent a special case?” It appears that nitrogen is a frequent “master variable” controlling estuarine phytoplanktonic primary production**.**
   b. There is a very substantial range in both SAV growing season and annual average chlorophyll-a concentration in surface waters. During the low flow year of 2002 concentrations were close to 10 µg/l for both computations. However, concentrations increased by about 400% during the very wet year of 2003, especially so for the SAV growing season average. During the most recent years concentrations were between 15 and 17 µg/l. Thus, the levels of interannual variability were large. In addition, during the drought year of 2002 chlorophyll-*a* concentration was below the Bay Program SAV criteria of 15 µg/l for the mesohaline Patuxent. During the wet year of 2003, concentration was far in excess of the criteria concentration and during more average flow conditions only slightly higher than criteria conditions. Considering only the chlorophyll-a criteria it appears that most of the mesohaline area would meet SAV chlorophyll-a criteria during dry

and average flow years if chlorophyll-*a* concentrations were reduced by relatively small amounts.

c. While we recognize that factors other than water column chlorophyll (e.g., turbidity, nutrient conditions, exposure to waves, grazing by swans and other herbivores) impact SAV survival, these data suggest that at the low end of contemporary TN loading rates chlorophyll levels are close to being consistent with SAV success. This further suggests that modest reductions in nutrient loading rates might well produce some ecosystem changes that would be positive, such as SAV re-invasion of the mesohaline estuary.

Submerged Aquatic Vegetation (SAV) Habitat Evaluation

In 1997, the EPC began an ambitious and diversified study of the near-shore water quality conditions important to SAV growth and survival. The primary goal of the near-shore water quality evaluation was to measure a suite of water quality parameters in the shallow near-shore habitat to assess compliance with established SAV habitat requirements and to directly measure epiphyte fouling rates using artificial substrates. In the 2005 field season, the EPC measured water quality conditions and epiphyte fouling rates at two locations in the lower Patuxent River Estuary. These locations, CBL (SV09) and Pin Oak (PXPO), were monitored for 4 consecutive weeks each, in the spring, summer and fall of 2005. These sites are under active consideration for large-scale SAV restoration. We summarize here the main management related points derived from this evaluation.

1. Growing season water column light attenuation (Kd) during 2005 continued the trend seen in 2004 with greatest water clarity in the spring at both sites. During the summer, water clarity at both sites frequently fell near or below the recommended habitat limit.
2. The temporal patterns of epiphyte fouling in 2005 were similar to those seen in previous years, with rapidly increasing fouling rates as water temperatures exceed 20ºC in the spring.
3. Summer and fall dry mass accumulation rates were high at both stations. Despite lower than normal river flow (and associated inputs of nutrients and sediments) in 2005, dry mass fouling rates were higher than those found in 2003 (high flow) and 2004 (average flow) during summer and fall.
4. Epiphyte total chlorophyll-*a* accumulation rates continued to show a strong link to nutrient availability.

Management Issues Based on Nutrient Budget Examination

There has been considerable effort expended to reduce nutrient inputs, mainly from point sources, and thereby restore the Patuxent estuary to a less eutrophic condition. However, there has not been a quantitative evaluation of all nutrient inputs, storages, internal losses, and exchanges with Chesapeake Bay before and after these management actions occurred. Nutrient budgets are a useful framework for such an evaluation and we summarize here the main management-related points derived from this budgeting effort.

1. There is clear evidence of nutrient load reduction at the head of the estuary. This pattern, for both TN and TP, is substantial and caused by decreased nutrient concentrations in point source discharges. Load reductions occurred earlier for P and were caused by the P-ban in detergents and improved P-removal at sewage plants. Reductions in N occurred later, were

not as large and were caused by use of biological N removal technologies at sewage treatment plants. These load reductions have been broadly touted as evidence of progress towards meeting Chesapeake Bay restoration goals.

2. There is no evidence that annual time-scale nutrient loads to the much larger lower estuary have declined in response to these management actions. Pre and post-BNR (Biological Nitrogen Removal) TN and TP fluxes from the upper to the lower estuary were almost identical. In fact, if TN and TP loads to this estuarine system were ranked from largest to smallest, the largest occurred during a wet year in the post-BNR period (1996) and the smallest during a dry year at the end of the pre-BNR period (1991). Thus, diffuse sources, particularly those from the middle portion of the drainage basin, dominate the nutrient input signature for this estuary. Water quality improvements will not likely occur until there are substantial reductions in diffuse source inputs.
3. Further reductions in N concentrations (to ~ 3 mg N l^{-1}) in point source discharges are planned; these reductions, if implemented, could reduce N loads by about 20-25 % to the upper estuary and about 9 % when all N sources to the estuary are considered.
4. There has been debate concerning the relative importance of Patuxent basin versus Chesapeake Bay nutrient sources contributing to the eutrophication of the Patuxent estuary. Some agencies claim that Patuxent basin nutrient reductions would be ineffective because large amounts of N and P are imported from the nutrient enriched Chesapeake Bay to the Patuxent estuary. Several estimates of nutrient exchange at the mouth of the Patuxent indicate that this is not the case; TN and TP are exported from the Patuxent to the Chesapeake Bay rather than the reverse. In addition, regression models relating nutrient loading rates to algal biomass accumulation and to hypoxic volumes account for much of the variability, suggesting that nutrients derived from the Patuxent basin are centrally involved. Finally, spring algal blooms and development of hypoxic waters first occur within the Patuxent rather than in the adjacent Chesapeake Bay; there is little evidence for importation of these features from the Bay to the Patuxent. Thus, nutrient load reductions in the Patuxent should, if of sufficient size, contribute to a lessening of eutrophic characteristics. However, recent work on the issue of Patuxent basin versus mainstem Chesapeake Bay as sources of N and P has indicated a trend wherein dissolved inorganic N is being imported into the Patuxent from the Bay and that this trend is intensifying. This is reason for concern, especially relative to water quality in the lower few miles of the estuary.
5. N and P budgets for about a dozen estuaries have been constructed in recent years. The magnitude and characteristics of inputs, losses and exports varied widely, as might be expected from a selection of estuaries that ranged from shallow lagoons to deeper, stratified coastal plain estuaries. However, a striking relationship was found between the percent of N and P exported and the log mean residence time of estuarine water. Thus, in rapidly flushed estuaries a large percent of inputs were exported while in more slowly flushed systems a smaller percent of inputs were exported. The Patuxent exported (as a percent of inputs) even less than predicted by this analysis. The practical issue here is that the Patuxent does not rapidly export nutrients. In fact, only about 13 % and 23% of TN and TP inputs, respectively, are exported. Most of the TN and TP exported are as dissolved or particulate organic compounds, indicating that they have been transformed from dissolved inorganic forms during transit through the estuary. Because of these large internal losses, the Patuxent contributes little to the eutrophication of Chesapeake Bay and probably even less

than suggested by export estimates because a large fraction of the TN and TP exported is in forms not immediately utilizable by phytoplankton communities.

6. One of the unexpected outcomes of this budget analysis was the importance of the tidal marshes as sinks for both N and P. Marshes removed about 30 and 31 % of all TN and TP inputs, respectively, despite the fact they are a small part of the land/seascape (1.3 %) of the Patuxent basin and 18% of the estuarine/marsh system. Thus, accreting marshes, such as those in the Patuxent, seem to act as an efficient "ecosystem-scale kidney" and should continue to be protected for the many values they provide. However, should the tidal marshes of the Patuxent fail to keep pace with rising sea level, as has occurred in about 50% of other Chesapeake Bay tidal marshes, the nutrient buffering effect of marshes would be lost; further still, eroding marshes could serve as a source of organic matter and nutrients, reversing the current role marshes appear to play.
7. There is substantial recycling of N and P from both the Patuxent estuary water column and sediments, especially during the warm periods of the year. Water column recycling, while large, can not support further increases in algal biomass but only maintain existing biomass. Nutrient releases from sediments, however, represent a "new" source of nutrients to the euphotic zone and can support increased algal standing stocks.
8. There is field evidence from the Patuxent that deep water hypoxic/anoxic conditions facilitate efficient recycling of N and P from estuarine sediments. We would expect sediment nutrient releases to diminish under conditions in which sediments remain oxidized through the summer months. Under such conditions P releases would be reduced due to reactions with oxidized iron at the sediment-water interface and N releases would also be reduced because coupled nitrification-denitrification would remain active. Thus, nutrient input reductions sufficient to relieve seasonal hypoxic/anoxic conditions might lead to larger improvements in water quality than expected because sediment nutrient recycling processes become less efficient. The quantitative impact of a drop in sediment nutrient recycling efficiency is not available at this time.
9. Our analyses indicate that major features of the estuary can be related to nutrient load changes. For example, the volume of hypoxic water and the size of algal standing crop were proportional to nutrient loading rates. In addition, time-series measurements of community metabolism and sediment releases of N also appear to be related to nutrient loading rates in the Patuxent and mainstem Chesapeake Bay. The practical aspect of these findings is that these processes, central to water quality, are very responsive to changes in nutrient inputs. There does not seem to be a large nutrient memory embedded in the sediments or water column of the Patuxent. Should substantial nutrient reductions occur, we would predict measurable improvements in water quality conditions within a year or slightly longer period.
10. A central issue concerning eutrophication of the Patuxent concerns how much nutrient load reduction is needed. The Patuxent is currently among the aquatic systems in Maryland cited as not being in compliance with water quality guidelines; a Total Daily Maximum Load (TMDL) computation is currently being developed for this estuary. Much of the TMDL result will be based on values computed from coupled land-use and water quality models and will thus be a function of how well those models capture features of the land and estuary. There are alternative approaches to estimating needed load reductions based on field measurements; in the long run, use of both approaches would be useful. Deep water dissolved oxygen concentrations in the Patuxent were examined for an 18 year period

(1986-2004). During summer average oxygen concentrations were below 1 mg l^{-1} for 6 of those years and below 2 mg l^{-1} for 10 additional years. During two drought years (1986 and 1992) summer dissolved oxygen concentration were at or slightly above 2 mg l^{-1}. Whole system TN and TP loads during those years averaged 5100 and 313 kg N and P day^{-1}, about 80 % and 70%, respectively, of average loads and 60 % and 45 %, respectively, of loads during high flow years. TN input reductions on the order of 1500 to 2500 kg N day^{-1} and TP reductions on the order of 100 kg P day^{-1} would be needed to be consistent with load conditions associated with deep water dissolved oxygen concentrations at or above 2 mg l^{-1}. We recognize that factors other than nutrient inputs play a role in determining water quality conditions so these values are most useful as a first approximation rather than as firm targets. An alternative approach is to examine nutrient loading rates when the estuary exhibited few symptoms of eutrophication. The earliest load estimates extend back to 1960, a period before sewage treatment plants were a significant feature of the basin and before intensive urban/suburban development was initiated in the watershed. TN and TP inputs at head of tide (HoT) averaged about 1200 kg N day-1 and 224 kg P day-1 during the decade of the 1960's. TP loads at the head of tide are now lower than during the 1960's by almost a factor of two. However, TN loads at the same location are still a factor of 1.6 greater than the earlier loads, despite BNR technology at the sewage treatment plants located above the head of tide. This comparison suggests the need for modest reductions in TN. However, about 70% of the contemporary TN load to the estuary comes from the basin located downstream of HoT. If we apply a modest diffuse TN yield for the basin area below HoT (areal rate = 5 kg N ha yr-1) to represent inputs appropriate for the 1960's, a total TN load to the estuary of 3100 kg N day^{-1} results. This is about half of average contemporary TN loads and about 30% higher than TN loads estimated for recent dry years. While also crude, this analysis reaches a conclusion not dissimilar from the previous one; TN loads need to be decreased on the order of 2500 - 3000 kg N day^{-1} to be comparable to loads associated with far less eutrophic conditions of the 1960's. The second estimate is somewhat larger than the first and this might reflect the fact that the first only required that deep water dissolved oxygen conditions be above 2 mg $^{-l}$ in summer while the latter estimate was associated with an ecosystem having a vibrant seagrass community, well developed benthos and oyster reefs as well as better deep water oxygen conditions.

11. Whatever nutrient input reductions are eventually agreed to during the TMDL process, several things seem clear. First, TN reduction will need to be substantial to reduce hypoxic conditions during normal and wet years and larger still to restore other community components (SAV, benthos) to this ecosystem in addition to improving oxygen conditions in deep waters. Second, further reductions in point source discharges are technically possible and, if instituted, will measurably reduce loads. However, most of the needed reductions will involve diffuse sources and to date there appears to have been little progress in dealing with this source of nutrients.

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1.0 Introduction

W.R. Boynton

1.1 Background

Two decades ago an historic agreement led to the establishment of the Chesapeake Bay Partnership whose mandate was to protect and restore the Chesapeake Bay ecosystem. The year 2000 saw the signing of *Chesapeake 2000,* a document that incorporated very specific goals addressing submerged aquatic vegetation (SAV) restoration and protection and the improvement and maintenance of water quality in Chesapeake Bay and tributaries rivers.

The first phase of the Chesapeake Bay Program was undertaken during a period of four years (1984 through 1987) and had as its goal the characterization of the existing state of the bay, including spatial and seasonal variation, which were keys to the identification of problem areas. During this phase of the program the Ecosystems Processes Component (EPC) measured sediment-water oxygen and nutrient exchange rates and determined the rates at which organic and inorganic particulate materials reached deep waters and bay sediments. Sediment-water exchanges and depositional processes are major features of estuarine nutrient cycles and play an important role in determining water quality and habitat conditions. The results of EPC monitoring have been summarized in a series of interpretive reports (Boynton *et al.* 1985, 1986, 1987, 1988, 1989, 1990, 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004 and 2005). The results of this characterization effort have confirmed the importance of deposition and sediment processes in determining water quality and habitat conditions. Furthermore, it is also now clear that these processes are responsive to changes in nutrient loading rates.

The second phase of the program effort, completed during 1988 through 1990, identified interrelationships and trends in key processes monitored during the initial phase of the program. The EPC was able to identify trends in sediment-water exchanges and deposition rates. Important factors regulating these processes have also been identified and related to water quality conditions (Kemp and Boynton, 1992; Boynton *et al.* 1991).

In 1991 the program entered its third phase. During this phase the long-term 40% nutrient reduction strategy for the bay was reevaluated. In this phase of the process, the monitoring program was used to assess the appropriateness of targeted nutrient load reductions as well as provide indications of water quality patterns that will result from such management actions. The preliminary reevaluation report (Progress Report of the Baywide Nutrient Reduction Reevaluation, 1992) included the following conclusions: nonpoint sources of nutrients contributed approximately 77% of the nitrogen and 66% of the phosphorus entering the bay; agricultural sources were dominant followed by forest and urban sources; the "controllable" fraction of nutrient loads was about 47% for nitrogen and 70% for phosphorus; point source reductions were ahead of schedule and diffuse source reductions were close to projected reductions; further efforts were needed to reduce diffuse sources; significant reductions in phosphorus concentrations and slight increases in nitrogen concentrations have been observed in some areas of the bay; areas of low dissolved oxygen have been quantified and living resource water quality goals established; simulation model projections indicated significant reductions in low dissolved oxygen conditions associated with a 40% reduction of controllable nutrient loads.

During the latter part of 1997 the Chesapeake Bay Program entered another phase of re-evaluation. Since the last evaluation, programs had collected and analyzed additional information, nutrient reduction strategies had been implemented and, in some areas, habitat improvements have been accomplished. The overall goal of the 1997 re-evaluation was the assessment of the progress of the program and the implementation of necessary modifications to the difficult process of restoring water quality, habitats and living resources in Chesapeake Bay. During this portion of the program, EPC has been further modified to include intensive examination of SAV habitat conditions in several regions of the Chesapeake Bay in addition to retaining long-term monitoring of sediment processes in the Patuxent estuary. The previous report, *EPC Level 1 Interpretive Report No. 20*, concluded the effort to monitor sediment-water oxygen and nutrient exchanges (Boynton, *et al.* 2003).

Chesapeake 2000 involves the commitment of the participants *“to achieve and maintain the water quality necessary to support aquatic living resources of the Bay and its tributaries and to protect human health."* More specifically, this Agreement focuses on: 1) living resource protection and restoration; 2) vital habitat protection and restoration; 3) water quality restoration and protection; 4) sound land use and; 5) stewardship and community engagement. The current EPC program has activities that are aligned with the habitat and water quality goals described in this agreement.

The Chesapeake Bay Water Quality Monitoring Program was initiated to provide guidelines for restoration, protection and future use of the mainstem estuary and its tributaries and to provide evaluations of implemented management actions directed towards alleviating some critical pollution problems. A description of the complete monitoring program is provided in:

Magnien *et al.* (1987),

Chesapeake Bay program web page http://www.chesapeakebay.net/monprgms.htm

DNR web page http://www.dnr.state.md.us/bay/monitoring/eco/index.html.

In addition to the EPC program portion, the monitoring program also has components that measure:

1. Freshwater, nutrient and other pollutant input rates,
2. chemical and physical properties of the water column,
3. phytoplankton community characteristics (abundances, biomass and primary production rates) and
4. benthic community characteristics (abundances and biomass).

1.2 Conceptual Model of Water Quality Processes in Chesapeake Bay

During the past two decades much has been learned about the effects of both natural and anthropogenic nutrient inputs (*e.g.*, nitrogen, phosphorus, silica) on such important estuarine features as phytoplankton production, algal biomass, seagrass abundance and distribution and oxygen conditions in deep waters (Nixon, 1981, 1988; Boynton *et al.* 1982; Kemp *et al.* 1983; D'Elia *et al.* 1983; Garber *et al.* 1989; Malone, 1992; and Kemp and Boynton, 1992). While our understanding is not complete, important pathways regulating these processes have been identified and related to water quality issues. Of particular importance here, it has been determined that (1) algal primary production and biomass levels in many estuaries (including Chesapeake Bay) are responsive to nutrient loading rates, (2) high rates of algal production and algal blooms are sustained through summer and fall periods by recycling of essential nutrients that enter the system during the high flow periods of the year, (3) the "nutrient memory" of estuarine systems is relatively short (one to several years) and (4) submerged aquatic vegetation (SAV) communities are responsive to water quality conditions, especially light availability, that is modulated both by water column turbidity regimes and epiphytic fouling on SAV leaf surfaces.

Nutrients and organic matter enter the bay from a variety of sources, including sewage treatment plant effluents, fluvial inputs, local non-point drainage and direct rainfall on bay waters. Dissolved nutrients are rapidly incorporated into particulate matter via biological, chemical and physical mechanisms. A portion of this newly produced organic matter sinks to the bottom, decomposes and thereby contributes to the development of hypoxic or anoxic conditions and loss of habitat for important infaunal, shellfish and demersal fish communities. The regenerative and large short-term nutrient storage capacities of estuarine sediments ensure a large return flux of nutrients from sediments to the water column that can sustain continued high rates of phytoplanktonic growth and biomass accumulation. Continued growth and accumulation supports high rates of deposition of organics to deep waters, creating and sustaining hypoxic and anoxic conditions typically associated with eutrophication of estuarine systems. To a considerable extent, it is the magnitude of these processes that determines water quality conditions in many zones of the bay. Ultimately, these processes are driven by inputs of organic matter and nutrients from both natural and anthropogenic sources. If water quality management programs are instituted and loadings of organic matter and nutrients decrease, changes in the magnitude of these processes are expected and will serve as a guide in determining the effectiveness of strategies aimed at improving bay water quality and habitat conditions. The schematic diagram in Figure 1-1. summarizes this conceptual eutrophication model where increased nitrogen (N) and phosphorus (P) loads result in a water quality degradation trajectory and reduced N and P loads lead to a restoration trajectory. There is ample empirical evidence for the importance of N and P load variation. For example, water quality and habitat conditions change dramatically between wet and dry years, with the former having degradation trajectory characteristics and the latter, restoration trajectory characteristics (Boynton and Kemp, 2000; Hagy *et al*. 2004). Within the context of this model a monitoring component focused on SAV and other near-shore habitat and water quality conditions has been developed and was fully operational in the Patuxent River estuary during 2005.

Specifically, this program involved monthly (March – November), detailed surface water quality mapping using the DATAFLOW system, high frequency (15 minute intervals) monitoring of selected water quality variables at four fixed sites located from tidal fresh to mesohaline portions of the Patuxent, and SAV planting (via seeds) and monitoring of SAV epiphytic growth at Patuxent River sites.

In all of these monitoring activities the working hypothesis is if anthropogenic nutrient and organic matter loadings decrease, the cycle of high organic deposition rates to sediments, sediment oxygen demand, release of sediment nutrients, continued high algal production, and high water column turbidity will also decrease. As a result, the potential for SAV re-colonization will increase and the status of deep-water habitats will improve.

1.3 Objectives of the Water Quality Monitoring Program

The EPC has undergone program modification since its inception in 1984 but its overall objectives have remained consistent with those of other Monitoring Program Components. The objectives of the 2005 EPC program were as follows:

1. Characterize the present status of the Patuxent River estuary (including spatial and seasonal variation) relative to ***near-shore habitat and water quality conditions***. This portion of the program (DATAFLOW) involved high-resolution water quality mapping in the Patuxent River estuary.

4. Evaluate the variation in spatial and temporal scales of water quality in both near-shore and off-shore areas of the Patuxent River estuary using the same DATAFLOW mapping system.

5. Measure ***epiphyte accumulation rates*** on SAV mimics and associated water quality conditions at several sites in the Patuxent River estuary, extending the developing time series of this important SAV habitat indicator process.

4. ***Integrate the information*** collected in this program with other elements of the monitoring program to gain a better understanding of the processes affecting water quality of the Chesapeake Bay and its tributaries and the maintenance and restoration of living resources.

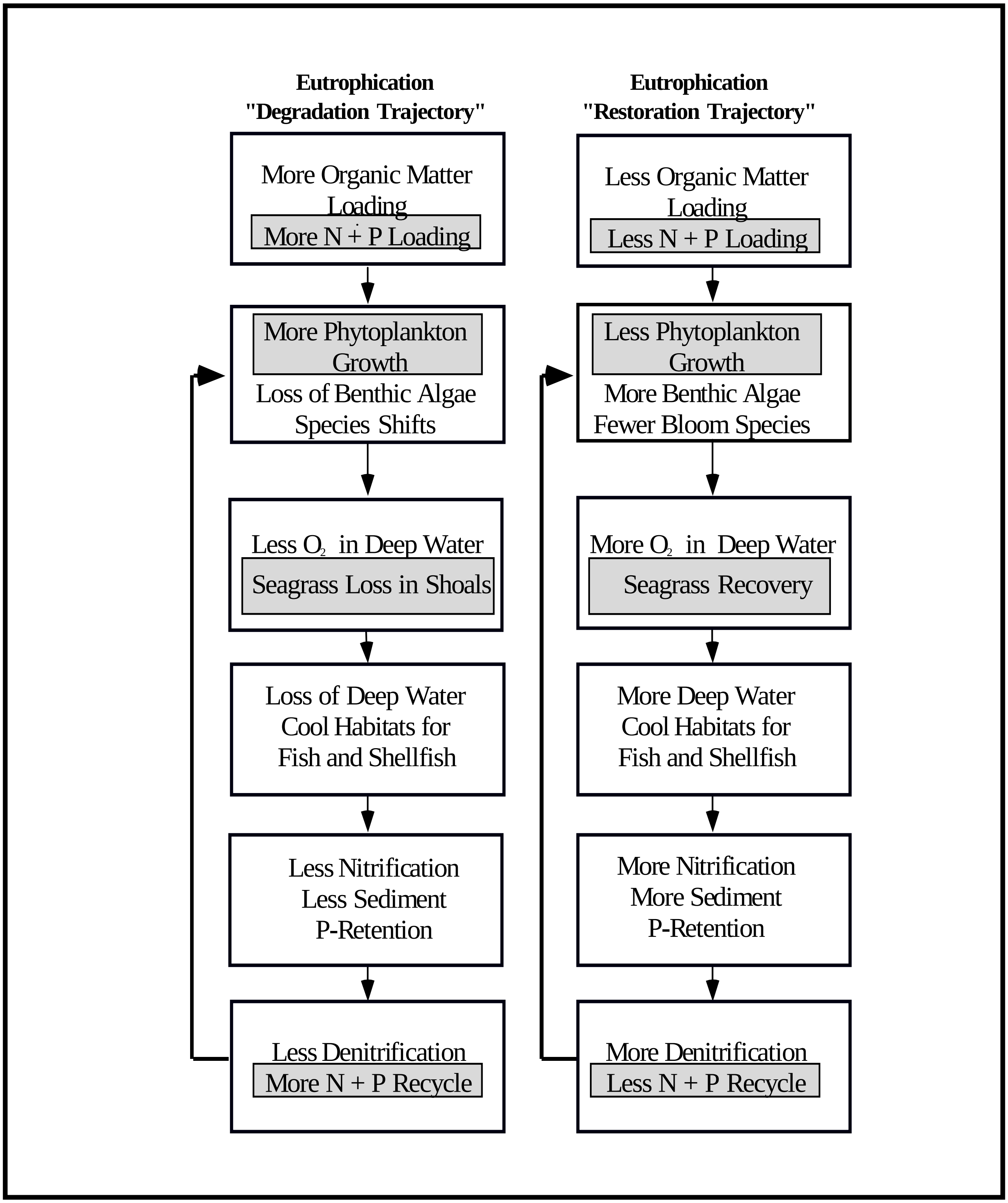

Figure 1-1. A simplified schematic diagram indicating degradation and restoration trajectories of an estuarine ecosystem. Lightly shaded boxes in the diagram indicate past and present components of the EPC program in the Patuxent River and Tangier Sound. (Adapted from Kemp *et al*. 2005)

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2.0 Patuxent River Flows and Total Nitrogen Loads

W.R. Boynton

2.1 Introduction

2.1.1 Background and Management Issues

One of the central features of the Chesapeake Bay Program and Maryland's component of this program is an emphasis on reduction of nutrient loading rates to the mainstem Bay and tributary rivers. It has become clear that the Bay ecosystem is nutrient over-enriched and that this leads to a variety of water quality, habitat and living resource problems (e.g., Kemp *et al*. 2005). It has also become clear that a large fraction of the nutrient load to the Bay and tributaries comes from diffuse sources (e.g., Boynton *et al*. 1995). Hence, consideration of river flow, the vehicle of diffuse source nutrient transport, is of central interest to those tasked with understanding the performance of these systems and deciding on appropriate management actions. Finally, it also appears that these ecosystems, such as the Patuxent River estuary, respond to changes in river flow and associated nutrient loads on relatively short time-scales (~year; Boynton and Kemp 2000; Hagy *et al*. 2004). An examination of multi-decade records of these parameters (flow and nutrient loads) is appropriate and useful.

2.1.2 Patterns of River Flow

There is a very substantial record of monitoring available for the Patuxent. River flows, a key variable regulating water quality and habitat conditions, are available at the fall line (Bowie, MD) since 1978. We have summarized average annual flows for the period of the monitoring Program (1985-2005) and these are shown in Figure 2-1. During this period of record, flows averages about 17.5 m^3 sec^{-1} but there were large departures from this average flow condition. Using one standard deviation of the mean as an index of strong departure from average conditions, there were five wet or very wet years, seven dry or very dry years and nine years of near average flow. The period before sewage treatment plants were upgraded to seasonally remove nitrogen (pre-BNR; before 1992) were dryer than the years following BNR (1993 to present). During the last four years river flow was highly variable with one year having the highest flow on record (2003), another year the lowest flow on record (2002), a low flow year (2005) and a near-average year (2004). Given this variability, we would expect similar variability in water quality and habitat conditions in the estuary during this period of time.

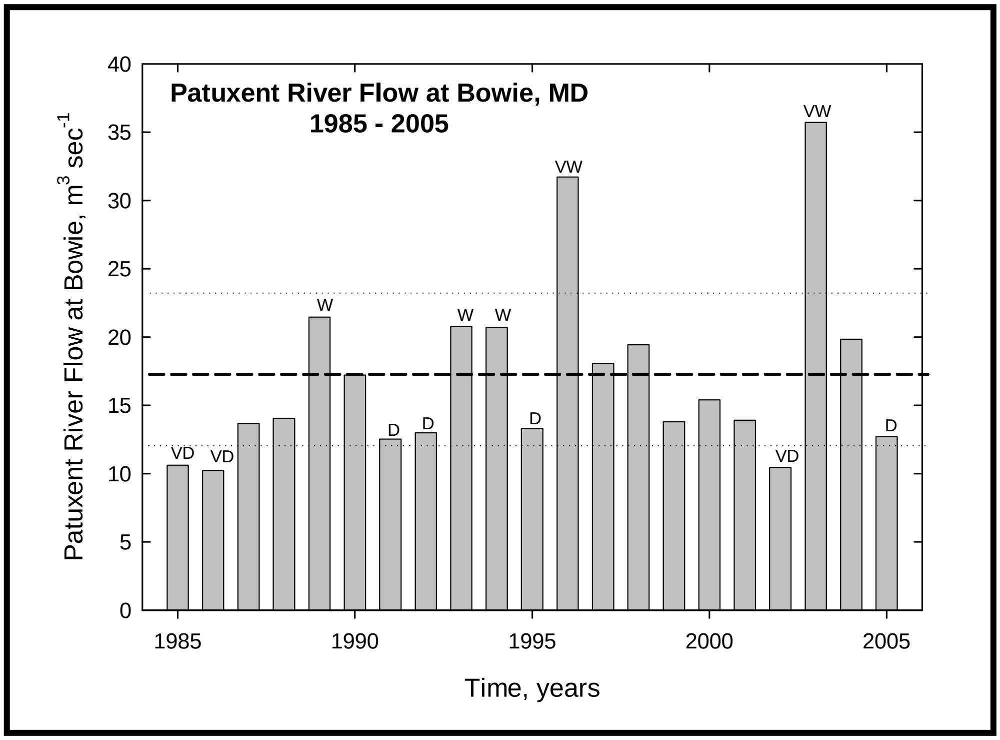

Figure 2-1. A time series of annual average river flows measured at the fall line (Bowie, MD) of the Patuxent River. The bold dashed line represents the 21 year average flow. The light dotted lines represent one standard deviation of the mean. Abbreviations are: VW = very wet; W = wet; VD = very dry; D = dry. Data were from USGS (2005).

2.2 Methods

2.2.1 Nutrient Loads to the Mesohaline Estuary: Use of Box Models

Until recently we made assessments of nutrient loads to the Patuxent River estuary by using the nutrient load at the fall line as an index of the actual, full loads to the entire estuarine system. In some limited instances, the full nutrient load was estimated using the load at the fall line for the upper portion of the drainage basin, output from landscape models for the portion of the basin below the fall line and estimates of atmospheric N deposition directly to surface waters of the estuary based on data collected at adjacent monitoring sites (e.g., Boynton *et al*. 2006; see Chapter 3.0 in this report). However, we did not until recently have the ability to routinely make such load estimates for distinct portions of the estuary. Hagy *et al* (2000) developed a box-model for the Patuxent River estuary and, more recentky, Testa (2006) coupled a version of this model with nutrient concentration data collected by the Biomonitoring Program. As we will demonstrate, while very useful, this effort is also a very good example of a synthesis of multiple aspects of the monitoring program. Freshwater inflows were estimated by USGS (2005), water quality developed by the Biomonitoring Program and river morphology (volumes) developed from earlier studies (e.g., Cronin and Pritchard 1975). The end result of this box modeling effort was a set of TN loading estimates for the head of the mesohaline estuary. The importance of this is that all sources of inputs upstream of Benedict are included in this estimate and there is no longer the need to use just the fall line load as an index of nutrient load magnitude or temporal pattern.

Monthly load estimates from 1985 – 2005 are shown in Figure 2-2. During this period of time loads averaged about 2700 kg TN day^{-1}and ranged from several hundred to more than 10,000 kg TN day^{-1}. Despite this very considerable variability, seasonal-scale patterns were distinct with lower input rates during summer and fall and much higher rates during winter and spring. Very high inputs (>8000 kg TN day^{-1}) occurred during 1989, 1993, 1994, 1996 and 2003, all associated with particularly wet periods indicating the importance of diffuse sources of nutrients in this system.

It should be noted that BNR technologies at the major sewage treatment plants were operational by about 1992. These plants operated (and with one exception; Western Branch Sewage Treatment Plant) BNR technology on a seasonal basis (April – October). Combined, these plants remove about 1100 kg N/day when they are operating BNR technologies. However, TN loads to the mesohaline portion of the Patuxent River estuary do not show a marked decline during the post-BNR period. In fact, 8 of the 9 highest load months in the data record occurred after BNR became operational. This observation points to two factors, one of which is quite certain and the other more speculative. The post-BNR period was wetter than the pre-BNR period and hence diffuse sources of N were larger during the more recent post-BNR period. Certainly the magnitude of loads indicates the importance of diffuse sources in this system. The second factor is changing land use. During the period 1960 – 1980 much of the development in the Patuxent was located in the upper portion of the basin. The fact that 8 of the 9 major sewage treatment plants are located in the upper basin supports this observation. However, since the 1990's development (e.g., loss of forested and pasture lands) has rapidly increased in the lower basin and could also have contributed to the very large loads estimated to have occurred during the wetter, post-BNR period.

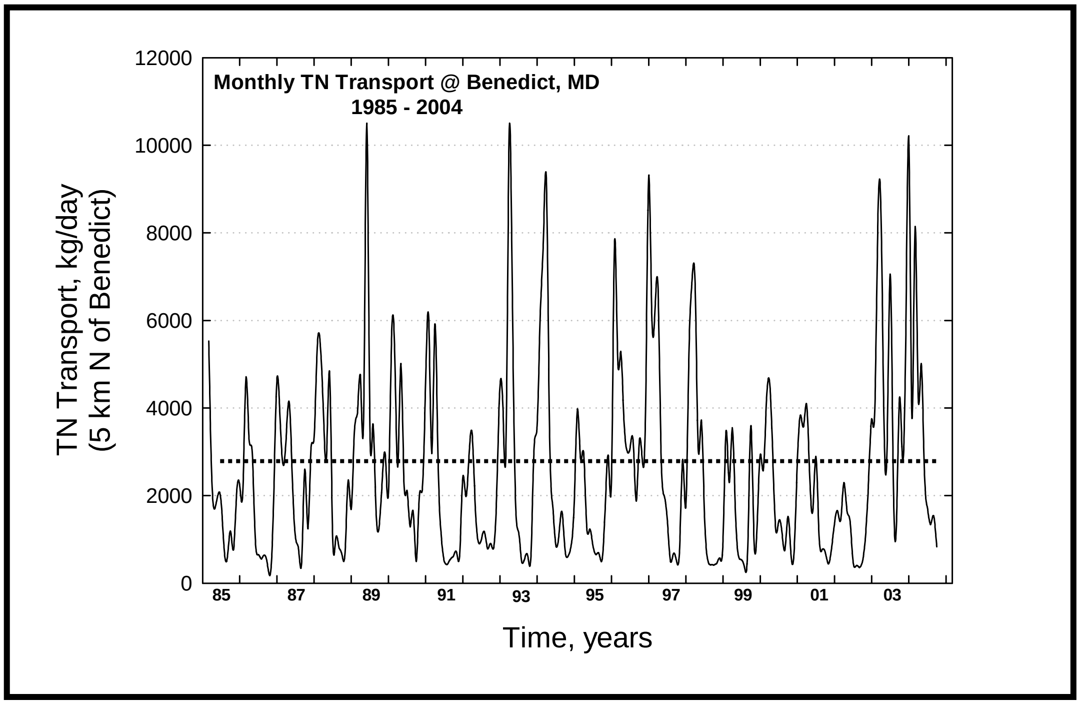

Figure 2-2. Monthly time series of total nitrogen (TN) loads computed for an estuarine cross-section located 4 km north of Benedict, MD at the head of the mesohaline estuary. Water transport was estimated using a box-model (Hagy *et al*. 2000; Testa 2006). Net nutrient flux was computed using the box model coupled to nutrient concentration data collected by the Biomonitoring Program (Chesapeake Bay Water Quality Monitoring Program 2005). Bold dotted line represents the long-term annual average TN input (~2700 kg TN day $^{-1}$). These rates were computed by Testa (2006).

2.3 Results and Discussion

2.3.1 TN Loads at the Fall Line versus Benedict, MD

To examine the relative proportion of loads (or transport; both have units of kg TN day^{-1}) coming from the upper and middle basins we developed a scatter plot of TN loads measured at the fall line versus loads computed at Benedict using the box model (Figure 2-3). In addition, loads were divided, as previously done, into pre and post-BNR periods. In both pre and post-BNR years these loads were strongly related one to the other. During the pre-BNR period loads at Benedict were slightly larger than those measured at the fall line. However, during the post-BNR years, loads at Benedict were 50% higher than those at the fall line. Several things are suggested by these relationships. First, the fact that there are substantial differences among years (e.g., wet vs dry years) indicates the importance of diffuse sources in this system. Second, the increase in loads at Benedict relative to those at the fall line suggests new nutrient sources, possibly related to land-use changes and also to the generally wetter conditions associated with the post-BNR period.

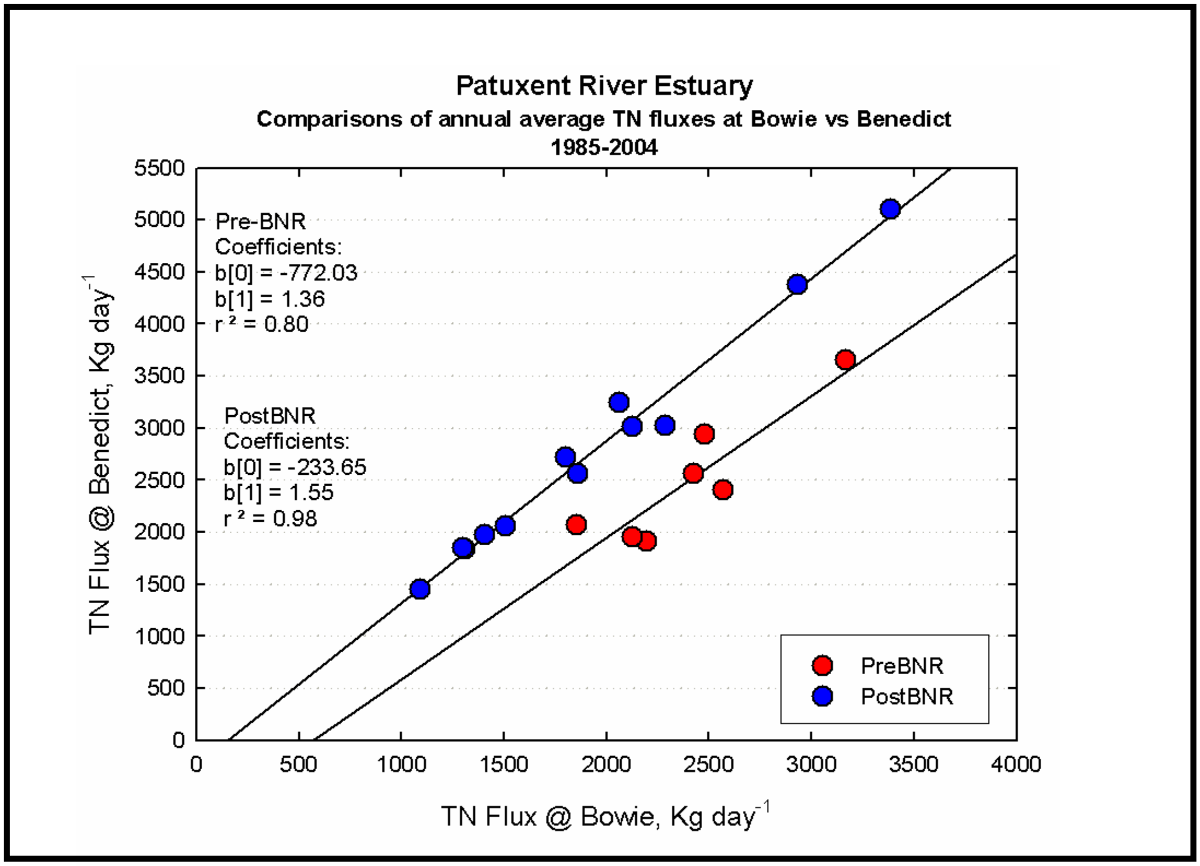

Figure 2-3. A scatter plot of average annual TN flux measured at the fall line of the Patuxent River versus TN flux estimated using a Box model for Benedict, MD. Data were separated in to pre (1985-1992) and post-BNR (1993 -2005) periods. Box model computations of TN flux were provided by Testa (2006) and fall line loads are from USGS (2005).

2.3.2 Estimation of Impact of Sewage Treatment Plant Upgrades on Nutrient Loads

Total nitrogen fluxes calculated via the box model for an estuarine cross-section in the vicinity of Benedict, MD were plotted as a function of average annual river flow for pre and post-BNR years. Several interesting points emerged. First and most importantly, TN fluxes at comparable river flows were lower during the post-BNR period than during the pre-BNR period. Said another way, per unit of river flow less TN entered the mesohaline estuary during the post-BNR period. As indicated in the diagram, at average river flow (~17.5 m3 sec -1) about 500 kg TN day $^{-1}$ less TN is delivered to the mesohaline estuary. Boynton *et al* (2006) have estimated that the total reduction in TN loads due to BNR at sewage treatment plants averages about 1100 kg TN day^{-1}. We have argued earlier that there may well have been increased TN loads coming from the middle basin due to several decades of land-use changes (e.g., conversion of forests to residential/urban uses) and we have shown that the post-BNR period was wetter, leading to generally higher diffuse source loads. In spite of these processes, at a given level of river flow, TN loads were still lower during the post-BNR period. The most reasonable explanation for this is that nitrogen removal at sewage treatment plants have contributed to measurable TN load reductions to the mesohaline estuary. While loads remain moderate to high compared to other estuarine ecosystems (Boynton and Kemp 2006), BNR has apparently caused modest load reductions. BNR reductions have helped, but are partially off-set by diffuse source loads coming from the basin between Bowie and Benedict.

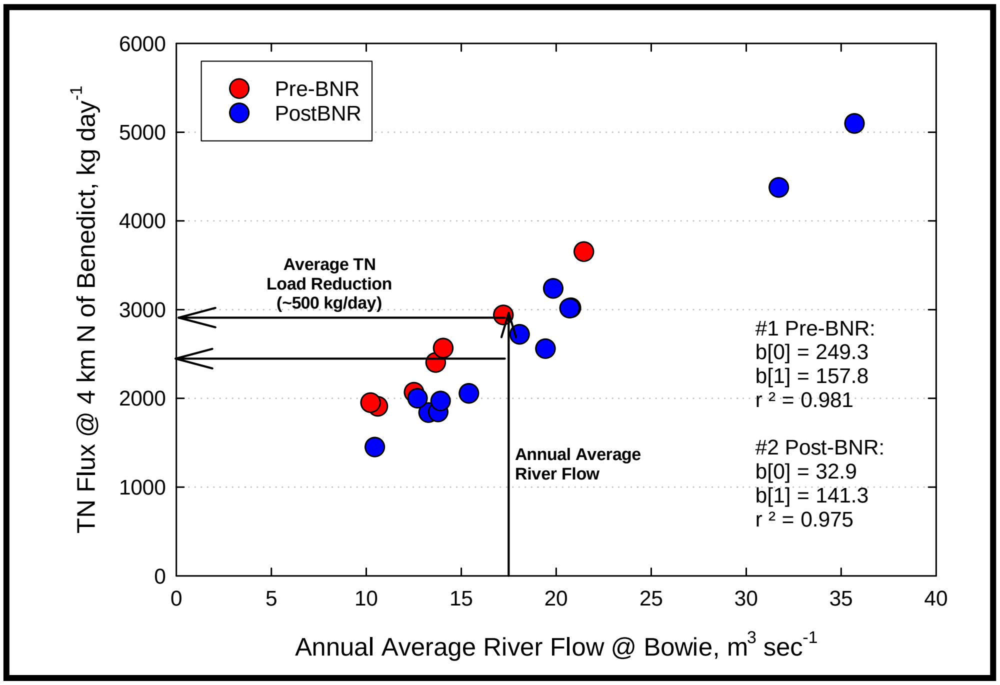

Figure 2-4. A scatter plot of average annual river flow at the fall line versus average annual TN flux computed at an estuary cross-section 4 km north of Benedict, MD. Pre and post-BNR periods are indicated by red and blue symbols, respectively. The vertical solid line indicates average river flow during the 21 year monitoring period. The two horizontal lines represent the average TN flux at Benedict, MD to the mesohaline estuary before and after BNR additions to sewage treatment plants in the basin. At average flow conditions, there appears to be a reduction in load of about 500 kg TN/day. River flow data were from USGS (2005) and TN flux estimates were made by Testa (2006).

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3.0 Community Metabolism: An Integrated Measure of Ecosystem Activity and an Additional Use of Continuous Monitoring Data for Estimating System Status, Trends and Responses to Nutrient Load Modifications

W. R. Boynton, K. V. Wood, D. A. Jasinski, and E. Perry

3.1 Introduction

3.1.1 Background

Rates of primary production and community respiration are fundamental characteristics of aquatic ecosystems. The late oceanographer J. D. H. Strickland (1961) once noted that a lack of interest and understanding of aquatic production would not be unlike a lack of interest in these processes in agricultural situations…not a likely occurrence. However, the production and respiration characteristics of estuarine systems have been far less well studied or monitored than is the case with portions of coastal waters and certainly of lakes. Since it is well-established that these rates are sensitive to nutrient loading rates (e.g., Nixon et at. 1992; Kemp *et al*. 2005; Boynton and Kemp 2006) reliable estimates of these rates would serve both as an index of system performance as well as an indicator of system response to nutrient load reductions.

The original method for making estimates of community production and community respiration was developed by Odum and Hoskins (1958) for estuarine waters. The original technique involved making several measurements of dissolved oxygen during a diel period with particular emphasis on sampling near dawn and near dusk so as to obtain DO minimum and maximum values, respectively. Temperature and salinity measurements also needed to be collected. In practice, investigators generally were able to obtain 4 to 6 observations during a diel period due to the laborious nature of sampling and making DO determinations. To compute production and respiration rates, DO concentration was plotted as function of time and the rate of change in DO was then computed. This rate of change curve was then "corrected" for DO diffusion between air and the water column. To make this correction, percent saturation of DO was computed using the temperature and salinity observations. When water was supersaturated during daylight periods (>100% saturated) DO diffuses from the water to the atmosphere and hence the rate of change curve was underestimating production. Under these circumstances the rate of change curve was increased by the amount of oxygen estimated to have diffused from the water to the atmosphere. Air-water diffusion was estimated by applying a diffusion coefficient to the gradient in DO saturation between water and atmosphere. Diffusion coefficients have been estimated with a variety of techniques and values of about 0.5 g O_2 m^{-2} hr^{-1} at 100% saturation gradient have often been used in shallow and generally protected estuarine situations (Caffrey 2004). In practice, this correction amounts to 5 -30% of the corrected rate of change curve. Once the curve has been corrected, the positive rate of change curve is integrated and is an estimate of community production. Similarly, the negative portion of the rate of change curve is integrated and is an estimate of nighttime respiration. Gross primary production (i.e., net production plus the respiratory losses associated with this production) is estimated by obtaining an average of hourly nighttime respiration, multiplying this value by the hours of daylight and then adding this value to the net daytime production estimate. While very useful, the original technique suffered because of the laborious nature of data collection and the time-consuming nature of the graphing and correcting rate of change curves. Nevertheless, numerous studies adopted the technique and confirmed the responsive nature of these rates to nutrient or organic matter inputs (Oviatt *et al*. 1993).

3.1.2 Current Motivations for Use of Open Water Technique

During the last several decades several things have changed in the monitoring/research world that have made it far more feasible and affordable to consider using open water community metabolism measurements as components of monitoring or research programs in estuarine systems. First, several generations of in-situ devices have come into common use, each providing more reliable measurements of DO, temperature, salinity, pH and more recently chlorophyll-a and turbidity. These devices now have the capability of making these measurements in a reasonably reliable fashion for periods of one to two weeks in nutrient-enriched estuarine ecosystems. The addition of wiper blades and other self-cleaning devises have further enhanced the reliability of these devices. Finally, these in-situ sondes are capable of making rapid (~ 20 measurements/minute; more frequently measurements are made at a frequency of 4/hour), repeated measurements thus ensuring that a fine-scale record of diel changes in concentrations is captured. Second, computational capacity and associated software have improved greatly. It is now possible to readily store and manipulate the large data files associated with a group of continuously recording sondes. It is also possible, as we will describe in detail later in this Chapter, to develop programs to compute metabolism variables, thus largely removing the time consuming nature of these analyses. Thus, reliable data sets collected at frequencies amenable for metabolism calculations and computer hardware and software more than capable of conveniently storing and making calculations have combined to make these community-scale processes very attractive.

3.1.3 Applications for Monitoring and Management

One of the central issues related to Chesapeake Bay restoration is the reduction of nutrient loading rates. This goal results from the fact that algal production of organic matter is often related to loading rates of both nitrogen and phosphorus. Further, this organic matter often sinks to deeper waters, decomposes via respiratory processes and oxygen is depleted in the process. Having in-situ measurements of these two processes (e.g., production and respiration) provides a strong empirical link to Bay Program goals, namely, the reduction of nutrient loading rates. Earlier work with this sort of measurement in the Patuxent River estuary indicted a strong linkage between loading rates and metabolic rates. In fact, Sweeney (1995) and Burger and Hagy (1998) found near-linear responses of production and respiration to nitrogen loading rate corrected for water residence time.

Moreover, in these studies metabolic variables exhibited a factor of 3-4 range in magnitude between periods prior to large nutrient loads and current times characterized by much larger loads. Similar results have been reported by other investigators (see D'Avanzo and Kremer 1994 and Boynton and Kemp 2006 for additional examples). In addition to changes in metabolic magnitude, it also appears that the day to day variability in these rates increase at higher nutrient loading rates and decreases substantially at lower loading rates. Finally, the seasonal pattern of metabolism also appears to be responsive to nutrient loading rates. At lower rates, metabolic variables tend to reach highest levels during or immediately after the spring phytoplankton bloom (April-May); rates during the summer (June – September) are lower and there is a small increase in metabolism during the early fall (October). Under more eutrophic conditions, metabolic rates increase during the spring but continue to increase further during summer into early fall before decreasing with the onset of winter. Thus, there are at least three indices derived from these metabolic rates that serve to tell us about system performance and these include magnitude of rates, variability of rates and seasonal pattern. We would expect all three to decrease as nutrient loading rates decrease.

3.1.4 Current Potential Data Sets

There are at present a very large number of sites for which metabolism computations might be applied. ConMon-like measurements began about 1998 at three sites in the Pocomoke River. During 2005 there were 39 sites being monitored in Maryland tributary rivers of Chesapeake Bay and the Maryland Coastal Bays. At most of these sites measurements are collected from April through October and sites remain active for three consecutive years; in a few cases more years of data are available. Thus, at a specific site there is the potential for about 210 measurements of production and respiration per year and a total of about 630 measurements during a three year deployment cycle. Such a relatively large set of rate process measurements would certainly help us better understand the status and trends of these systems as nutrient and sediment loads are modified by management actions.

3.2 Methods

3.2.1 Description and Operation of Metabolism Macro: Preliminary Program

Based on earlier work by Burger and Hagy (1998) for calculating water column metabolism from near-continuous monitoring data, an automated Excel spreadsheet (Metabolism.xls) was developed. The worksheet was automated using Microsoft's Visual Basic for Applications (VBA) programming language. Briefly, the steps the spreadsheet undertakes are as follows:

1. An excel file, containing the continuous monitoring data configured by the user in a requisite format (Figure 1) is read into the spreadsheet.

2. Dates and times are reformatted into a continuous time variable or serial number.

3. Sunrise and Sunset times for each date are calculated based on the latitude and longitude of the station.

4. Rows are inserted into the dataset to create an observation at sunrise and sunset on each day.

5. Each observation in the dataset is assigned a daypart – Sunrise, Day, Sunset, or Night

6. Each observation is assigned to a “Metabolic Day”. Each metabolic day begins at sunrise on the current day and continues to the observation immediately before sunrise on the following day.

7. For sunrise/sunset observations created in Step 4, values for water temperature, salinity, dissolved oxygen and dissolved oxygen saturation are calculated by taking the mean of the observations immediately before and after sunrise and sunset.

8. The change in DO, time, air/sea exchange and oxygen flux is calculated between each consecutive observation.

9. The minimum and maximum DO values are calculated between sunrise and sunset on each day and these values are labeled “metabolic dawn” and “metabolic dusk”.

10. Sums of the changes in DO, time, air/sea exchange and DO flux (step 8) are calculated for each metabolic day for the periods between sunrise and metabolic dawn, metabolic dawn and metabolic dusk, metabolic dusk and sunset, and sunset and the following sunrise.

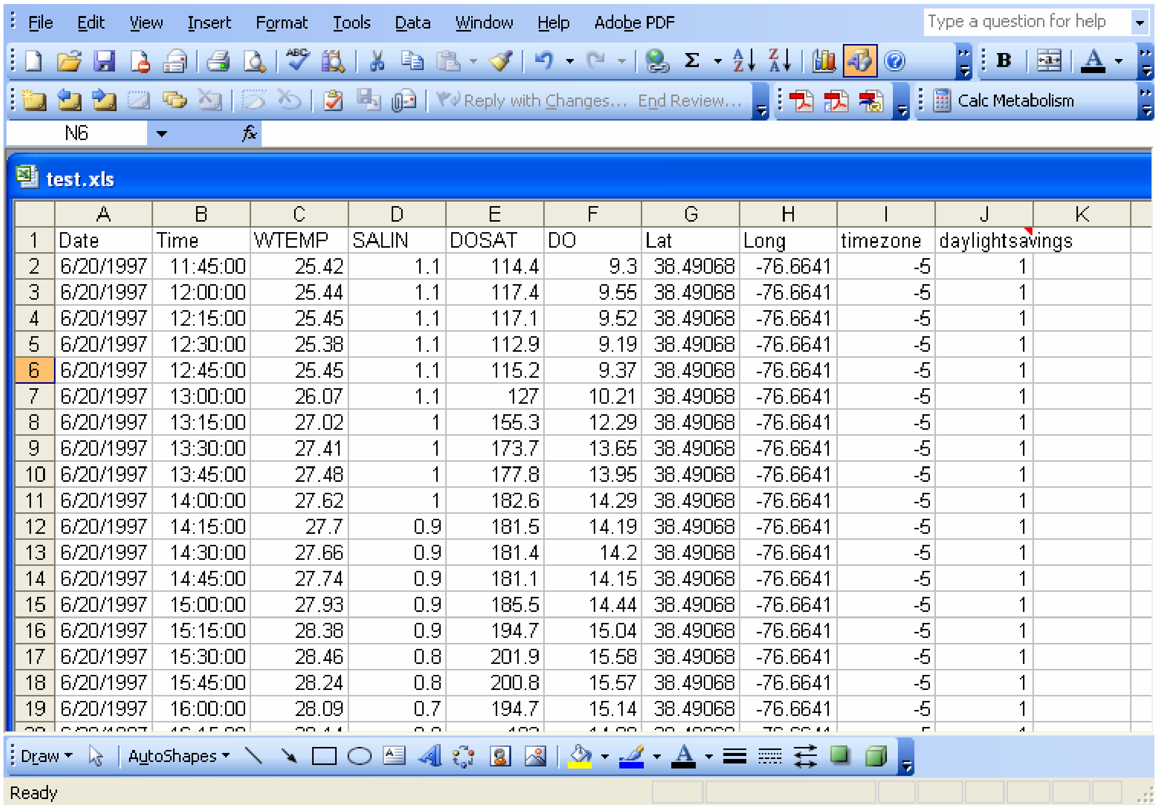
11. From these sums, 6 metabolic variables are calculated and these include: rn, rnhourly, pa, pa_star, pg, pg_star.

These variables are defined as follows:
rn = Nighttime (sunset to following sunrise) summed rates of DO flux corrected for air/water diffusion.
rnhourly = rn divided by the number of nighttime hours
pa = The sum (both positive and negative) of oxygen flux (corrected for air-water diffusion) for the dawn, day and dusk periods.
pa_star = summed oxygen flux (corrected for air-water diffusion) for the day period
pg = pa + daytime respiration. Daytime respiration = rnhourly * (number of hours of daytime+dawntime+dusktime).
pg_star = pa_star + daytime respiration as defined above.

Air-water diffusion of oxygen is considered in these computations and the diffusion correction is based on the difference between observed DO percent saturation and 100% saturation multiplied by a constant diffusion coefficient. For these preliminary computations a diffusion coefficient of 0.5 g O2m-2 hr-1 was selected as generally representative of conditions frequently encountered in tributary situations (Caffrey 2004).

One of the primary assumptions of this method is that temporal changes in DO measured by the continuous monitors are due solely to metabolism (i.e., oxygen production from photosynthesis and oxygen loss from respiration) occurring at the station and not due to advection of water masses with different oxygen conditions moving past the instrument. Because Chesapeake Bay is a tidal system, this may not always be the case. Depending on the hydrodynamics of a given station, this assumption may be more or less realistic and may also be variable from date to date. One way of censoring dates where DO is affected by advection is to preview the data graphically prior to metabolism calculations and determine if there is a relationship between salinity and DO. Large changes in salinity suggest moving water masses and therefore, advection. These dates could then be flagged and reviewed before metabolism variables are calculated.

Another way of dealing with advection is to incorporate in the code a method of detecting changes DO associated with changes in salinity. It might then be possible to apply a site specific correction factor to remove the advection affect on DO. These possibilities could be investigated further in the future.



	A	B	C	D	E	F	G	H	I	J
1	Date	Time	WTEMP	SALIN	DOSAT	DO	Lat	Long	timezone	daylightsavings
2	6/20/1997	11:45:00	25.42	1.1	114.4	9.3	38.49068	-76.6641	-5	1
3	6/20/1997	12:00:00	25.44	1.1	117.4	9.55	38.49068	-76.6641	-5	1
4	6/20/1997	12:15:00	25.45	1.1	117.1	9.52	38.49068	-76.6641	-5	1
5	6/20/1997	12:30:00	25.38	1.1	112.9	9.19	38.49068	-76.6641	-5	1
6	6/20/1997	12:45:00	25.45	1.1	115.2	9.37	38.49068	-76.6641	-5	1
7	6/20/1997	13:00:00	26.07	1.1	127	10.21	38.49068	-76.6641	-5	1
8	6/20/1997	13:15:00	27.02	1	155.3	12.29	38.49068	-76.6641	-5	1
9	6/20/1997	13:30:00	27.41	1	173.7	13.65	38.49068	-76.6641	-5	1
10	6/20/1997	13:45:00	27.48	1	177.8	13.95	38.49068	-76.6641	-5	1
11	6/20/1997	14:00:00	27.62	1	182.6	14.29	38.49068	-76.6641	-5	1
12	6/20/1997	14:15:00	27.7	0.9	181.5	14.19	38.49068	-76.6641	-5	1
13	6/20/1997	14:30:00	27.66	0.9	181.4	14.2	38.49068	-76.6641	-5	1
14	6/20/1997	14:45:00	27.74	0.9	181.1	14.15	38.49068	-76.6641	-5	1
15	6/20/1997	15:00:00	27.93	0.9	185.5	14.44	38.49068	-76.6641	-5	1
16	6/20/1997	15:15:00	28.38	0.9	194.7	15.04	38.49068	-76.6641	-5	1
17	6/20/1997	15:30:00	28.46	0.8	201.9	15.58	38.49068	-76.6641	-5	1
18	6/20/1997	15:45:00	28.24	0.8	200.8	15.57	38.49068	-76.6641	-5	1
19	6/20/1997	16:00:00	28.09	0.7	194.7	15.14	38.49068	-76.6641	-5	1

Figure 3-1. Screen shot showing the requisite input format needed by Metabolism.xls for calculation of metabolism variables.

3.3 Results

3.3.1 Previous Metabolism Results from the Bay and Elsewhere

The longest time-series record of data suited for metabolism calculations that we are aware of in Chesapeake Bay was initially collected by Cory working for the USGS at a bridge site in the Patuxent River estuary (MD Rt. 231 Bridge at Benedict, MD). Cory started making measurements in 1963 and his record continued until 1969. Cory used an arrangement of pumps, manifolds, early YSI probes and strip-chart recorders to develop the data set. Fortunately, Cory was very attentive to calibration concerns and he devoted considerable effort to ensuring good quality data. This data set was then used by Sweeney (1995) to compute metabolism for the 1963-1969 period and he also deployed a more modern instrument at the same location during 1992. We later deployed instruments during the late-1990's, again at the same location. Data were also available for this area of the Patuxent for 1978 but these data were not collected at the Rt. 231 bridge site.

We have summarized much of these data in a scatter plot where summer metabolism was plotted as a function of nitrogen loading rate corrected for water residence time. The results suggest that this site in the Patuxent is sensitive to changes in nutrient loading rate and that the response is quite large. Note that metabolism rates were considerably lower in recent years following the institution of Biological Nitrogen Removal (BNR) at sewage treatment plants in the upper basin (after 1992). In addition, the red dots represent data collected during the 1960's and there is a clear indication of increasing metabolism through that decade as sewage treatment plants began discharging and land-use changes became large-scale.

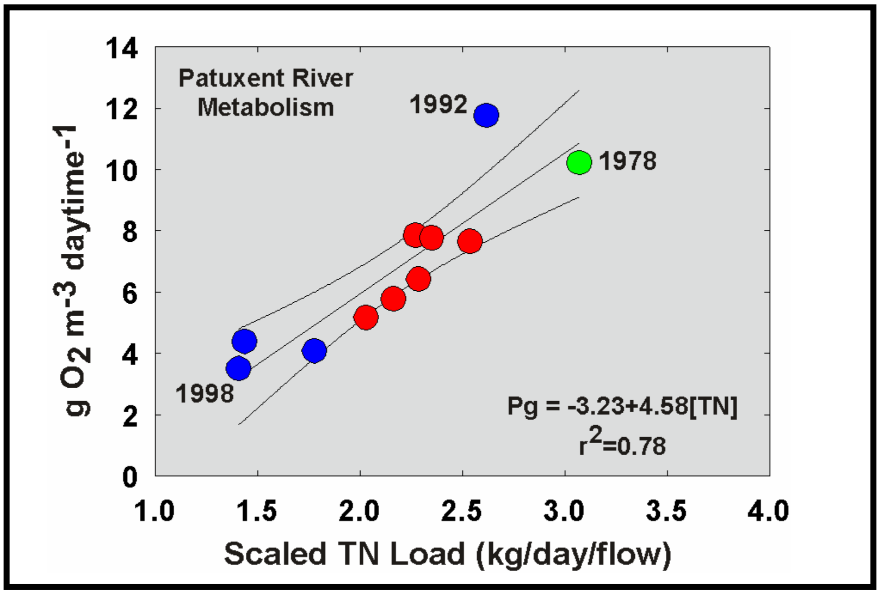


Figure 3-2. A scatter plot of summer Pg* versus nitrogen loading rate scaled for water residence time in the vicinity of Benedict, MD. Red dots represent years between 1963 and 1969 and blue dots are observations from the 1990's. Data are from Sweeney (1995).

In addition to the system metabolism work done in the Patuxent, this technique has been gaining much broader applications in estuarine and near-coastal areas. Perhaps the best single example of this was reported by Caffrey (2004). Caffrey assembled high frequency DO, temperature and salinity data from 42 sites located within 22 National Estuarine Research Reserves between 1995 and 2000. She computed the same sorts of metabolism estimates as described here and found the following: 1) highest production and respiration rates occurred in the SE USA during summer periods; 2) temperature and nutrient concentrations were the most important factors explaining variation in rates within sites; 3) freshwater sites were more heterotrophic than more saline sites; 4) nutrient loading rates explained a large fraction of the variance among sites and; 5) metabolic rates from small, shallow, near-shore sites were generally much larger than in adjacent, but larger, deeper off-shore sites. The fact than nutrient loading rates and concentrations were strong predictors of rates is especially relevant to efforts being made in Chesapeake Bay tributaries.

Finally, Danish investigators have been using this technique in a variety of shallow Danish systems and they have, quite importantly, started to use four different approaches for estimating the metabolic parameters of interest here (Gazeau *et al*. 2005), including the open water DO approach. Significantly, their evaluations suggest that all techniques produce the same estimates with regard to magnitude and direction (production or respiration). A convergence of estimates, using different techniques, suggests a robust set of variables and that is consistent with the needs of a monitoring program.

3.3.2 Preliminary Results for Maryland Chesapeake Bay Tributaries

For purposes of this preliminary exercise we selected ConMon and other sites that would provide some indications of the utility of making these computations as a routine part of shallow water monitoring. First, several very nutrient impacted sites were selected and these included two sites on the Back River estuary located just north of Baltimore and one site on the Corsica River estuary, a tributrary of the Chester River. Both have large nutrient loading rates are frequently have substantial algal blooms. A site located on the St Mary's River, a tributary of the lower Potomac, was also used as it appeared that nutrient loading rates at this site were considerably lower than in the Corsica and Back River locations. We also selected two sites on the Patuxent River estuary where nutrient enrichment effects were substantial but lower than at the heavily enriched sites. In this case we used data from off-shore (ACT Buoy sites) and shallow water (Pin Oak ConMon site) for comparative purposes. Finally, we made these metabolism computations for a tidal freshwater site in the Potomac River estuary (Mattawoman Creek). In most cases data were collected during 2005.

Metabolism estimates for a range of sites are shown in Figures 3-3 and 3-4. Rates of production and respiration at the highly enriched sites (Back River and Corsica River) were very large. Estimates of Pg* approached 18 g O_2 m^{-3} day^{-1} at these sites during summer periods and values of Rn ranged from 1 to 5 g O_2 m^{-3} day^{-1}, again, very large rates. To put respiration values in some perspective, volumetric rates of this magnitude could consume all of the oxygen in a 1 meter water column in just over one day if there were no other sources of oxygen. Thus, we would predict periods of hypoxia in these areas based on metabolism measurements and, indeed, this is the case. In contrast, metabolism rates in the St Marys River were generally much smaller; Pg* ranged from about 5 to 8 g O_2 m^{-3} day^{-1} and respiration from 1 to 3 g O_2 m^{-3} day^{-1}. In addition, variability among days was generally lower at the St Marys River site than at more enriched locations, as predicted, based on observations made in the Patuxent River during the pre-eutrophication years (prior to 1970). We suspect that lower variability is the result of generally smaller algal biomass and more severe nutrient limitation, both of which would effectively preclude very high rates.

We also developed metabolism estimates for the Pin Oak ConMon site in the mesohaline region of the Patuxent River and for the adjacent off-shore buoy site maintained by the ACT-NOAA program. The motivation for this comparison was to examine the same processes in deep and shallow areas and come to some conclusions regarding rate differences. In general, rates of production were slightly higher at the off-shore site, as was algal biomass. However, volumetric respiration rates were higher at the shallow site, probably because benthic respiration added substantially to the water column rate. Despite some difference, these preliminary volumetric rates suggest strong similarities between deep and shallow zones of the mesohaline estuary.

Finally, we examined ConMon data collected at a tidal freshwater site in the upper portion of the tidal Potomac River estuary (Mattawoman Creek). We have little experience interpreting rates from such environments. Rates of Pg* and Rn were small to modest at this site. We were not expecting such modest rates because of the proximity of this creek to major nutrient inputs associated with the Potomac River and metropolitan Washington, DC. It is possible that water exchange between the creek and river are sufficiently small that river nutrient loads do not make their way into this in quantities sufficient to support high metabolic rates. In the future we may be able to examine data from additional ConMon sites in the upper Potomac River estuary.

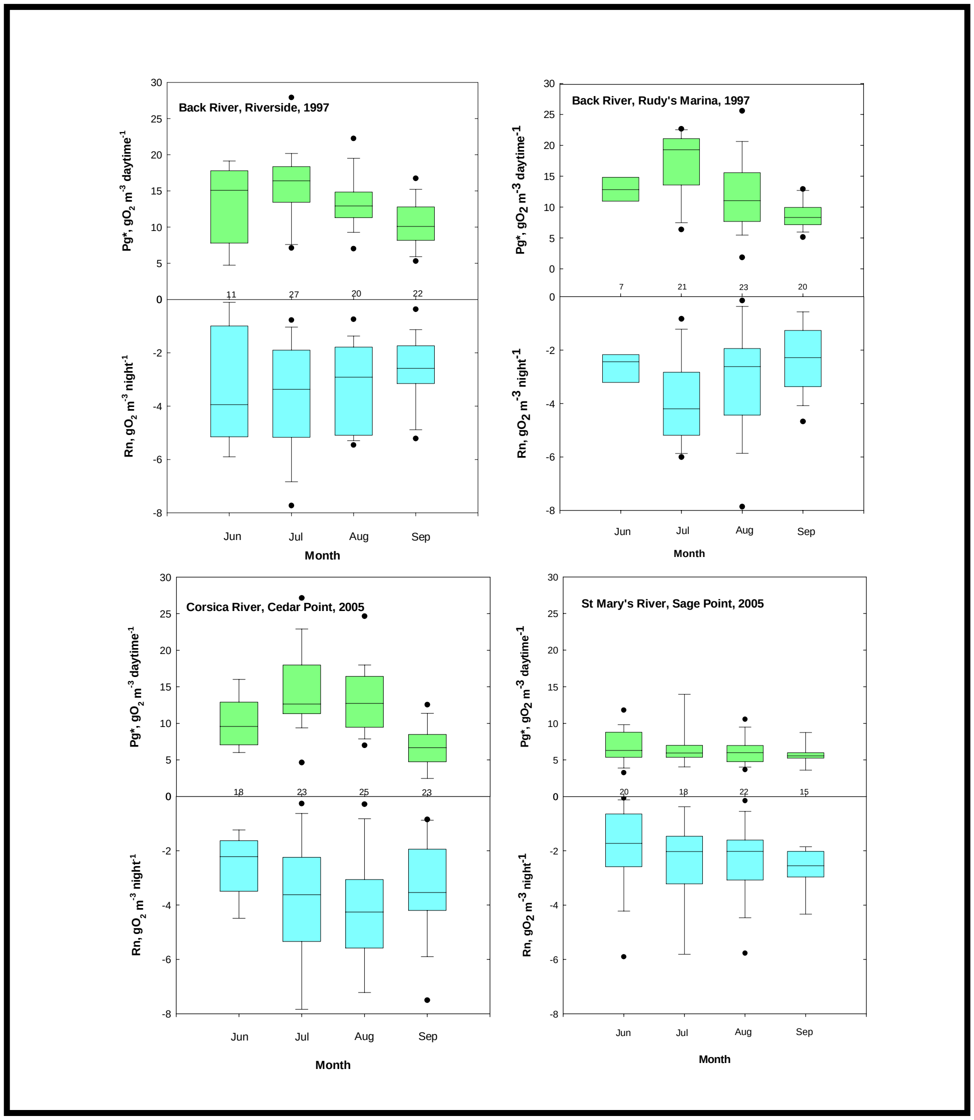


Figure 3-3. Monthly box and whisker plots of metabolism (Pg* = gross primary production; Rn = nighttime respiration) from three heavily nutrient enriched sites (two sites in the Back River and one site in the Corsica River) and from a less enriched site in the St. Marys River, a tributary of the lower Potomac River estuary. The horizontal line in the box represent the median, top and bottom of the box the 75th and 25th percentiles, top and bottom of the solid vertical lines 5th and 95th percentile and small crosses are outlier observations. Data used in this computation were collected at a variety of ConMon sites during 2005.

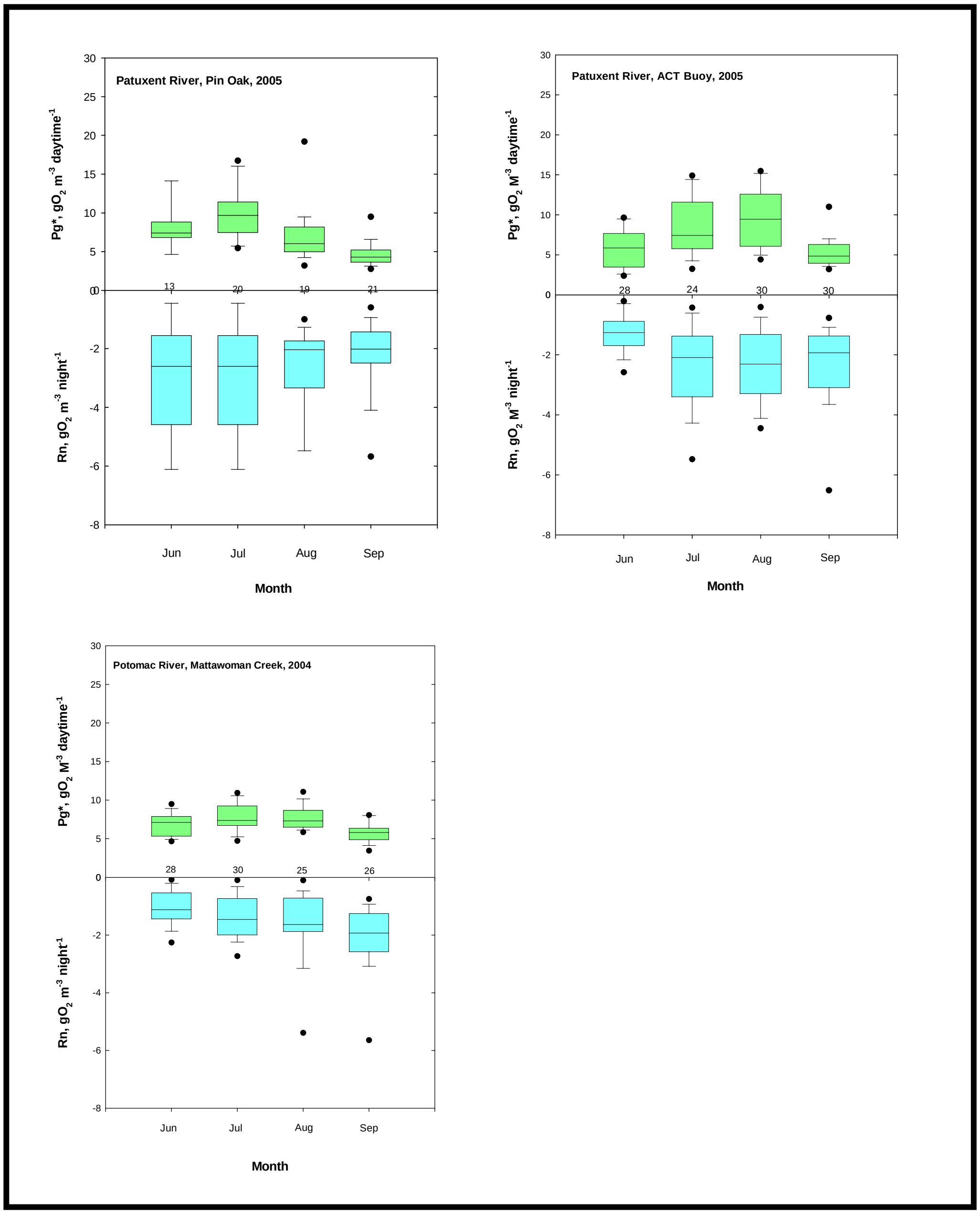


Figure 3-4. Monthly box and whisker plots of metabolism (Pg* = gross primary production; Rn = nighttime respiration) from an inshore ConMon site in the mesohaline Patuxent River estuary (Pin Oak), an off-shore site adjacent to Pin Oak (CBL-NOAA-ACT Buoy site), and Mattawoman Creek, a tributary of the upper Potomac River estuary. The horizontal line in the box represent the median, top and bottom of the box the 75th and 25th percentiles, top and bottom of the solid vertical lines 5th and 95th percentile and small crosses are outlier observations. Data used in this computation were collected at a variety of ConMon sites during 2005.

3.4 Discussion

3.4.1 Data Examination Using Spectral Densities

We have mentioned several times problematic issues related to advection of water mass past a sensor system. This advection is not an issue in many cases if the water mass has reasonably homogeneous DO properties. However, if the water mass has different DO properties (e.g., much lower or higher concentrations and possibly larger or smaller rates of DO change due to differing biological communities in the water) then there are errors generated in the metabolism calculation. We wish to minimize these errors and, if needed, eliminate some days of observations at a site or even ConMon sites if this problem is frequently encountered. We have just begun considering how best to attack this issue. One approach is to visually inspect data before making the computation. However, this is time consuming and it is not clear just what criteria would be used to exclude data sets. Other approaches, including using salinity/DO change as a “correction factor” are also being considered. However, we have examined two distinct sites in the Patuxent River estuary using spectral analysis to determine the spectral frequency at which most of the DO varaiance is associated. Spectral analysis is a numerical technique designed to identify the frequency (time in this case) where variability is greatest. At the mesohaline site (ConMon Pin Oak site) there is a very clear signal associated with 24 hour frequency, the frequency expected in biological production (daytime photosynthesis) and consumption (nighttime respiration) was the dominant driver of the diel DO pattern. Visual inspection of some data from this site is consistent with results of spectral analysis. In addition, salinity gradients in the mid-mesohaline are quite small so the likelihood of very different water masses moving past the sonde during one tidal cycle are also relatively small.

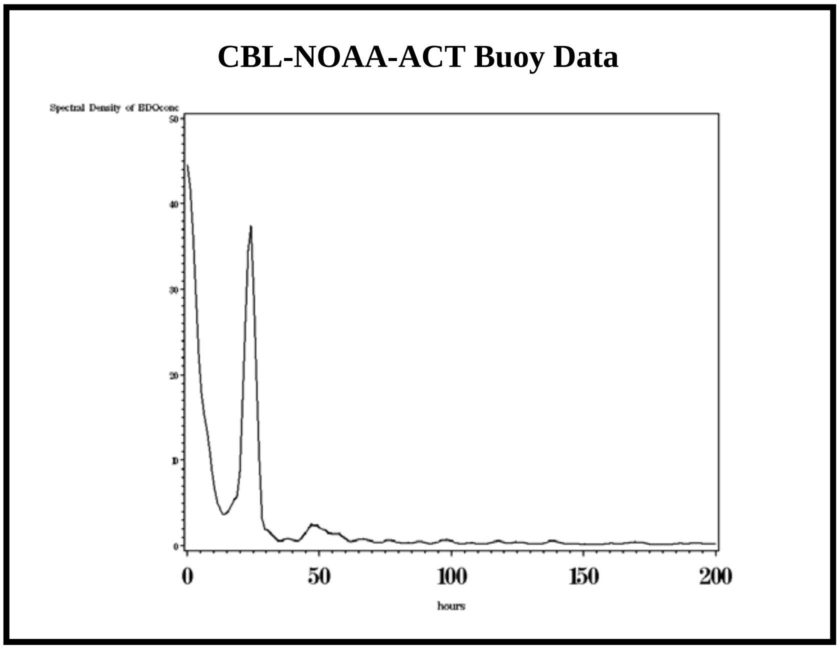

CBL-NOAA-ACT Buoy Data

Figure 3-5. Spectral analysis of continuously (4/hour) measured dissolved oxygen (DO) concentration shows a strong spectral signal at a frequency of 24 hours (day/night period). Data were collected at the CBL-NOAA-ACT buoy located in the mesohaline region of the Patuxent River estuary.

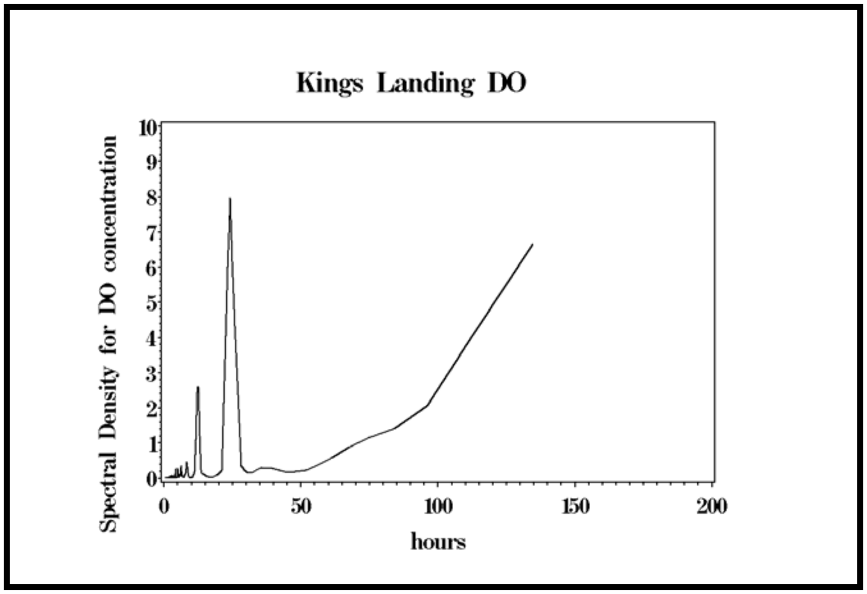


Figure 3-6. Spectral density of DO concentration for the period 7/31/05-8/28/05 at the Kings Landing ConMon site in the oligohaline portion of the Patuxent River estuary. At this site the diel signal is again the strongest but there is some variance explained at tidal frequencies (12 hrs). Such a result is not surprising given that longitudinal water quality gradients are strongest in this portion of the estuary. Sites such as Kings Landing may not be good candidates for open water metabolism computations because of DO variability associated with tidal advection.

However, at the Kings Landing ConMon site spectral analysis identified a portion of the variance as being associated with tidal frequencies (12.25 hours) as well as diel frequencies. Inspection of DO concentrations from this site indicate sharp salinity changes during a diel period and associated DO changes. This is not surprising since this site is located at the salt front in this estuary and strong salt gradients are to be expected in this zone of the estuary.

As indicated above, we are at the beginning of this exercise to determine the most efficient ways to compute metabolism from ConMon data. We want to maximize the number of observations used and, at the same time, avoid using portions of data sets that have DO patterns too complex for use in this methodology.

3.4.2 A Preliminary Predictive Model of Metabolism: Analysis of Corsica River production and respiration data

One of the goals of this effort to routinely use ConMon data to compute estuarine metabolism is to improve our understanding of factors controlling these rates. Data collected at ConMon sites gives us an unusual opportunity to conduct such analysis. In addition to the variables needed to compute metabolism (temperature, salinity and oxygen concentration) ConMon data also include turbidity, pH and algal biomass, all of which can influence production rates. In addition, we obtained daily PAR flux from the Horn Point Laboratory meteorology station.

3.4.3 Correlation analysis

Initial graphical analysis shows that production, respiration, turbidity, and chlorophyll all have a distribution that is skewed right and variability that tends to increase with the mean. Because these are properties associated with the log normal distribution, these variables have been transformed by base 10 logarithms for analysis. The prefix Ln precedes logarithm transformed variables.

To assess the associations among the variables in the Corsica River data file, we begin with simple product moment correlations between all possible pairs. From this it is clear that Log Production shows some association with all other variables. Respiration on the other hand seems to be associated only with production and temperature. When we think in terms of production and respiration as dependent variables and the remaining variables as independent variables, then it is important to note that while production is positively correlated with temperature and PAR, temperature and PAR are correlated with each other. Thus it will be difficult to discern whether temperature or PAR (or both) is having an operative effect on production. Similarly, production is positively correlated with turbidity and chlorophyll, but turbidity and chlorophyll are correlated with each other. Thus there is also a problem identifying the effect of these two variables.

Table 3-1. Product-moment correlation coefficients between variables of the Corsica River Respiration (Rn) and Production (Pg*) data set. In each cell of the table, the correlation is the upper number and the p-value for the correlation is the lower number. P-values less than 0.05 appear in *italics*.

Variable	LnProd	LnResp	Temp	LnTurb	LnChl	PAR
Log Production (LnProd)	1.00 _	0.45 *0.0000*	0.64 *0.0000*	0.25 *0.0073*	0.37 *0.0000*	0.38 *0.0000*
Log Respiration (LnResp)	0.45 *0.0000*	1.00 _	0.22 *0.0143*	0.16 .0827	0.02 .8238	-0.11 .2206
Water Temperature C (Temp)	0.64 *0.0000*	0.22 *0.0143*	1.00 _	0.06 .5010	0.08 .3663	0.39 *0.0000*
Log Turbidity (LnTurb)	0.25 *0.0073*	0.16 .0827	0.06 .5010	1.00 _	0.35 *0.0001*	0.12 .2163
Log Chlorophyll (LnChl)	0.37 *0.0000*	0.02 .8238	0.08 .3663	0.35 *0.0001*	1.00 _	0.18 .0513
Incident Light (PAR)	0.38 *0.0000*	-0.11 .2206	0.39 *0.0000*	0.12 .2163	0.18 .0513	1.00 _

3.4.4 Stepwise regression analysis

For both productivity and respiration, stepwise regression was used to select important predictor variables from among the set: temperature, ln turbidity, ln chlorophyll-*a*, and PAR. The enter selection criterion was set at a p-value of 0.15 and the criterion to stay in the model was set at 0.05.

For the production dependent variable, temperature was selected as the most important predictor and ln-chlorophyll was selected as the variable that improves prediction most when added to temperature. Use of turbidity and PAR does not result in significant improvement over temperature and chlorophyll. The cumulative r-square is 0.51 and both variables have a positive coefficient indicating that each has a positive association with production.

Dependent Variable: ln Prod
Independent Variables: temp ln turb ln chl par

Summary of Stepwise Selection

Step	Variable Entered	Partial R-Square	Model R-Square	F Value	Pr > F
1	Temp	0.3983	0.3983	73.47	<.0001
2	ln Chl	0.1113	0.5096	24.96	<.0001

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	3.89306	1.94653	57.15	<.0001
Error	110	3.74683	0.03406		
Corrected Total	112	7.63989			

Parameter estimates of final stepwise model

Variable	Standard Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	-0.56785	0.14217	0.54338	15.95	0.0001
Temp	0.04036	0.00443	2.83271	83.16	<.0001
ln Chl	0.34763	0.06958	0.85031	24.96	<.0001

For the respiration dependent variable, three of the four potential predictors were selected: temp, PAR, and ln turbidity. The cumulative r-square is an unimpressive 0.14. Thus while these independent variables have an association with respiration that is stronger than is likely to occur by chance, the strength of the relation is not adequate for useful prediction.

Dependent Variable: ln Resp
Independent Variables: temp ln turb ln chl par

Summary of Stepwise Selection

Step	Variable Entered	Partial R-Square	Model R-Square	F Value	Pr > F
1	Temp	0.0447	0.0447	5.24	0.0239
2	PAR	0.0631	0.1078	7.85	0.0060
3	ln Turb	0.0310	0.1388	3.96	0.0490

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	1.99485	0.66495	5.91	0.0009
Error	110	12.37353	0.11249		
Corrected Total	113	14.36838			

Parameter estimates of final stepwise model

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	-0.31311	0.24288	0.18695	1.66	0.2000
Temp	0.02805	0.00865	1.18143	10.50	0.0016
ln Turb	0.27343	0.13734	0.44589	3.96	0.0490
PAR	-0.00802	0.00265	1.02852	9.14	0.0031

A seasonal means model was also used with these data, but results did not change to any significant degree. We will continue to explore these data sets with the goal of producing models capable of useful, seasonal-scale forecasting.

3.4.5 Scatter plots

Scatter plots were prepared for each dependent variable (LnProd and LnResp) against each of the potential independent variables (Temp, LnChl, LnTurb, and Par). Where Ln precedes a variable name, the variable has been transformed by base 10 logarithms. In addition to plotting the dependents versus the independents, the dependents were plotted versus each other and selected independents were paired and plotted to address specific questions. A LOESS regression curve is fitted to each plot to help the eye identify the central tendency among the noise.

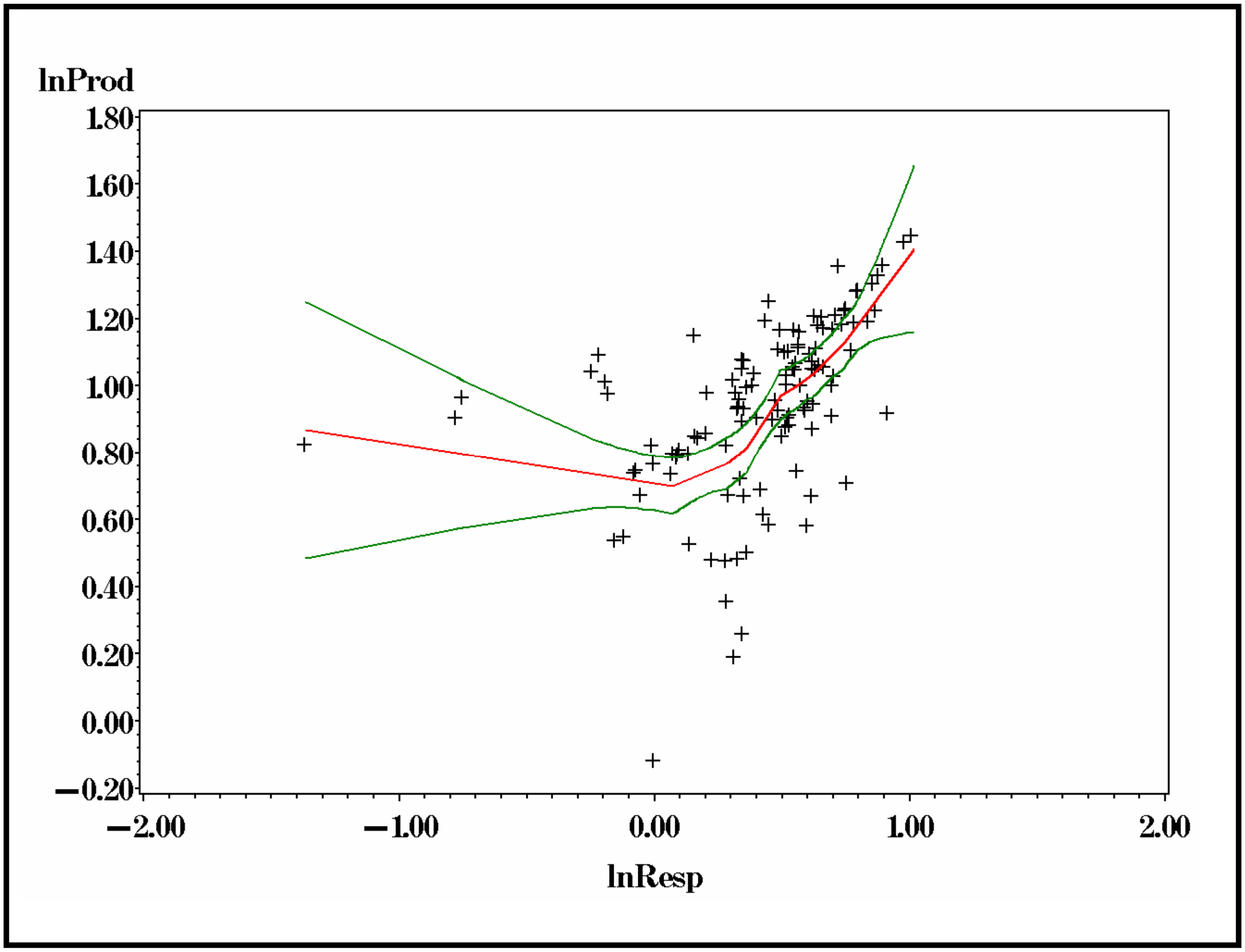


Figure 3-7. LnProd vs. LnResp. In general the association between Prod and Resp is positive. An exception is a trend associated with very low (might be classed as outliers) values of Resp.

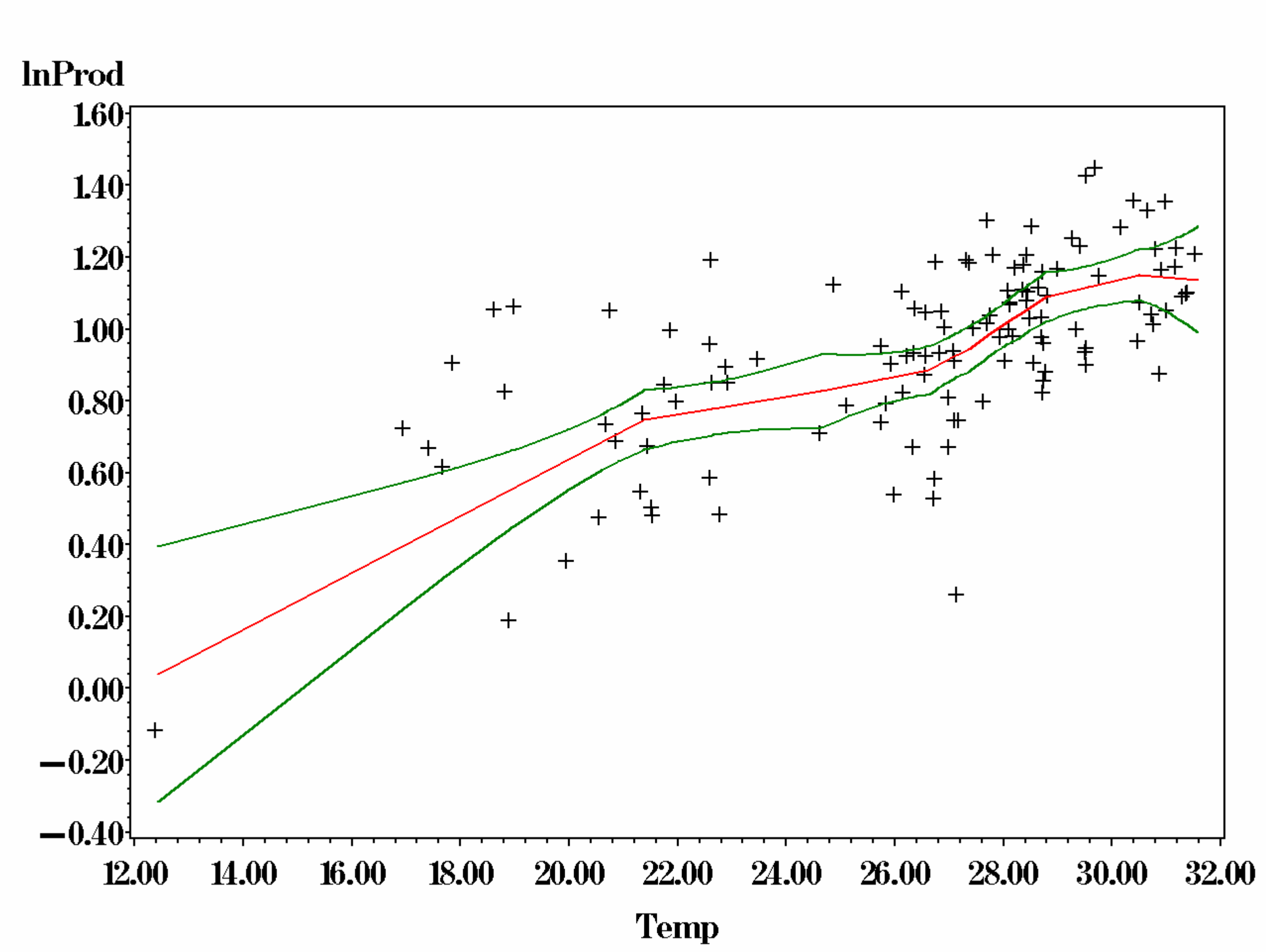


Figure 3-8. LnProd vs Temp. A clear positive association between these variables is evident. Such results have been reported in the phytoplankton literature for many years and this relationship is not unexpected.

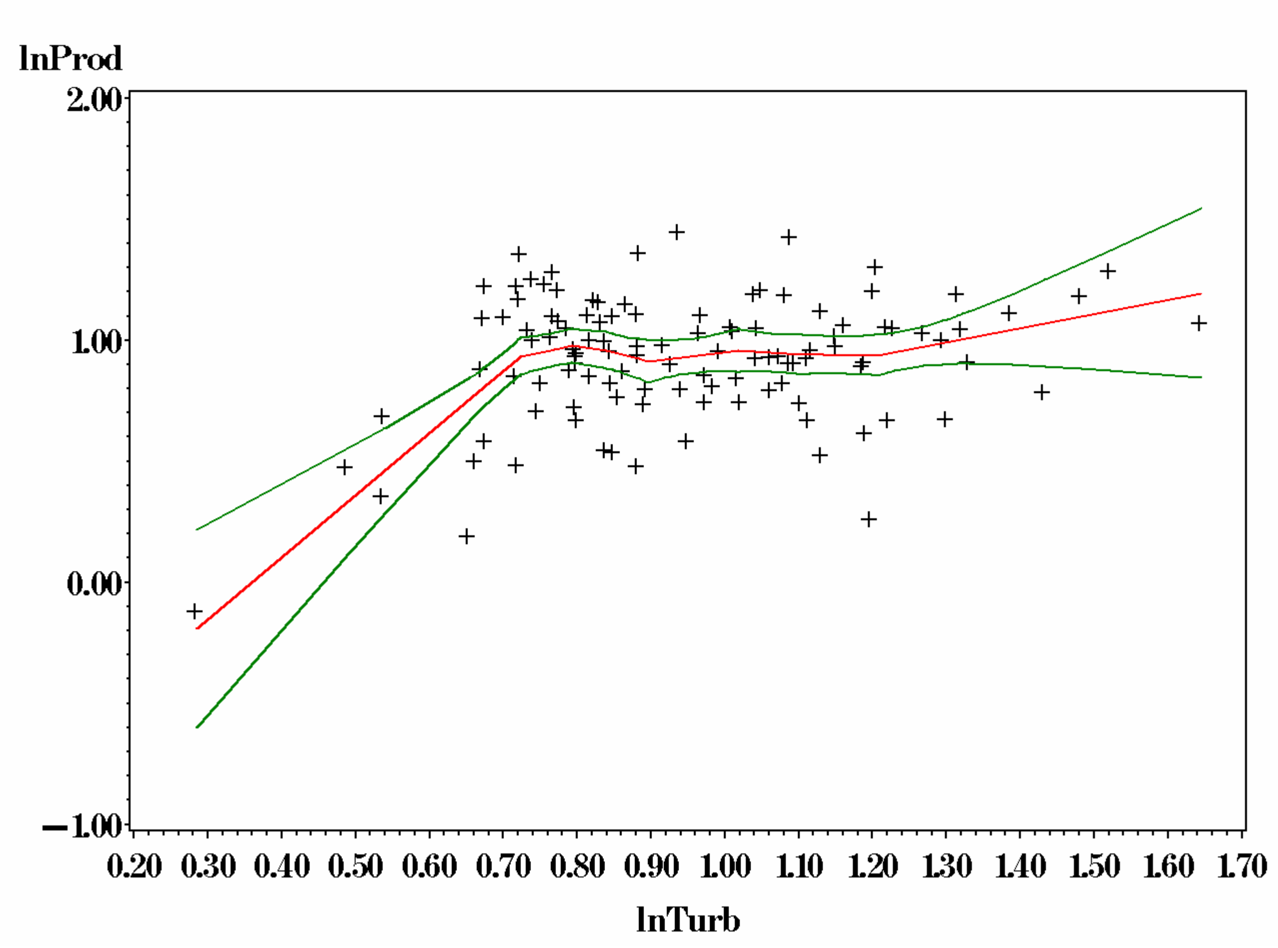


Figure 3-9. LnProd vs Turb. Generally, no association was evident. However, Prod drops with very low values of Turb. This seems counter intuitive unless it means that the chl component of Turb has dropped out.

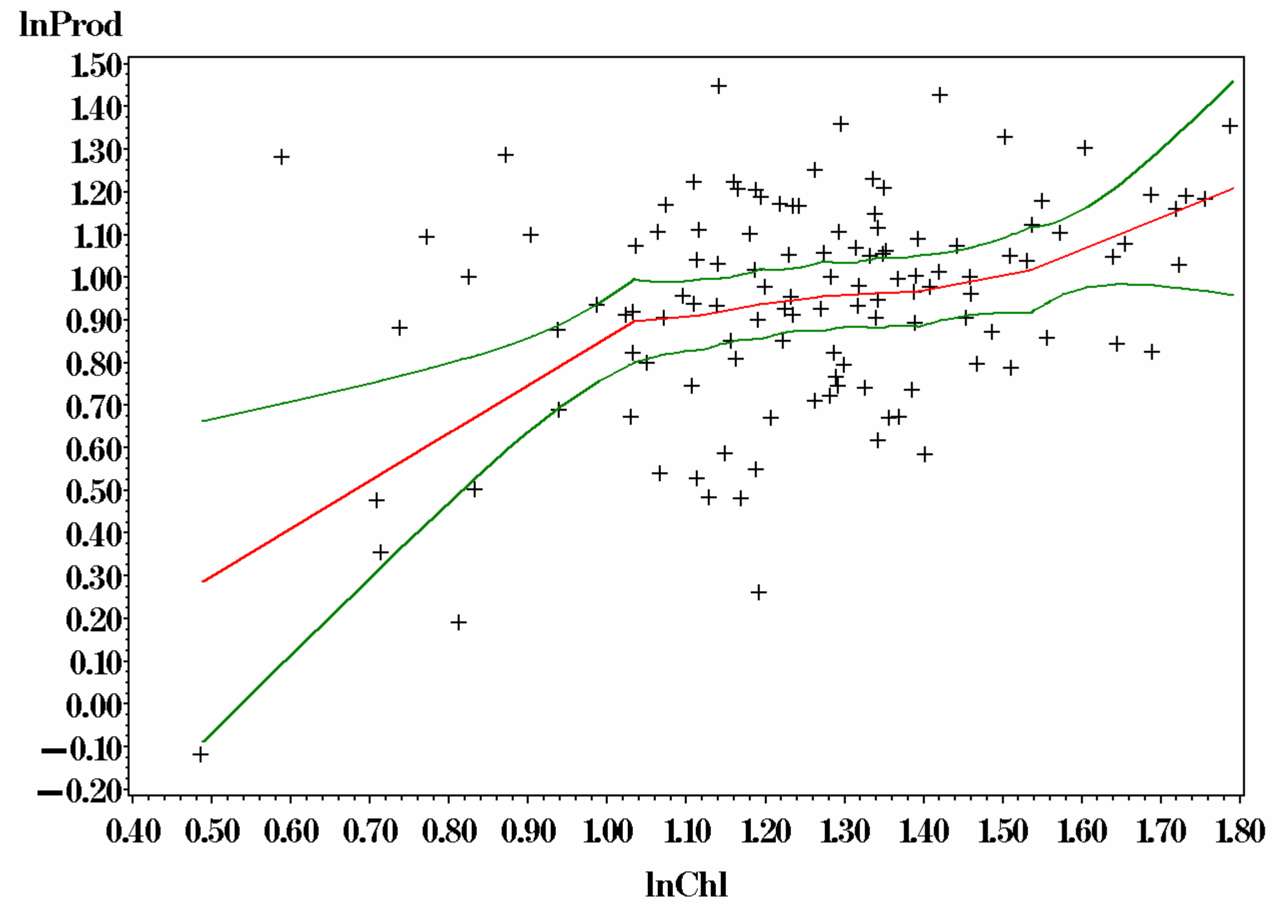


Figure 3-10. LnProd vs lnChl. Prod is generally increasing with chlorophyll. The lower tail on the left seems to confirm conjecture above that the low Turb-Prod association is driven by Chl.

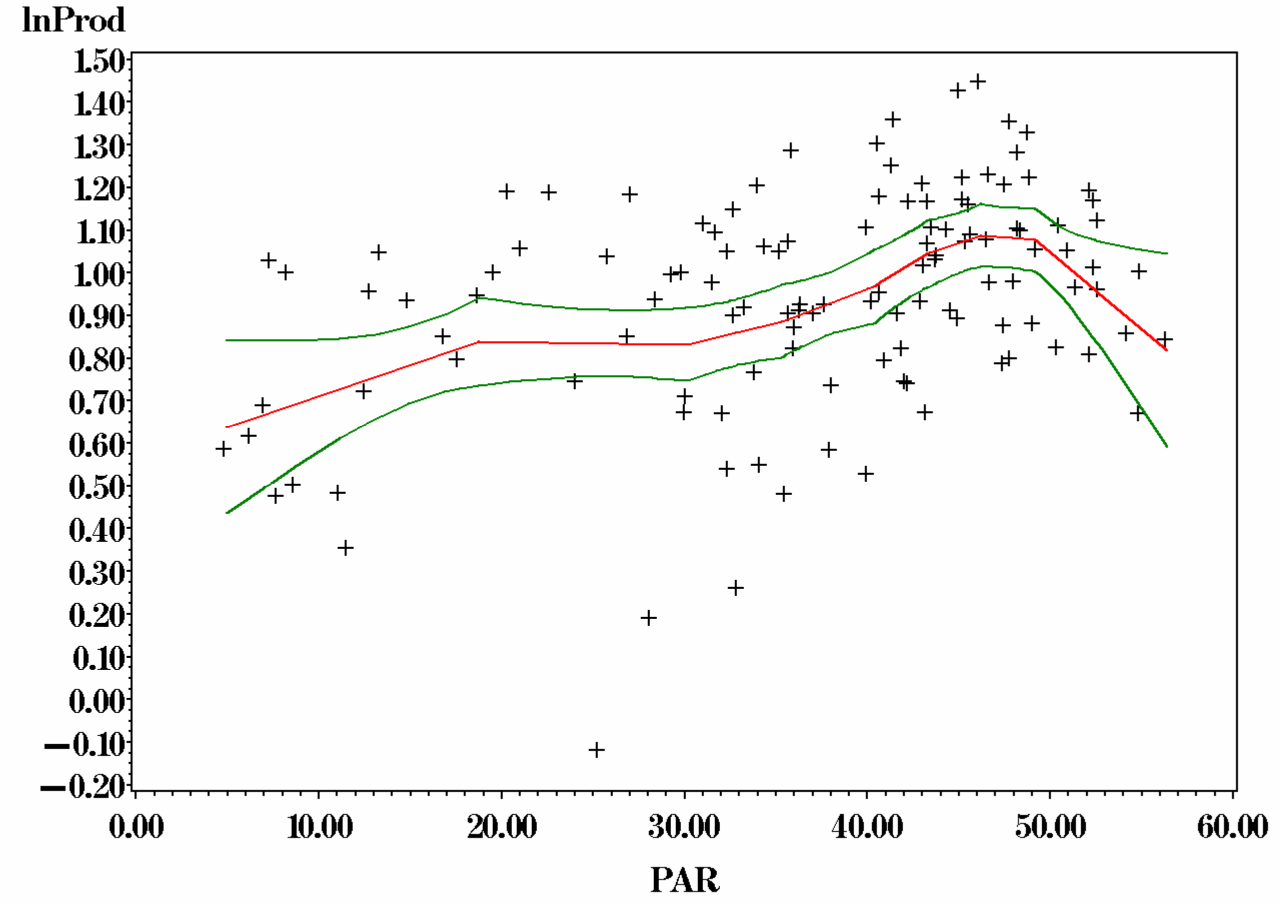


Figure 3-11. LnProd vs PAR. Here there is a generally increasing trend up to PAR ~ 48 and the association becomes negative for higher PAR. These high PAR records seem to come from the early part of the data record when temperature was low. It is possible that at high PAR levels some light inhibition came into play.

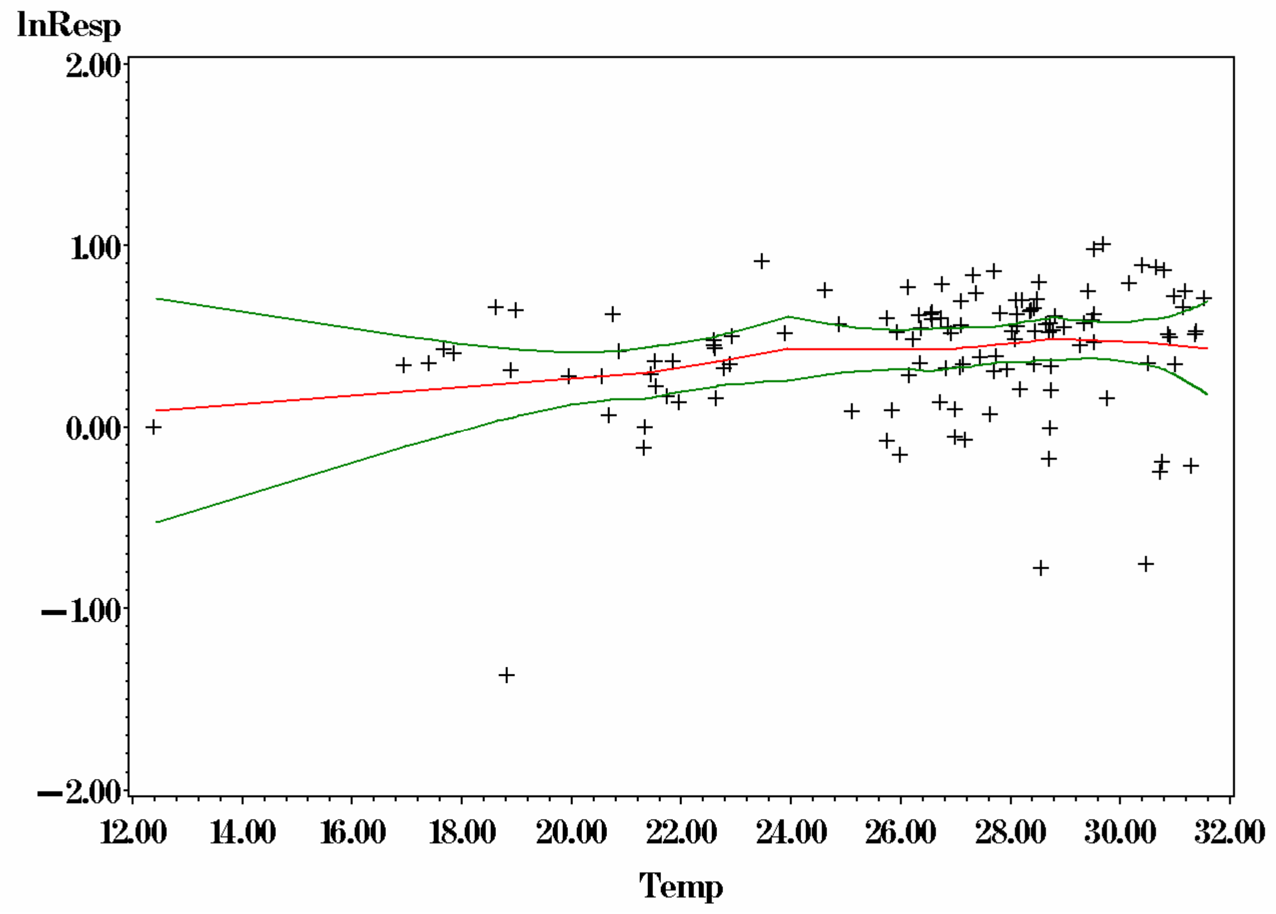


Figure 3-12. LnResp vs Temp. Generally increasing trend but trend is slight relative to noise.

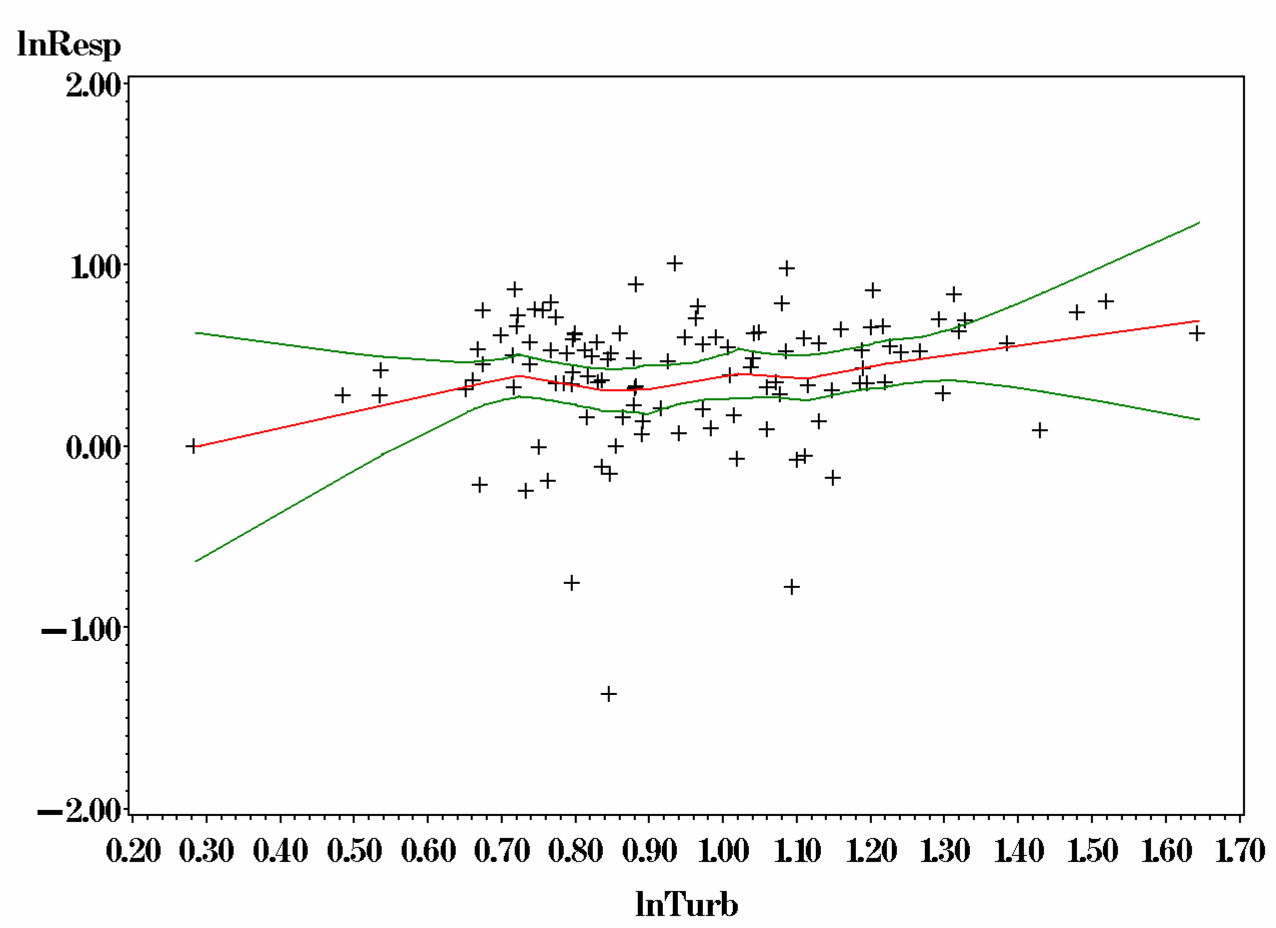


Figure 3-13. LnResp vs Turb. Generally increasing trend but trend is slight relative to noise.

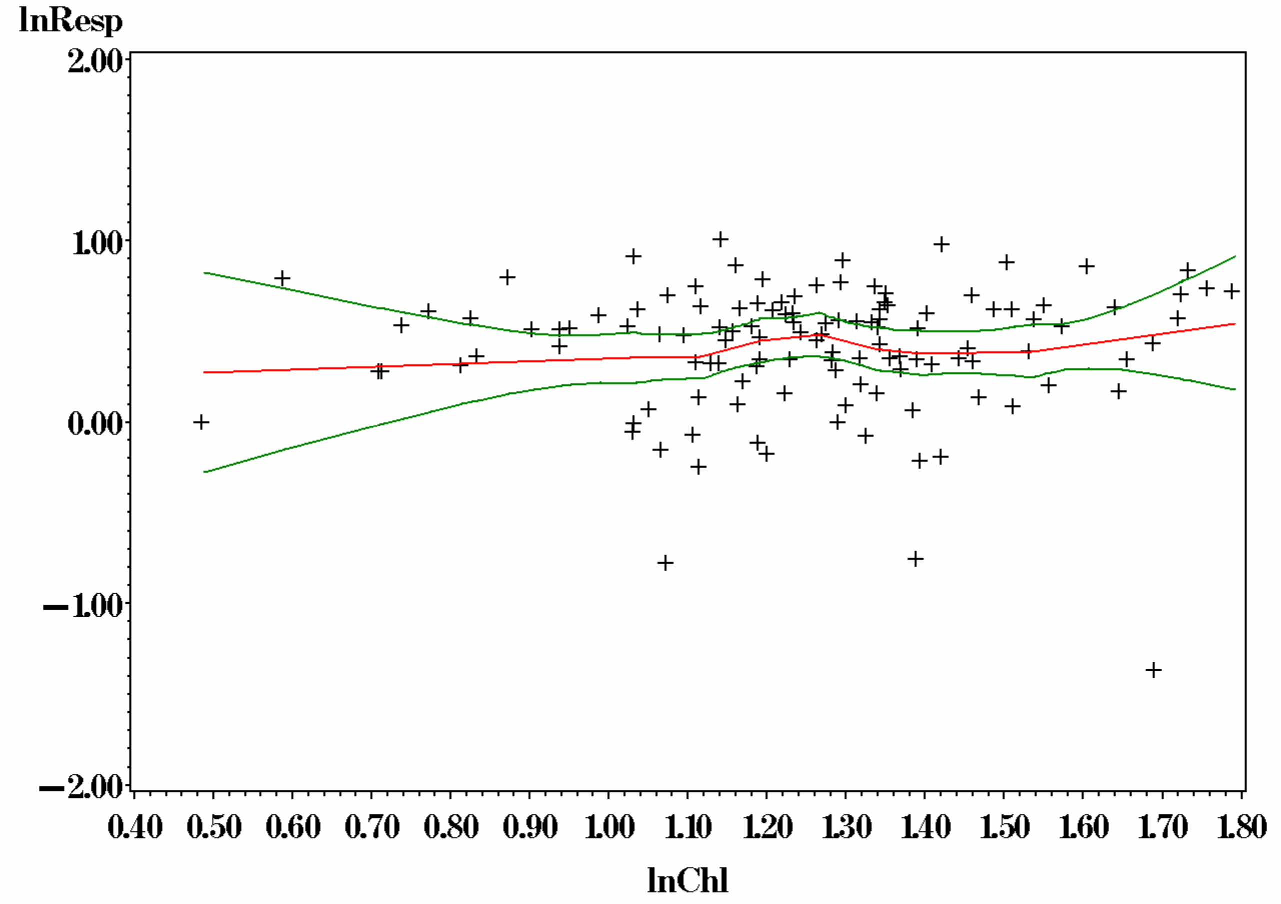


Figure 3-14. LnResp vs LnChl. No apparent association.

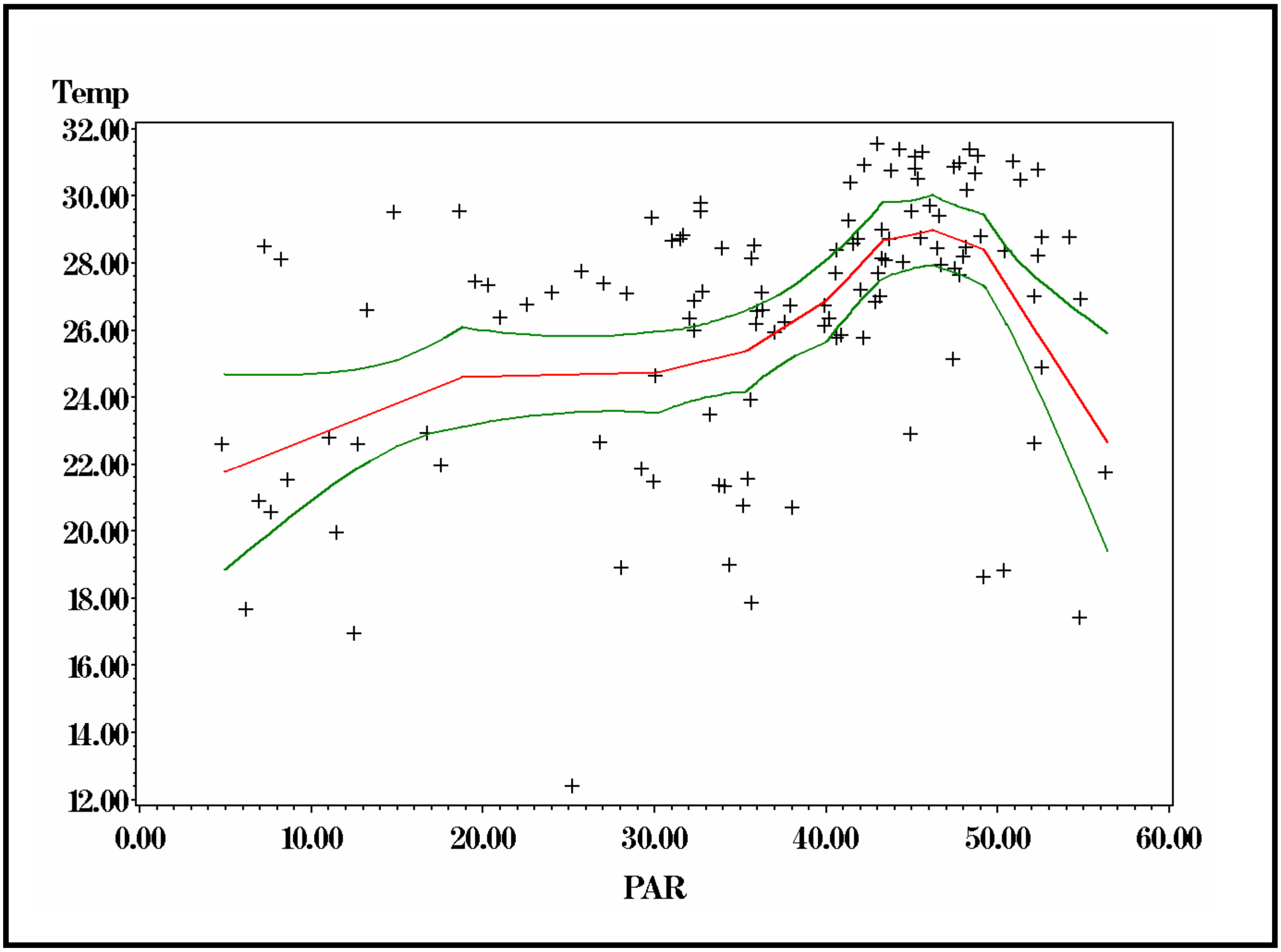


Figure 3-15. Temp vs PAR. These data show a generally positive association up to PAR ~ 48 and then it becomes negative. While one might conjecture an inhibition of biotic variables in response to high light, this would not seem logical for temperature. There appears to be some "quirk" in the subset of data where PAR > ~48.

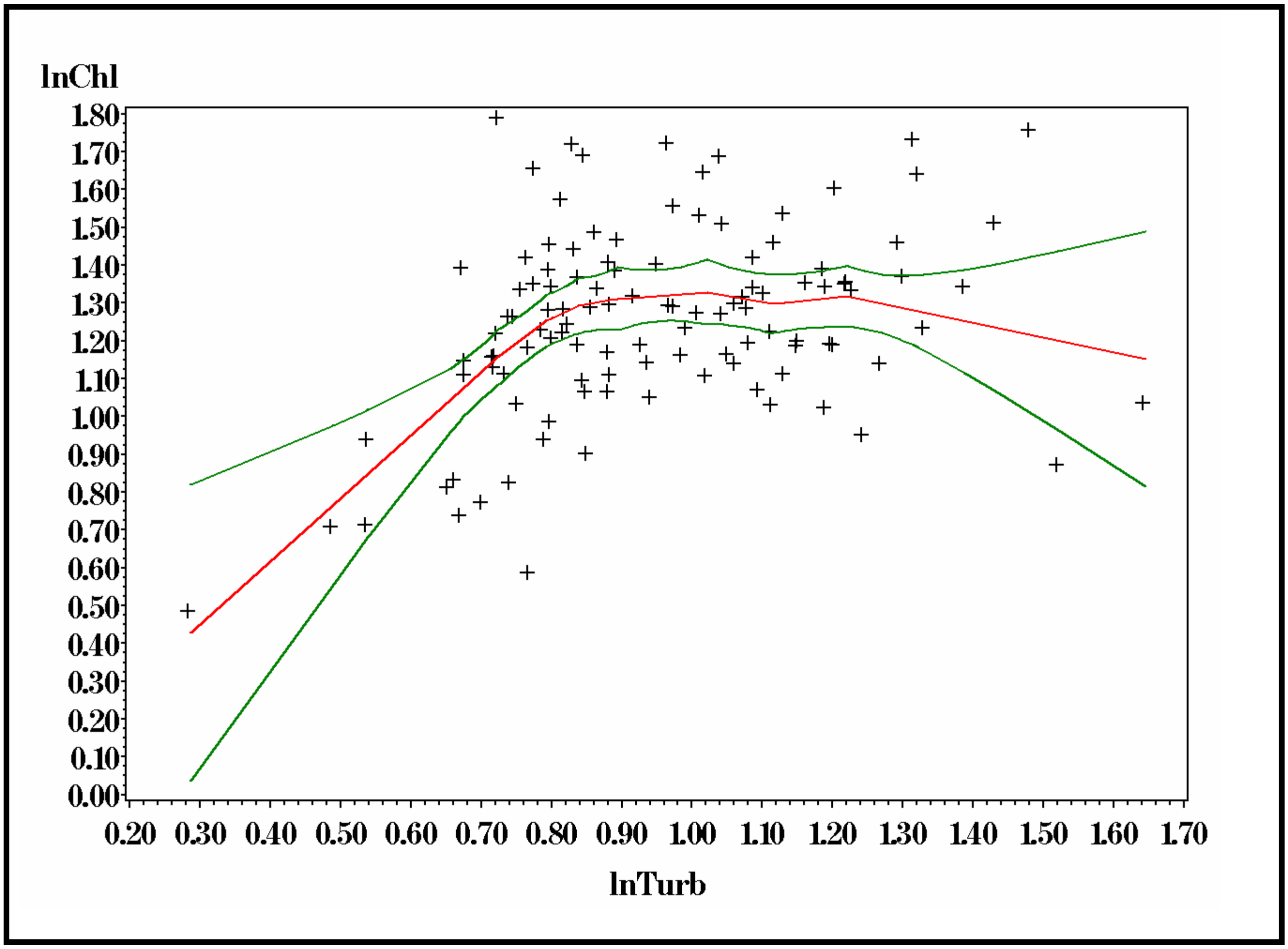


Figure 3-16. LnChl vs LnTurb. Indicates that low turbidity is associated with low chlorophyll, as conjectured above.

3.4.6 Time series plots

To study the association between the dependent variables and the independent variables as they occur through time, time series plots for the dependent variables overlay with plots of each independent variable were prepared. In each plot, LnProd and LnResp are measured by the left ordinate and the independent variable is measured on the right ordinate. For each variable, the time trend is illustrated by a spline fit with a small degree of smoothing. Where Ln or ln preceeds a variable name, the variable has been transformed by base 10 logarithms. For example: lnProd = log 10 (prod).

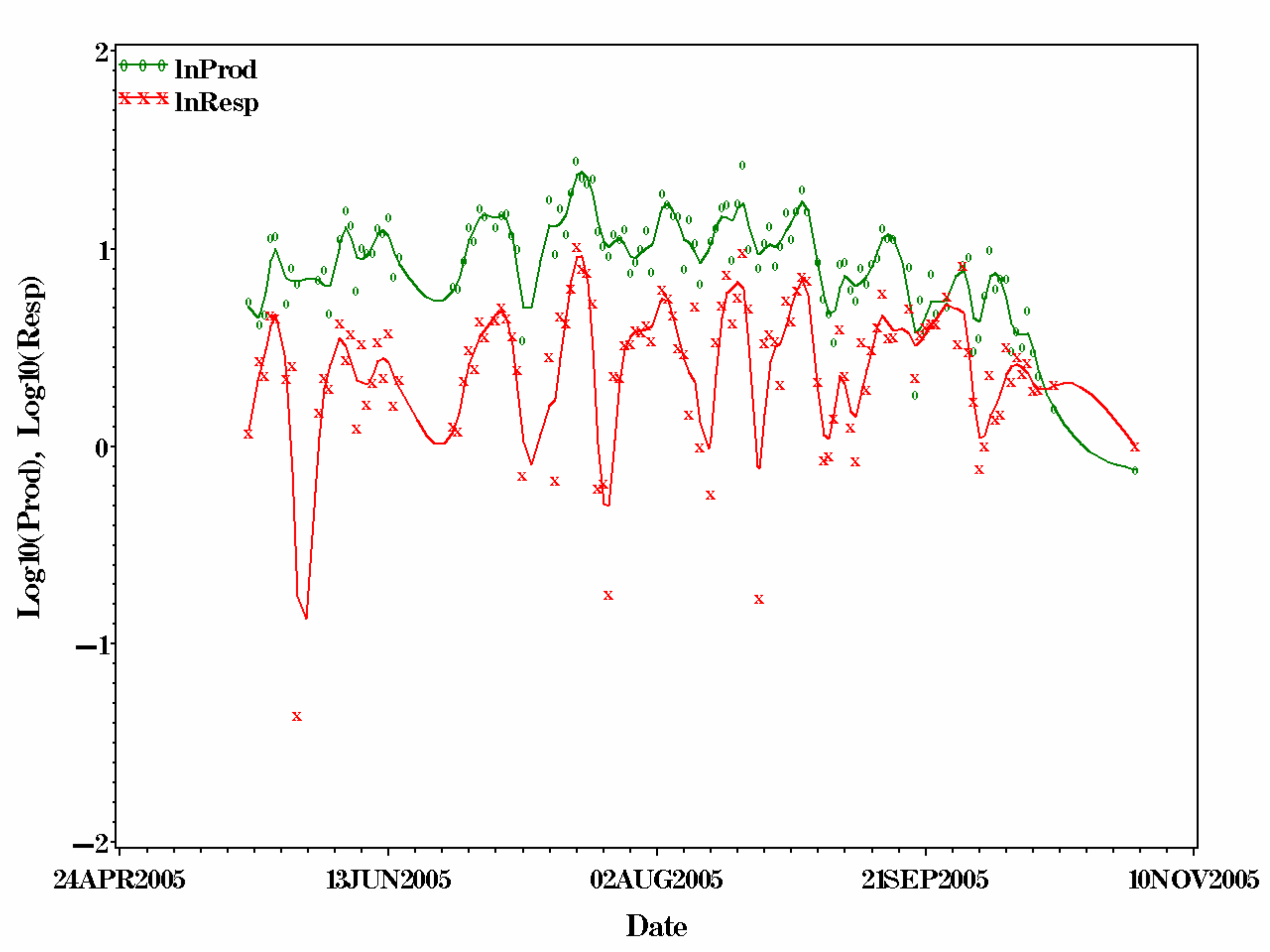


Figure 3-17. Clear concordance of Production and Respiration over time.

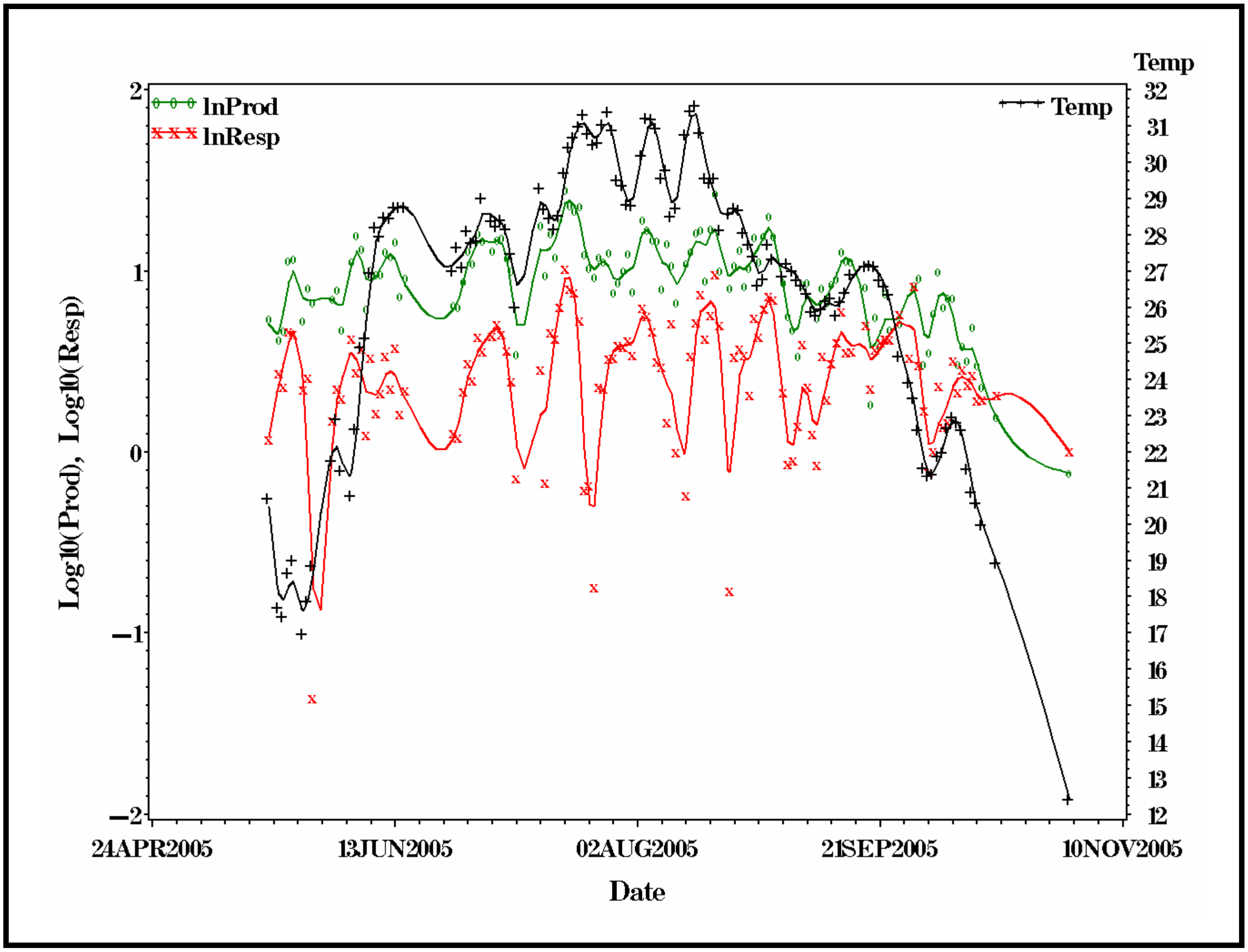


Figure 3-18. Temperature. Production and Respiration appear to be responding positively to temperature. This seems generally true with the exception of one event in late July when temperature first shoots above 30degC. In this case, both Prod and Resp appear to have a negative response to temperature. Temperature exceeds 30 twice more soon after this first event. For each of the later events, both Prod and Resp show a slight positive response. Was there a regime shift with the first high temperature excursion?

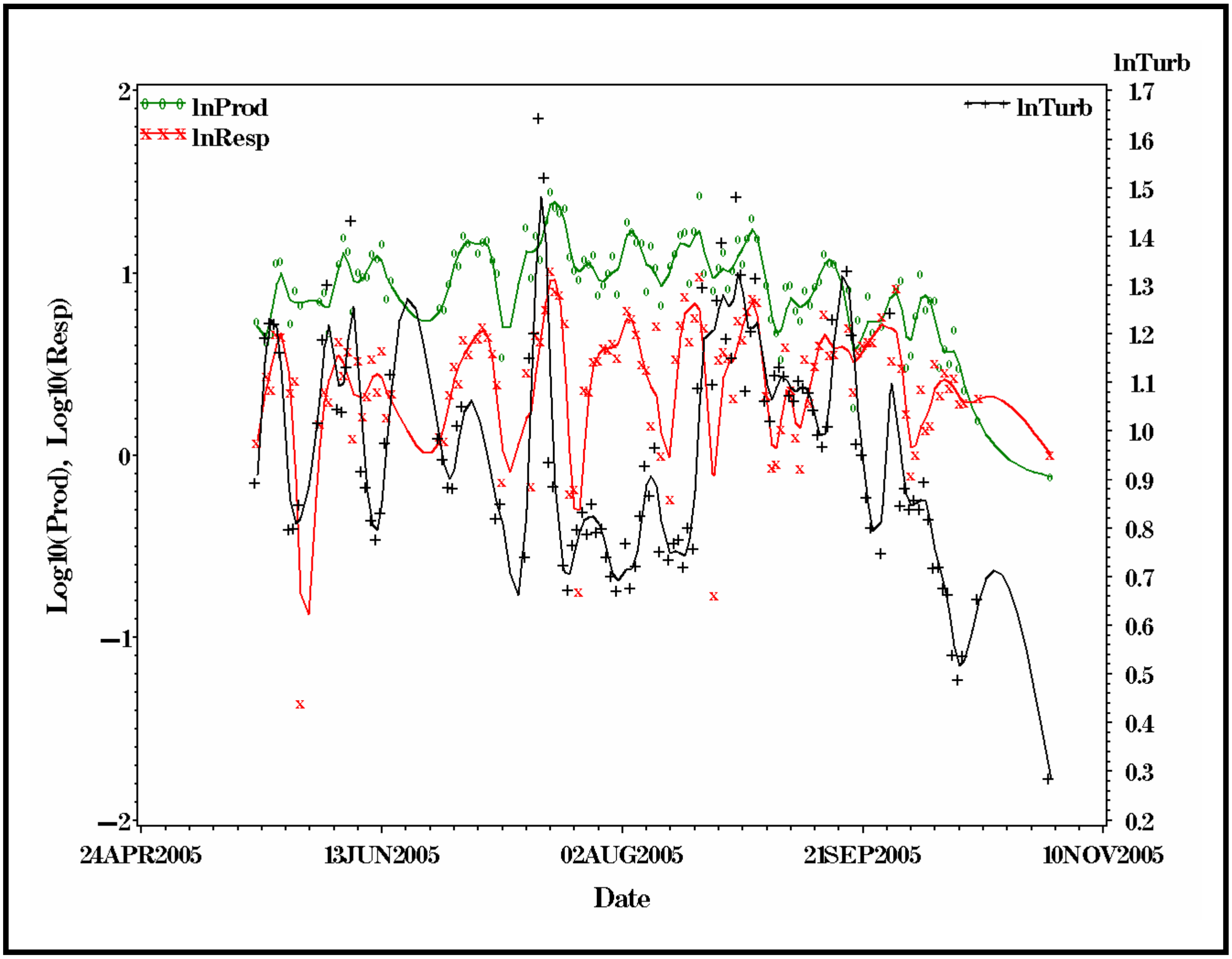


Figure 3-19. Turbidity. It almost appears that spikes in Turbidity slightly precede positive responses in Prod and Resp. This might be a trick of they eye. The responses in Prod and Resp come fairly regularly so any deviation in Turbidity will soon be followed by a response. The lag does not seem consistent.

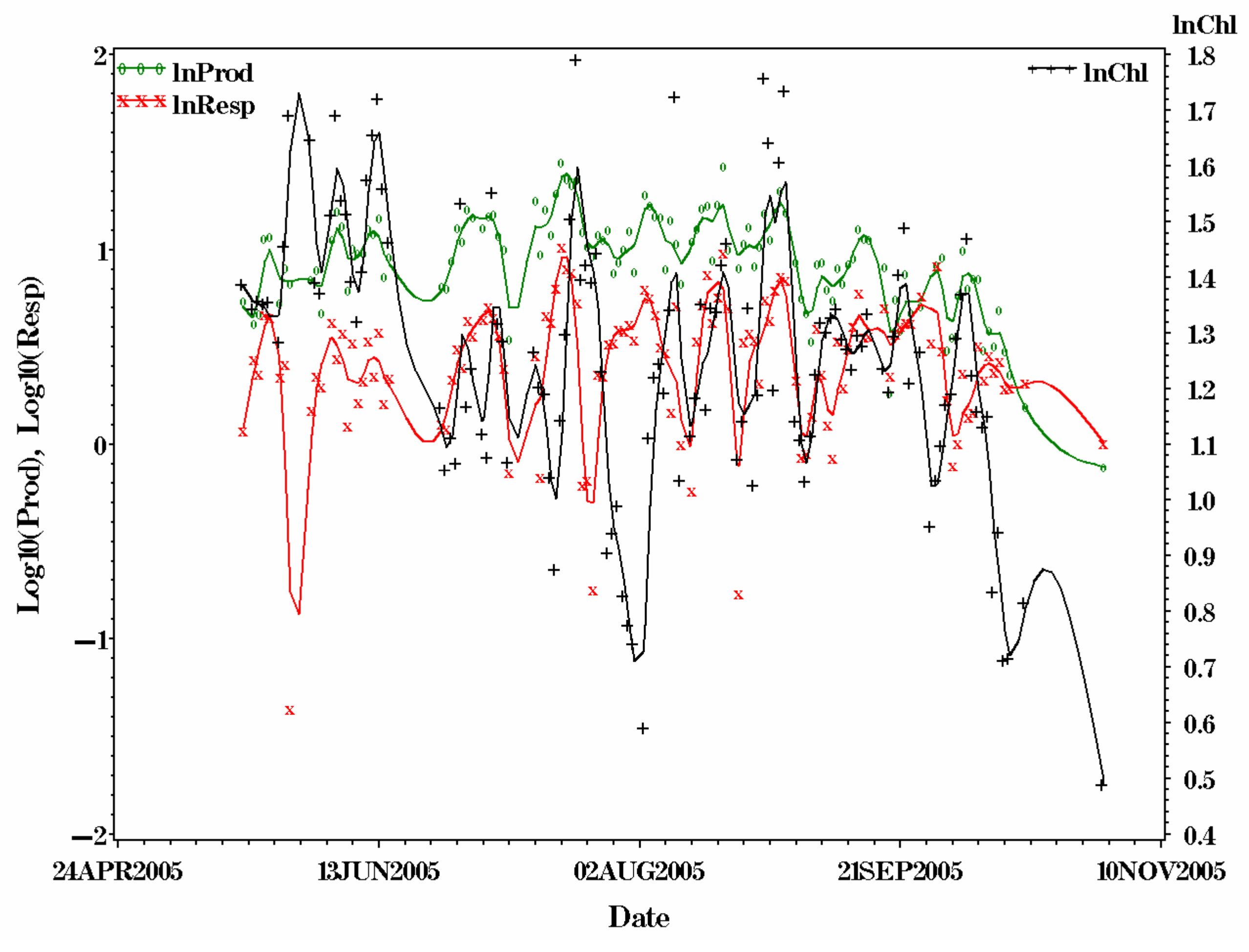


Figure 3-20. LnChl. It appears the peaks in lnchl might be following peaks in Prod. As noted above, this could be a trick of the eye. Note that there is a plunge in chl associated with the first excursion of temperature>30. With the next two events where temperature goes above 30, chl peaks slightly after prod peaks and might well be the result of net algal biomass growth.

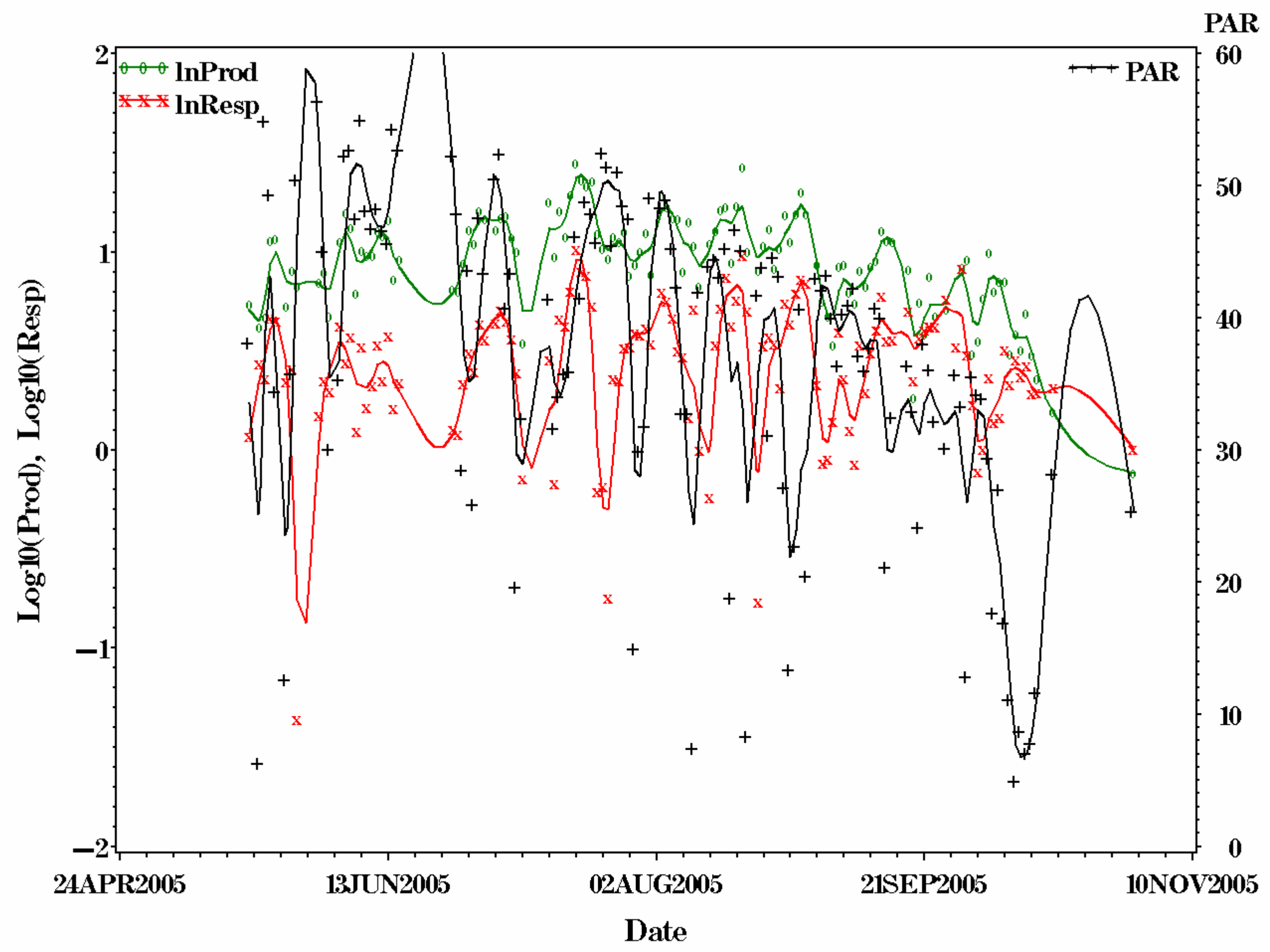


Figure 3-21. PAR. It appears that the response of Prod and Resp to PAR is more often negative than positive. In fact the Stepwise regression picks up PAR as having a weak association with Resp. It seems counter intuitive that Prod is not positively associated with light and just curious that Resp has any association with light. Is it possible that the simple explanation is that this part of the estuary is not light limited? Or that clarity is so poor that the light response is inhibited?

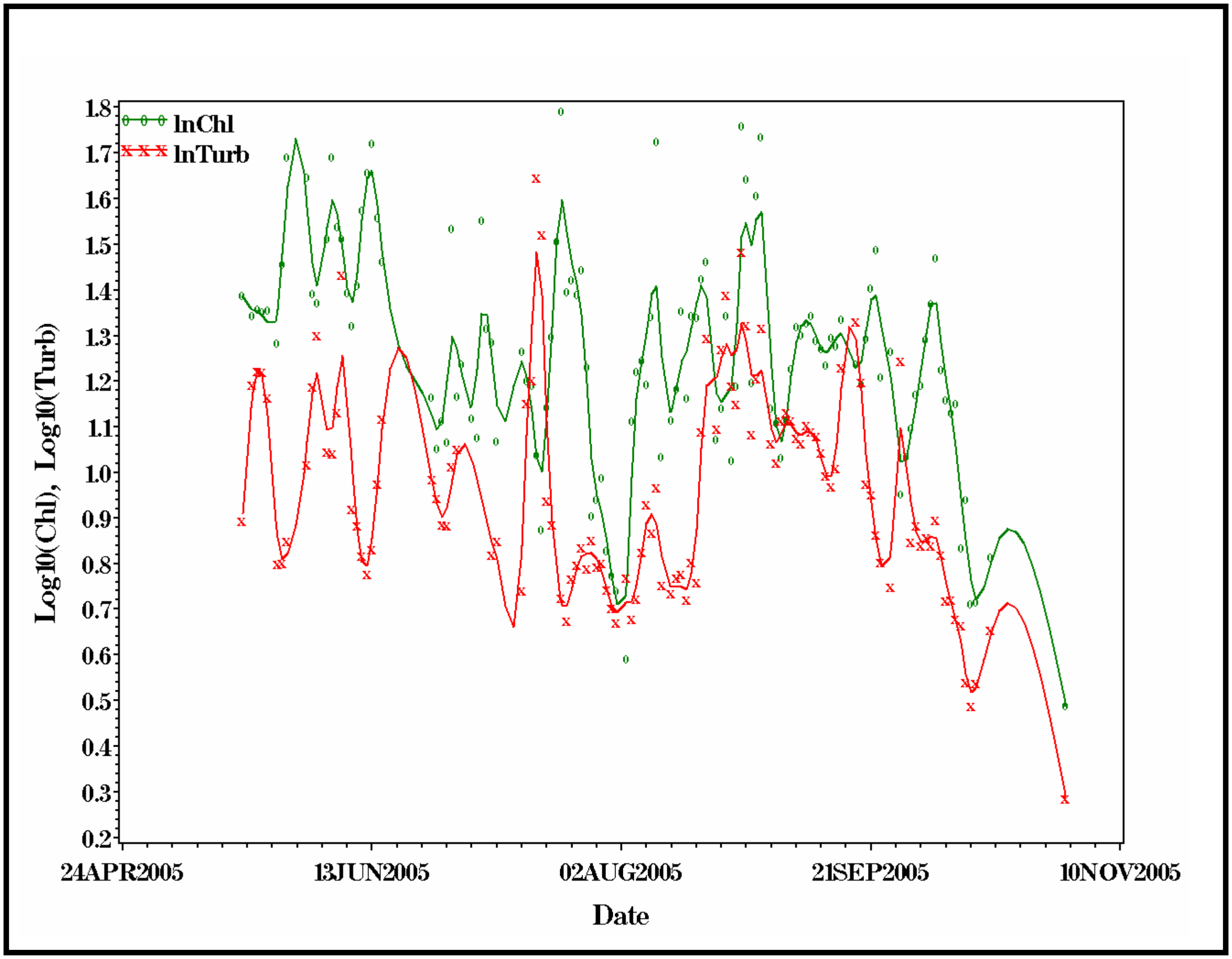


Figure 3-22. Chlorophyll and Turbidity. This may not have much to do with predicting Production or Respiration, but it appears in the times series plot above that spikes in turbidity are often followed by spikes in chlorophyll. This is supported by examining the lag-correlations. It appears that the ln Turb ln Chl correlation peaks with a lag of 4-5 days.

Table 3-2. Correlations of ln Chl against ln Turb with 1 to 10 days of lag.

Variable	lag	correlation	p-value
LnTurb	1	0.23826	0.0110
LnTurb	2	0.24567	0.0090
LnTurb	3	0.39600	<.0001
LnTurb	4	0.48548	<.0001
LnTurb	5	0.45588	<.0001
LnTurb	6	0.42225	<.0001
LnTurb	7	0.32288	0.0007
LnTurb	8	0.22081	0.0229
LnTurb	9	0.21025	0.0313
LnTurb	10	0.16558	0.0930

3.4.7 Parallel Axis Plots

Parallel axis plots are useful for searching out specific multivariate relationships and we have used them here in a preliminary fashion as a "relationship mining" tool. In these plots, each variable has been scaled (indicated by the 's' added to the beginning of the variable name) by subtracting the mean and dividing by the variance. This scaling process produces data that can be plotted against a single vertical axis. The units of this vertical axis are numbers of standard deviations above or below the mean.

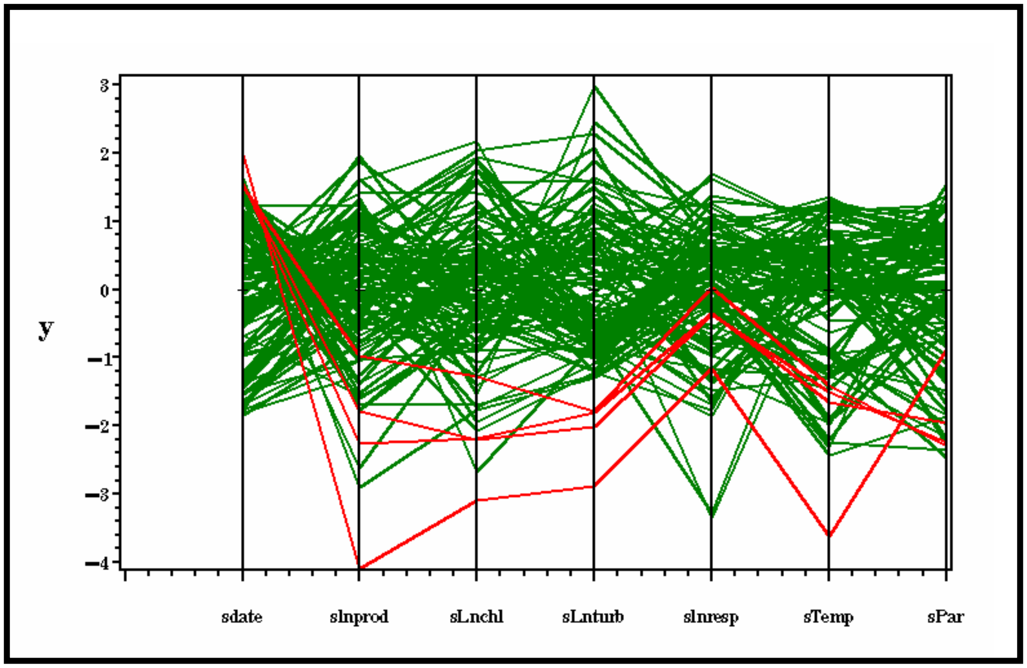


Figure 3-23. This plot shows that the low turbidity - low Production values shown in the Production vs turbidity scatter plot are also associated with low chlorophyll, low temperature, and low PAR and that they occur late in the sampling period.

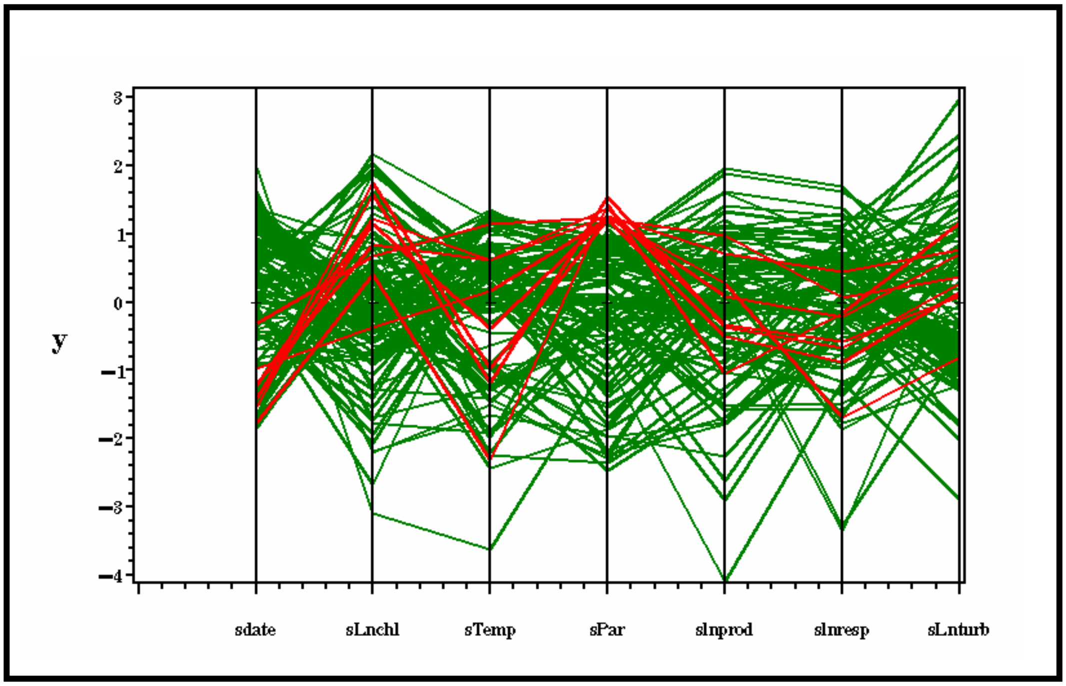


Figure 3-24. This plot shows that the high PAR-mid production values that cause the production vs. PAR plot to turn down at the end are from the early part of the sampling period and are mostly associated with low temperature.

3.4.8 Next Steps

We have been working with this method of computing important estuarine rate processes for a relatively short time. Our initial impressions are that we have data collection platforms that produce a large amount of data suitable for these analyses. Furthermore, ConMon sites are situated in a broad array of Bay habitats so the potential for comparative ecology is very great. Finally, there is strong support in the literature for the linkage between the magnitude, seasonal pattern and variance of metabolic rates and nutrient loading rates, thus making these measurements a useful index of system performance and a gauge of management action effectiveness. However, we have a number of steps to take before we would recommend adding this approach to the arsenal of analyses currently being used. To date we have accomplished the following and plan to continue additional analyses as listed below:

1) We have confirmed the internal reliability of the metabolism algorithym using very simple data sets and compared results to traditional hand-based graphical analyses.

2) We have considered several pre-testing schemes to help eliminate inappropriate data.

3) We have considered several other computational schemes and will continue to investigate these in the coming months.

4) We have initiated an effort to model these rates using ConMon and other data and at this early stage are optimistic about results. We may consider selecting a range of stations and attempt modeling efforts in a comparative context.

5) We have concluded at this stage that there are important ecosystem changes captured with this approach and that these will serve as indices of change in these shallow water ecosystems.

6) Finally, if we can develop a reliable and operational computation system we would like to move these measurements to the Eyes on the Bay web site along with readily understood graphics and text explaining the significance of these measurements.

3.5 Cited Literature

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4.0 Temporal Adjustments of DATAFLOW Observations: A case study using ConMon, DATAFLOW and ACT Buoy data in the Patuxent River estuary

Elgin Perry, Research Statistician

4.1 Introduction

4.1.1 Concept

The use of a relatively new technology, DATAFLOW, in the Chesapeake Bay Biomonitoring program has led to advances in describing spatial pattern in many Chesapeake Bay tributaries, especially in shallow water areas not previously directly monitored in the traditional monitoring program. While limited to surface water quality measurements, use of DATAFLOW has increased observations of important water quality variables, such as water clarity, dissolved oxygen and algal biomass (as indexed by chlorophyll-a) by several orders of magnitude. However, as with any measurement technology, there are technical and other issues that must be addressed. In the case of DATAFLOW, calibration of sensor-derived values with traditional laboratory-based values is critical and is the focus of on-going analyses. In addition, there are temporal issues to be resolved with DATAFLOW measurements. Specifically, DATAFLOW cruises generally start in early morning and conclude by late afternoon. While relatively synoptic, there are some variables collected with DATAFLOW that change considerably during a cruise period. Thus, we can obtain a somewhat distorted view of spatial distribution of these variables. For example, surface water DO can change considerably during the course of a cruise, in some areas changing by as many as 5 mg/l in 6 – 7 hours. In other systems the change is not that large but still important. The focus of this Chapter is to present an analysis of data collected from three different measurement platforms in the Patuxent River estuary towards the goal of adjusting DATAFLOW observations to a single base time during each cruise and thereby obtain an unbiased set of observations.

4.1.2 Adjustment for Short Term Temporal Signal

A statistical model has been implemented that is based on a concept of adjusting DATAFLOW data to a point in time. The ConMon data will accompany each DATAFLOW cruise and gives information about the temporal signal at a single location. With the assumption that the temporal signal at this location is a reasonable approximation of the temporal signal at all locations traversed by the data flow cruise, an algorithm for removing the temporal variation from the DATAFLOW data can be developed. The approach implemented here (which is similar to that used by Mark Trice at MD-DNR) is to estimate the temporal trend from the ConMon data and to use that temporal trend estimate to adjust the DATAFLOW data. If the target is to estimate the spatial pattern of DO at 7:00 am, DATAFLOW data collected after 7:00 am would be adjusted to reflect the 7:00 am DO. For example, the DATAFLOW datum collected at 8:00 am would be adjusted based on the estimated difference between the ConMon mean at 8:00 and the ConMon mean at 7:00. If the trend at the ConMon site shows that DO increased from 4 ppm to 5 ppm between 7:00 and 8:00, then the DATAFLOW data would be adjusted by subtracting 1 ppm from the 8:00 am measurement to yield an estimate of the 7:00 am DO. In what follows, the time that data are being adjusted to is called the base-time which is 7:00 am in this example. The time at which the DATAFLOW observation is actually taken is called the observation-time which is 8:00 am in this example.

As noted above, a key assumption underlying this adjustment for short term temporal signal is that the temporal signal at the ConMon site is representative of temporal signal over the area surveyed by a DATAFLOW Cruise. One test of this assumption is to implement the adjustment algorithm at a location where data for the observation-time (time at which data are collected) and the base-time (time to which data are being standardized) are both known. The test involves implementing the adjustment using the observation-time data to obtain an estimate of the base-time data. The estimated and known base-time data are compared to assess the efficacy of the adjustment.

The CBL-ACT buoy data provide a location for which both the observation-time data and base-time data are known. These two terms are more fully described below. Data from this location are available for the period for the period Aug. 02 to Aug. 23, 2005. This buoy is located within the cruise field of the ConMon site at Pin Oak which adds to the realism of using the buoy data as a surrogate for the DATAFLOW data. To construct the test, assume that the CBL-ACT Buoy is on the cruise track of the DATAFLOW collection. The analysis is conducted using DO data. The buoy data record tells the true base-time DO reading (e.g. DO at 7:00 am). It also tells what the DATAFLOW instrumentation would observe if it were at the Buoy at a subsequent observation-time (e.g. 8:00 am). Thus the buoy data record provides the means to compare estimated base-time DO to the true base-time DO. This validation can be repeated for a sequence of observations within one day as if the DATAFLOW boat passed the buoy at 9:00 am, 10:00 am, and so on. This sequence of adjusted data provides perspective on how the lag time of the adjustment affects the precision of the adjustment.

4.3 Methods

4.3.1 Estimating Temporal Trend

As described above, a key component of the adjustment process is the estimation of the temporal trend over the period of time that it takes to complete a cruise. For this analysis, it is assumed that the cruise window is less than 8 hours. One of the first questions to address with respect to estimating short term temporal trend is whether the estimate should be unique for each day or an estimate of trend aggregated over days. Based on the variability of trends observed in plots of both ConMon data and the Buoy data, this effort implements the adjustment using a “unique for each” day approach. Other averaging windows might be explored in future research.

To estimate the trend for each day, a LOESS regression curve (Cleveland, 1993) was fitted to the ConMon data collected between the hours of 6:00 am and 3:00 pm (see Figures at end of Chapter pgs. 71-89; x-axis is time in hours; y-axis is dissolved oxygen concentration in mg l^{-1}; + = measured DO, • = LOESS regression model; dates are provided at the top of each figure, 1Aug-23Aug 2005). The LOESS regression approach was chosen because of the variety of trends observed in plots of the ConMon data. It was clear that a simple linear model and even low order polynomial models would not be sufficiently flexible to follow the central tendency of the data over time. LOESS regression fits a regression line that makes no a priori assumption about the mathematical form of the fitted curve. The interval 6:00am - 3:00pm was chosen for several reasons. Because cruises typically start in the morning, it is the most relevant window from an operations point of view. Dissolved oxygen concentrations typically reach a nadir in the early part of this interval, thus it is the most important interval of time for estimating the most severe environmental stress due to low oxygen conditions. Looking at the daily time series plots (see Figures at end of Chapter), the DO trends at the ConMon site and the Buoy site seem most parallel for the morning period. The variability of DO concentrations is lower in the morning period. The choice of the 6:00 am to 3:00 pm window is based primarily on the first two reasons; the second two reasons being convenient happen-stance.

4.3.2 Adjusting the Data

Once the trend line estimate is computed, the adjustment is simple. From this trend line, obtain the estimated DO for the base-time ($BTDO_C$) and the estimated DO for the observation-time ($OTDO_C$) and compute their difference ($OTDO_C$ - $BTDO_C$) to estimate the change in DO between the base-time and the observation-time at the ConMon location. Now assuming that the observed difference at the ConMon location is a reasonable estimate of the difference for the Buoy location (which is serving as a surrogate for a DATAFLOW location) subtract this difference from the observation-time DO ($OTDO_B$) in the Buoy record to obtain the time adjusted DO for the base-time ($BTDO_{B/A} = OTDO_B - (OTDO_C - BTDO_C)$). This procedure was conducted using 7:00 a.m. as the base-time and the integer hours from 8:00 a.m. to 2:00 p.m. as the observation times. For each observation-time, we obtain 1 adjusted DO for each day of data.

To assess the efficacy of this adjustment process, we compare the bias and precision of the adjusted data to the bias and precision of unadjusted data. That is, is it better to use the DATAFLOW data as observed in spite of the temporal trend or is it better to attempt to adjust for the temporal trend? For each day, we compute two differences: the adjusted DO minus the true base-time DO ($BTDO_{B/A} - BTDO_B$) and the unadjusted DO minus the true base-time DO ($OTDO_B - BTDO_B$).
Bias is assessed by computing the mean of the daily differences. Precision is assessed by computing the mean squared error of the differences. In addition, we compare the minima and maxima of the true base-time DO and each of the estimates.

Variable definitions:

$BTDO_C$ = base-time dissolved oxygen at ConMon site.
$OTDO_C$ = Observation-time dissolved oxygen at ConMon site.
$BTDO_B$ = base-time dissolved oxygen at Buoy site.
$OTDO_B$ = Observation-time dissolved oxygen at Buoy site.

$BTDO_{B/A}$ = estimated base-time dissolved oxygen at buoy site obtained by adjusting $OTDO_B$
= $OTDO_B - (OTDO_C - BTDO_C)$

4.4 Results

Figures 4-1 and 4-2 are box-and-whisker plots for each hour for both the ConMon data and the Buoy data. By tracking the median (horizontal bar in the box) or the mean (the + symbol in the box) one can discern the average diel trend for the available data. The boxes represent the interval that contains 50% of the data. The whiskers (vertical lines) show the typical range of the data while the symbols beyond the whiskers show outliers. It is clear that variability over days is smallest in the morning hours and is greater in the mid-day through early evening. At the buoy there are substantial spikes to the high side starting as early as mid-morning and continuing until dark. At the ConMon location, there are spikes to the low side during darkness.

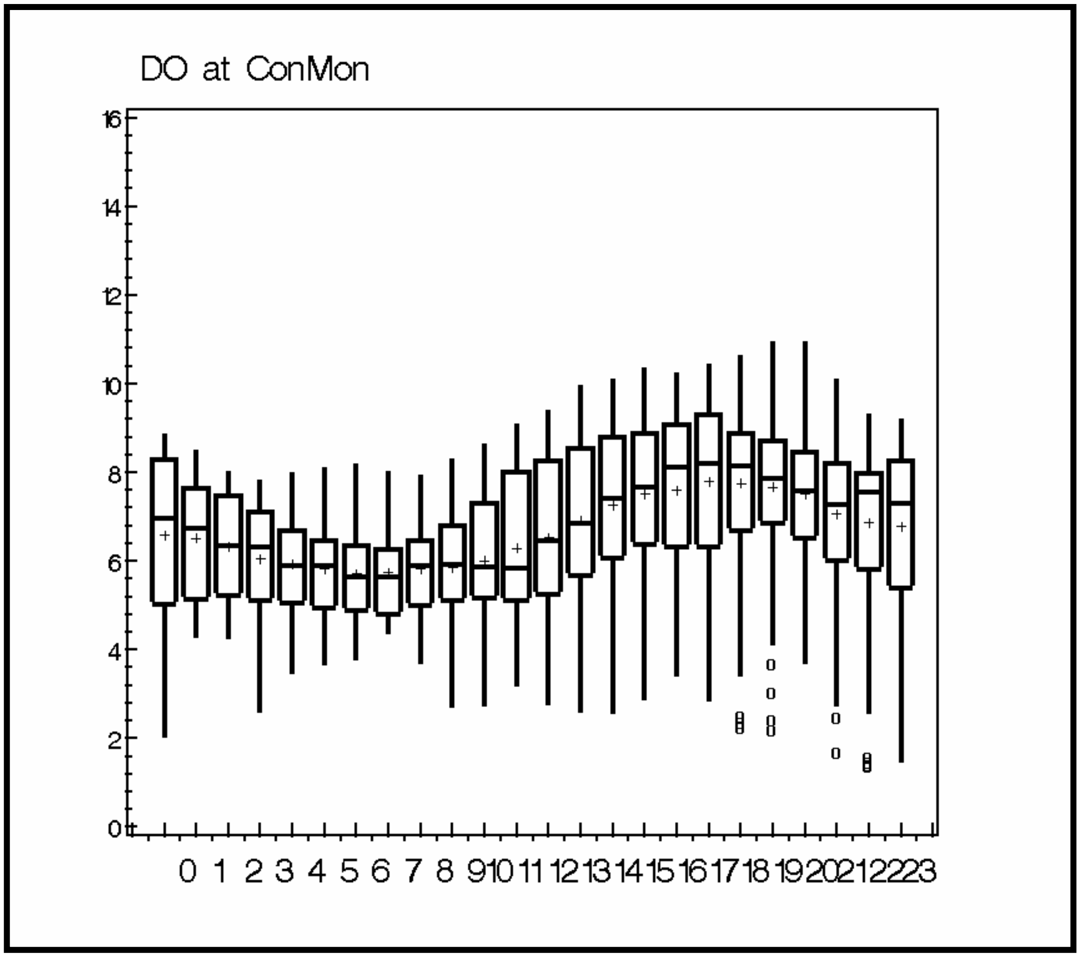


Figure 4-1. Box and Whisker plot of hourly data for the Pin Oak ConMon site for the periods of record.

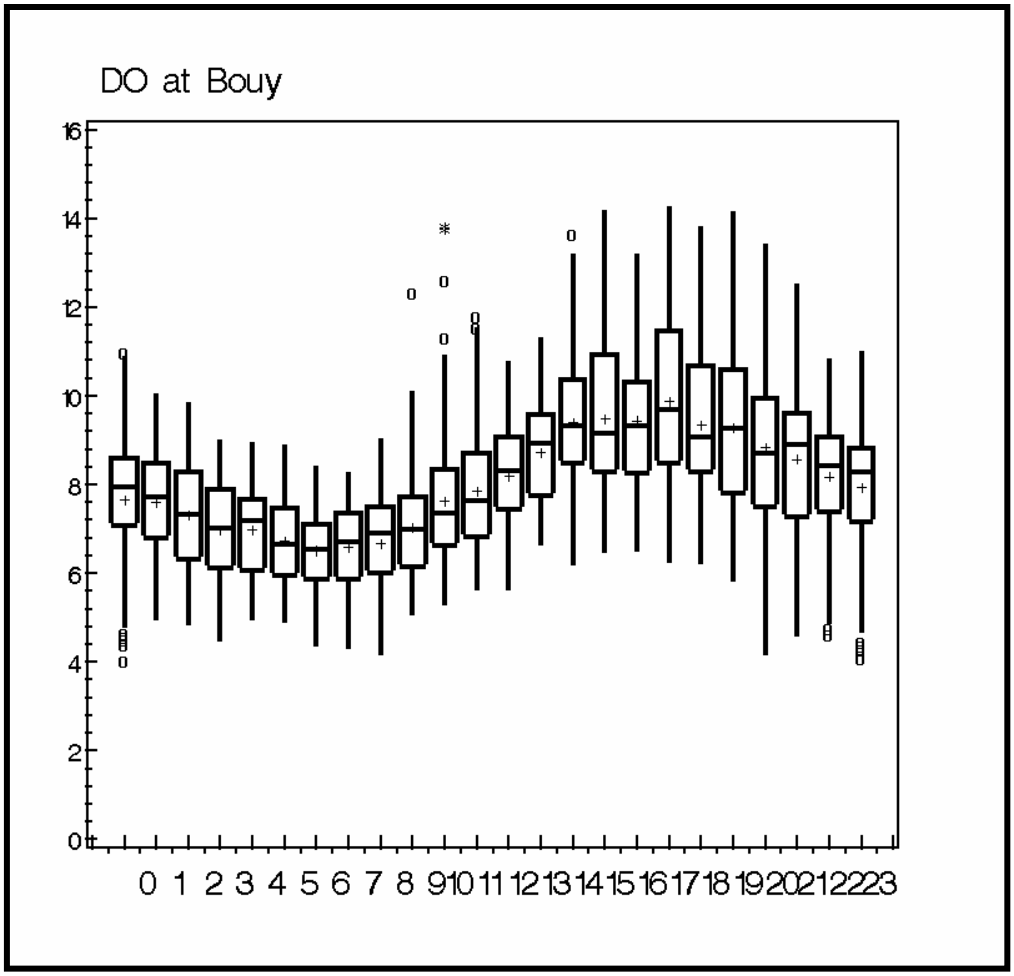


Figure 4-2. Box and Whisker plot of hourly data for the ACT Buoy site for the period of record.

4.4.1 Assessment Endpoints

When assessing estimates, it is important to consider both the bias and the precision of the estimate. The primary question is "does the adjustment process reduce bias?". In answering this question, both the observed data ($OTDO_B$) and the adjusted data ($BTDO_{B/A}$) are considered estimates of the known base-time observations ($BTDO_B$). Bias is assessed using the mean over days of the difference between the known base-time data and each of the estimates of base-time data. (Table 4-1) These means are computed where the difference between the base-time and the observation time increases in sequential integer hours. This gives perspective on how well the adjustment process performs for increasing degrees of temporal adjustment.

Looking at bias, it is clear that the bias of both the adjusted data and the observed data increases with the lag-time, but the increase for the observed data is greater than for the adjusted data.

Table 4-1. Assessment of bias for adjusted data and observed data as a function of hours of lag.

hours of lag	mean base-time DO	mean observed DO	mean adjusted DO	mean residual for observed	mean residual for adjusted
1	6.64	6.63	6.58	-0.01	-0.06
2	6.64	6.82	6.70	0.18	0.06
3	6.64	7.32	7.05	0.68	0.41
4	6.72	7.88	7.34	1.16	0.62
5	6.72	8.02	7.22	1.30	0.51
6	6.74	8.47	7.37	1.73	0.63
7	6.74	9.41	7.95	2.67	1.21

In addition to comparing means, maxima and minimum over days can be compared as well. Looking at these extremes (Table 4-2), both the observed DO and the adjusted DO overestimate the minimum and overestimate the maximum as compared to the base-time DO. While the adjusted DO minimum is consistently closer to the base-time minimum than the observed minimum, this relation does not hold for the maximum.

Table 4-2. Comparison of Maxima and Minima for adjusted data and observed data as a function of hours of lag.

hours of lag	minimum base-time DO	minimum observed DO	minimum adjusted DO	maximum base-time DO	maximum observed DO	maximum adjusted DO
1	4.28	4.78	4.78	8.19	8.63	8.34
2	4.28	5.05	4.96	8.19	9.08	9.51
3	4.28	5.26	5.43	8.19	11.36	12.22
4	4.28	5.80	4.95	8.19	11.58	11.66
5	4.28	5.68	5.31	8.19	10.77	9.91
6	4.28	6.82	4.70	8.19	10.60	10.22
7	4.28	7.05	5.74	8.19	11.39	10.30

To address total prediction error (bias + precision), mean square prediction error (Equations 4-1.1 and 4-1.2) is computed using the same layout of comparing observed data versus adjusted data over the hours of lag (Table 4-3). The square root of the MSPE measures the average deviation from the true base-time measurement. The trend over lag in the total prediction error shows that the adjusted data outperforms the observed data as lag increases. For 3 hours of lag and less, the observed data have smaller prediction error than the adjusted data. For 4 hours of lag and more, the adjusted data have smaller prediction error than the observed.

Table 4-3. Comparison of Mean Squared Prediction Error (MSPE) for adjusted data and observed data as a function of hours of lag.

hours of lag	MSPE for Observed DO	MSPE for adjusted DO	root MSPE for Observed DO	root MSPE for adjusted DO
1	0.36	0.29	0.60	0.54
2	0.81	1.03	0.90	1.01
3	1.68	2.43	1.30	1.56
4	3.24	2.70	1.80	1.64
5	3.09	1.89	1.76	1.37
6	4.34	2.64	2.08	1.62
7	8.95	3.99	2.99	2.00

Eqn. 4-1.1

$$MSPE_O = \sum_{DAYS} \left(OTBT_B - BTDO_B \right)^2$$

Eqn. 4-1.2

$$MSPE_A = \sum_{DAYS} \left(BTDO_{B/A} - BTDO_B \right)^2$$

Where:
$MSPE_O$ = Mean square prediction error for observed data,
$MSPE_A$ = Mean square prediction error for adjusted data, and
other variables are defined above.

4.5 Discussion

This assessment studies the efficacy of using ConMon data from a single site to adjust for the short term temporal signal that influences DATAFLOW measurements during a synoptic cruise. The case studied here uses the diel trend of DO at the shallow ConMon location to adjust surface DO observations made by a continuous Buoy monitor in the mid-channel nearby. By comparing the day by day overlay plots of the buoy and ConMon data, it is readily apparent that DO in these two locations is responding differently to the local habitat. Both have a diel signal of high DO during the day and low DO at night. However, DO at the ConMon location tends to go lower at night presumably in response to the more proximate benthic community. At the buoy location, daytime DO can be highly variable and often exceeds saturation by considerable amounts. Because of these differences, this is a difficult case for the adjustment procedure to perform well. A more reasonable case would be to use the trend in the ConMon data to adjust a comparable shallow water location. The expectation is that more similar habitat would produce more similar diel trends.

Even though the habitat of these two locations is quite different and leads to predictable differences in the diel trends in DO at the two locations, the adjustment process shows limited success. Bias of the adjusted data is reduced relative to the unadjusted data when the lag between the observation-time and base-time exceeds one hour. Thus on average over many surveys the adjustment process leads to improvement. Looking at MSPE, the adjustment process leads to improvement when the lag exceeds 3 hours. Thus at the level of a single survey, it seems that it is best not to adjust if the lag is less than 3 hours and to adjust when the lag exceeds 3 hours. If the habitat of the two sites were more comparable, the adjustment algorithm might lead to improvement at shorter lags.

By comparing the root MSPE (Table 4-3) and the bias (Table 4-1), one can assess the relative contribution of bias and precision to total error. At 2 hours of lag, the bias of adjusted data is 0.06 and the total root MSPE is 1.01. From these it is inferred that lack of precision or variance contributes on average the greatest part of error (1.01 - 0.06) = 0.95. At 7 hours of lag the bias is 1.21 and the MSPE is 2.00. On average, variance contributes 0.79 to the error. Thus as lag increases, bias becomes a larger part of the prediction error problem. This is because the diel trends at the two locations tend to diverge through the day.

This assessment shows that the adjustment process shows promise in that the adjusted data are improved relative to unadjusted data. However, a prediction error of 1.0 to 2.0 mg/l of DO is large compared to criteria of 3.0 to 5.0 mg/l. Research to improve on this should be pursued. As noted above, this test case might be classed as a fairly difficult one. One line of research would be to investigate test cases where the data serving as a model for diel trend and the data being adjusted come from more similar habitats.

While this assessment allows the evaluation of trends in adjustment over time by computing the adjustment with different degrees of lag, it provides no information on the effect of space because the buoy location and the ConMon location are a fixed distance apart. One would expect that adjustment error would increase with distance from the ConMon location. It would be interesting to test this conjecture.

Future research should attempt to address all three dimensions that might affect the accuracy of adjustment: time, space, and changes of habitat. A simple experiment that would provide information on these three dimensions could be conducted by using the DATAFLOW boat to repeatedly run a cruise track near a ConMon monitor. For example, start near the monitor and run a cruise track along shore, move to mid-channel, and return to the monitor. The cruise track should be designed to be repeated every hour. Data from the first run would serve as the base-time data. Data from subsequent runs could be adjusted using the diel trend from the monitor and compared to the base-time run.

In addition to obtaining data that allows for quantification of spatial, temporal, and habitat aspects of the adjustment process, additional research is needed to refine the mathematics of the adjustment procedure. Examples include: is it better to estimate the diel trend using ConMon data from the single day of the cruise or using data for a neighborhood of days around the cruise? What degree of smoothing is best for quantifying the diel trend? Can the diel trend be adjusted for habitat differences in a useful way?

It is clear that these new technologies that allow the collection of temporally and spatially dense data offer many opportunities for improving the resolution of assessing the shallow water environment. With this opportunity comes the discovery of problems that have been ignored in the past. Adjusting for the diel trend in a synoptic survey is one such problem that remains to solved. It is shown by this assessment that the problem is significant and that it is possible to some extent to use the ConMon data to adjust for the diel trend in the synoptic data. As noted above, there is room for improvement and several lines of research to improve this improvement are suggested.

4.6 Cited Literature

Cleveland, W. S. (1993) Visualizing Data. AT&T Bell Laboratories, Murray Hill, NJ. pp360.

4.7 Appendix

4.7.1 Supplemental Data Tables and Figures

Table 4-5. Day by Day comparison of base-time DO; observed DO; and adjusted DO for 1 hour lag.

date	base time	hours of lag	base-time DO	observed DO	adjusted DO	improvement
01AUG2005	7:00	1	5.86	5.04	4.78	Worse
02AUG2005	7:00	1	5.99	6.98	6.75	Better
03AUG2005	7:00	1	8.16	7.59	7.56	Worse
04AUG2005	7:00	1	8.19	8.63	8.34	Better
05AUG2005	7:00	1	7.58	7.21	7.08	Worse
11AUG2005	7:00	1	6.28	7.35	6.93	Better
12AUG2005	7:00	1	8.18	7.53	7.54	Better
13AUG2005	7:00	1	7.72	7.71	8.03	Worse
14AUG2005	7:00	1	6.81	7.47	7.39	Better
15AUG2005	7:00	1	7.00	6.12	7.26	Better
16AUG2005	7:00	1	5.89	5.62	5.29	Worse
17AUG2005	7:00	1	5.23	4.78	5.01	Better
18AUG2005	7:00	1	5.30	5.89	5.52	Better
19AUG2005	7:00	1	6.94	6.92	6.96	Better
20AUG2005	7:00	1	4.28	4.99	4.95	Better
21AUG2005	7:00	1	6.90	6.43	6.21	Worse
22AUG2005	7:00	1	6.93	6.81	6.55	Worse
23AUG2005	7:00	1	6.28	6.19	6.27	Better
percent improved						61

Table 4-6. Day by Day comparison of base-time DO; observed DO; and adjusted DO for 2 hour lag.

date	base time	hours of lag	base-time DO	observed DO	adjusted DO	improvement
01AUG2005	7:00	2	5.86	5.85	5.37	Worse
02AUG2005	7:00	2	5.99	6.76	6.03	Better
03AUG2005	7:00	2	8.16	8.45	8.36	Better
04AUG2005	7:00	2	8.19	7.25	6.33	Worse
05AUG2005	7:00	2	7.58	6.88	6.16	Worse
11AUG2005	7:00	2	6.28	8.46	7.62	Better
12AUG2005	7:00	2	8.18	9.08	9.51	Worse
13AUG2005	7:00	2	7.72	7.73	8.20	Worse
14AUG2005	7:00	2	6.81	7.60	7.44	Better
15AUG2005	7:00	2	7.00	6.21	8.75	Worse
16AUG2005	7:00	2	5.89	5.22	5.04	Worse
17AUG2005	7:00	2	5.23	5.47	6.03	Worse
18AUG2005	7:00	2	5.30	6.98	6.01	Better
19AUG2005	7:00	2	6.94	6.09	6.46	Better
20AUG2005	7:00	2	4.28	5.05	4.96	Better
21AUG2005	7:00	2	6.90	7.24	6.61	Better
22AUG2005	7:00	2	6.93	5.93	5.26	Worse
23AUG2005	7:00	2	6.28	6.46	6.39	Better
percent improved						50

Table 4-7. Day by Day comparison of base-time DO; observed DO; and adjusted DO for 3 hour lag.

date	base time	hours of lag	base-time DO	observed DO	adjusted DO	improvement
01AUG2005	7:00	3	5.86	6.19	5.51	Worse
02AUG2005	7:00	3	5.99	6.75	5.43	Better
03AUG2005	7:00	3	8.16	8.74	8.91	Worse
04AUG2005	7:00	3	8.19	7.52	5.97	Worse
05AUG2005	7:00	3	7.58	7.13	5.74	Worse
11AUG2005	7:00	3	6.28	8.74	7.15	Better
12AUG2005	7:00	3	8.18	11.36	12.22	Worse
13AUG2005	7:00	3	7.72	9.38	9.38	Worse
14AUG2005	7:00	3	6.81	8.41	8.11	Better
15AUG2005	7:00	3	7.00	6.72	9.66	Worse
16AUG2005	7:00	3	5.89	5.62	5.67	Better
17AUG2005	7:00	3	5.23	5.26	6.07	Worse
18AUG2005	7:00	3	5.30	7.17	5.88	Better
19AUG2005	7:00	3	6.94	6.24	7.29	Better
20AUG2005	7:00	3	4.28	5.78	5.50	Better
21AUG2005	7:00	3	6.90	6.66	5.63	Worse
22AUG2005	7:00	3	6.93	7.00	5.87	Worse
23AUG2005	7:00	3	6.28	7.13	6.92	Better
percent improved						44

Table 4-8. Day by Day comparison of base-time DO; observed DO; and adjusted DO for 4 hour lag.

date	base time	hours of lag	base-time DO	observed DO	adjusted DO	improvement
01AUG2005	7:00	4	5.86	7.01	6.07	Better
02AUG2005	7:00	4	5.99	7.14	5.34	Better
03AUG2005	7:00	4	8.16	8.51	9.68	Worse
04AUG2005	7:00	4	8.19	8.75	6.67	Worse
05AUG2005	7:00	4	7.58	8.16	6.21	Worse
10AUG2005	7:00	4	8.08	6.99	6.32	Worse
11AUG2005	7:00	4	6.28	9.95	7.99	Better
12AUG2005	7:00	4	8.18	11.58	11.66	Worse
13AUG2005	7:00	4	7.72	10.10	9.34	Better
14AUG2005	7:00	4	6.81	9.20	8.76	Better
15AUG2005	7:00	4	7.00	7.57	9.18	Worse
16AUG2005	7:00	4	5.89	6.67	7.09	Worse
17AUG2005	7:00	4	5.23	5.84	6.73	Worse
18AUG2005	7:00	4	5.30	7.96	6.35	Better
19AUG2005	7:00	4	6.94	5.80	7.10	Better
20AUG2005	7:00	4	4.28	7.30	6.71	Better
21AUG2005	7:00	4	6.90	6.30	4.95	Worse
22AUG2005	7:00	4	6.93	7.84	6.44	Better
23AUG2005	7:00	4	6.28	6.98	6.80	Better
percent improved						53

Table 4-9. Day by Day comparison of base-time DO; observed DO; and adjusted DO for 5 hour lag.

date	base time	hours of lag	base-time DO	observed DO	adjusted DO	improvement
01AUG2005	7:00	5	5.86	6.69	5.37	Better
02AUG2005	7:00	5	5.99	7.71	5.48	Better
03AUG2005	7:00	5	8.16	7.65	9.91	Worse
04AUG2005	7:00	5	8.19	8.61	6.23	Worse
05AUG2005	7:00	5	7.58	8.47	6.11	Worse
10AUG2005	7:00	5	8.08	8.64	7.82	Better
11AUG2005	7:00	5	6.28	9.24	6.94	Better
12AUG2005	7:00	5	8.18	10.77	9.39	Better
13AUG2005	7:00	5	7.72	9.81	8.60	Better
14AUG2005	7:00	5	6.81	9.41	8.68	Better
15AUG2005	7:00	5	7.00	7.71	7.65	Better
16AUG2005	7:00	5	5.89	7.09	7.81	Worse
17AUG2005	7:00	5	5.23	6.02	7.64	Worse
18AUG2005	7:00	5	5.30	8.04	6.30	Better
19AUG2005	7:00	5	6.94	5.68	6.92	Better
20AUG2005	7:00	5	4.28	7.44	6.69	Better
21AUG2005	7:00	5	6.90	6.96	5.31	Worse
22AUG2005	7:00	5	6.93	8.85	7.28	Better
23AUG2005	7:00	5	6.28	7.52	7.15	Better
percent improved						68

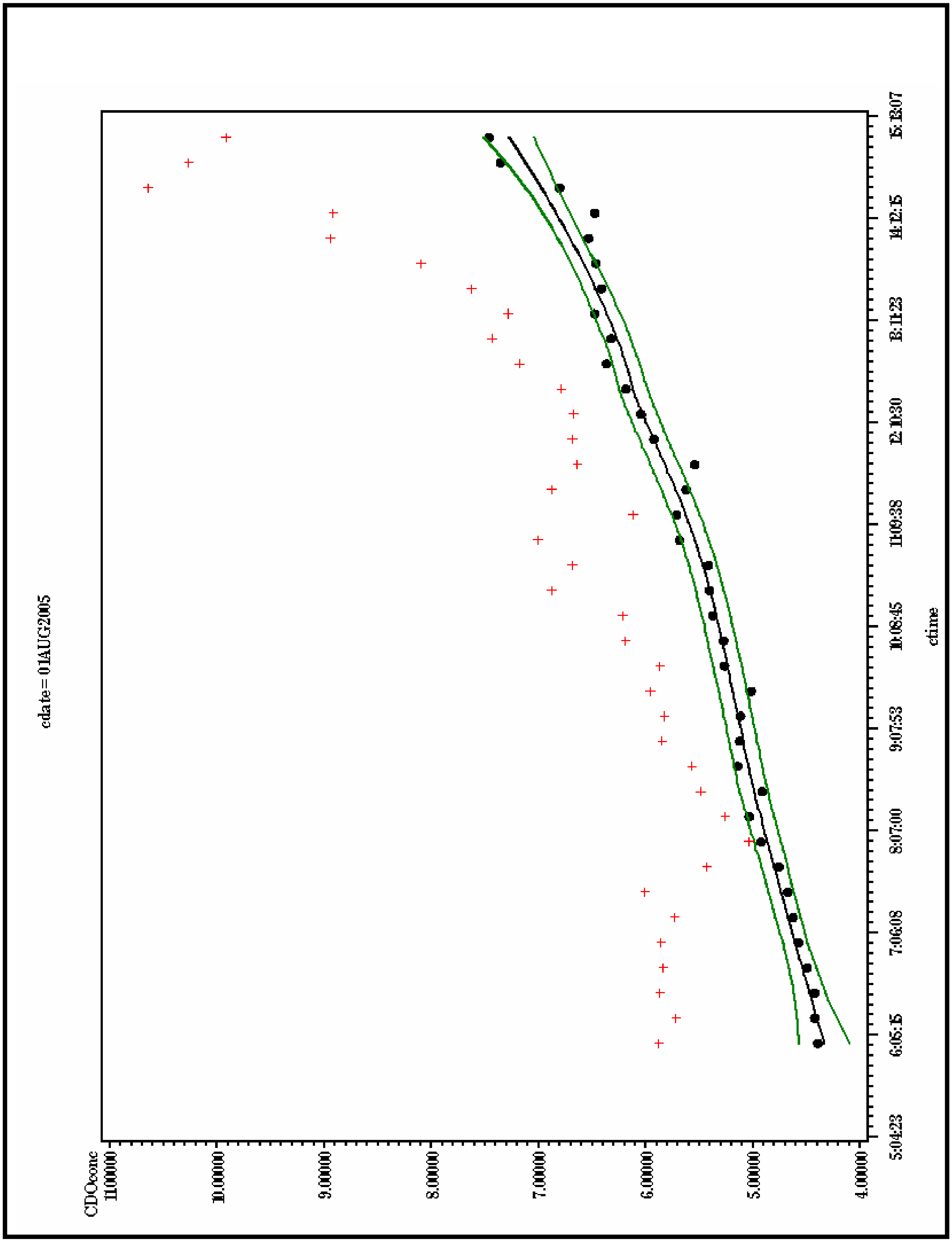
Table 4-10. Day by Day comparison of base-time DO; observed DO; and adjusted DO for 6 hour lag.

date	base time	hours of lag	base-time DO	observed DO	adjusted DO	improvement
01AUG2005	7:00	6	5.86	7.44	5.78	Better
02AUG2005	7:00	6	5.99	9.06	6.44	Better
03AUG2005	7:00	6	8.16	7.85	10.22	Worse
04AUG2005	7:00	6	8.19	9.53	6.95	Better
05AUG2005	7:00	6	7.58	9.55	7.00	Better
10AUG2005	7:00	6	8.08	8.28	6.69	Worse
11AUG2005	7:00	6	6.28	7.16	4.70	Worse
12AUG2005	7:00	6	8.18	10.54	8.21	Better
13AUG2005	7:00	6	7.72	10.60	9.09	Better
14AUG2005	7:00	6	6.81	9.09	7.91	Better
15AUG2005	7:00	6	7.00	7.87	6.59	Better
16AUG2005	7:00	6	5.89	7.60	7.99	Worse
17AUG2005	7:00	6	5.23	7.06	9.36	Worse
18AUG2005	7:00	6	5.30	9.53	7.71	Better
19AUG2005	7:00	6	6.94	6.82	8.02	Worse
20AUG2005	7:00	6	4.28	7.26	6.37	Better
21AUG2005	7:00	6	6.90	7.89	6.26	Better
22AUG2005	7:00	6	6.93	9.34	7.40	Better
percent improved						67

Table 4-11. Day by Day comparison of base-time DO; observed DO; and adjusted DO for 7 hour lag.

date	base time	hours of lag	base-time DO	observed DO	adjusted DO	improvement
01AUG2005	7:00	7	5.86	8.95	6.85	Better
02AUG2005	7:00	7	5.99	9.81	6.87	Better
03AUG2005	7:00	7	8.16	8.35	10.30	Worse
04AUG2005	7:00	7	8.19	9.99	7.15	Better
05AUG2005	7:00	7	7.58	11.34	8.71	Better
10AUG2005	7:00	7	8.08	9.18	5.74	Worse
11AUG2005	7:00	7	6.28	9.22	6.90	Better
12AUG2005	7:00	7	8.18	11.39	8.65	Better
13AUG2005	7:00	7	7.72	10.37	8.53	Better
14AUG2005	7:00	7	6.81	10.77	9.16	Better
15AUG2005	7:00	7	7.00	9.23	7.25	Better
16AUG2005	7:00	7	5.89	7.71	7.15	Better
17AUG2005	7:00	7	5.23	7.18	9.57	Worse
18AUG2005	7:00	7	5.30	9.30	7.27	Better
19AUG2005	7:00	7	6.94	7.05	8.16	Worse
20AUG2005	7:00	7	4.28	9.84	8.98	Better
21AUG2005	7:00	7	6.90	10.19	8.59	Better
22AUG2005	7:00	7	6.93	9.54	7.27	Better
percent improved						78

The following figures show the within day progression of the DO trend at both the ConMon site and the buoy site. In the figures, black dots represent individual observations at the ConMon site, the red + indicates individual observations at the buoy site, the black line follows the LOESS regression trend in the ConMon data and the green lines indicate confidence intervals on the regression line. The regression line of the ConMon data is used to compute the temporal adjustment which is applied to the buoy data.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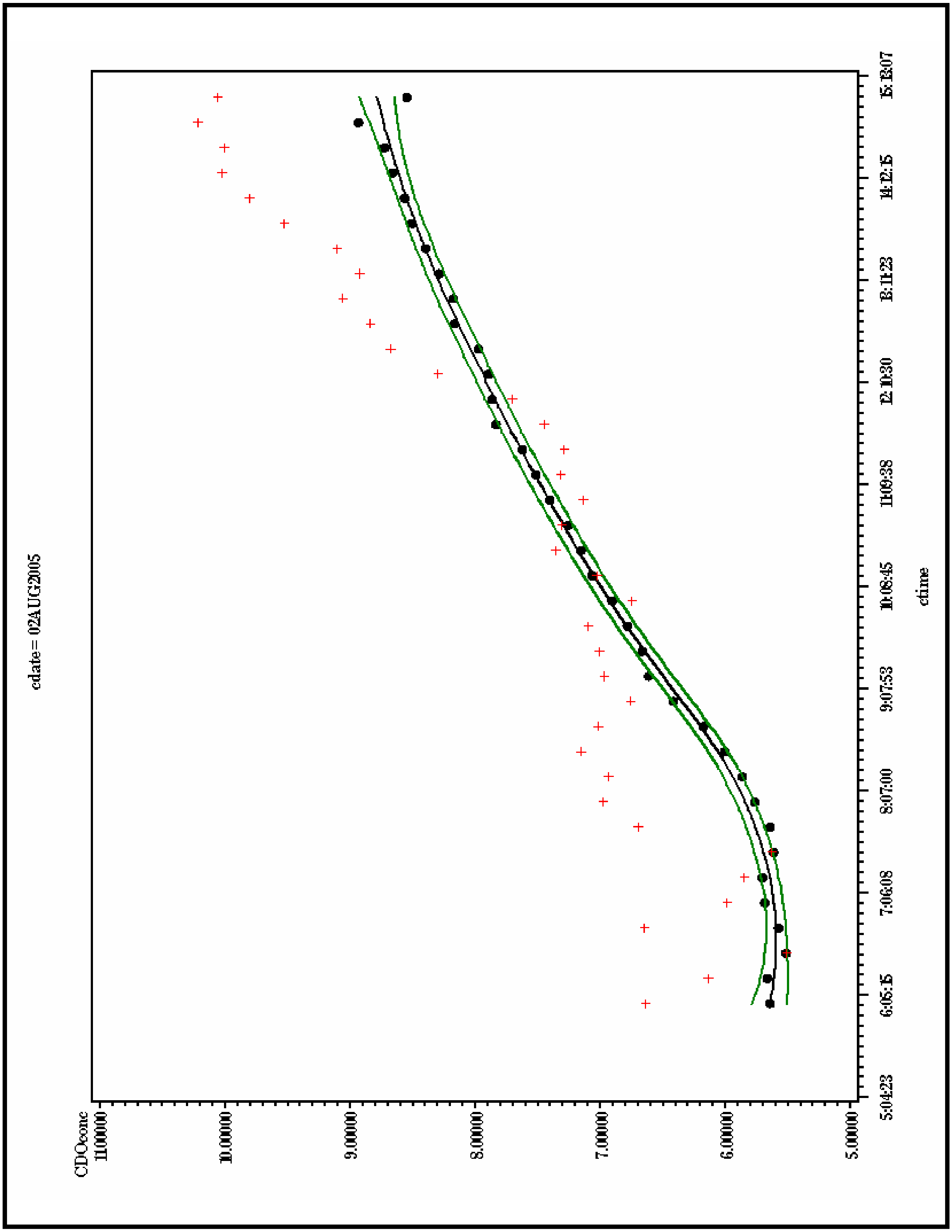
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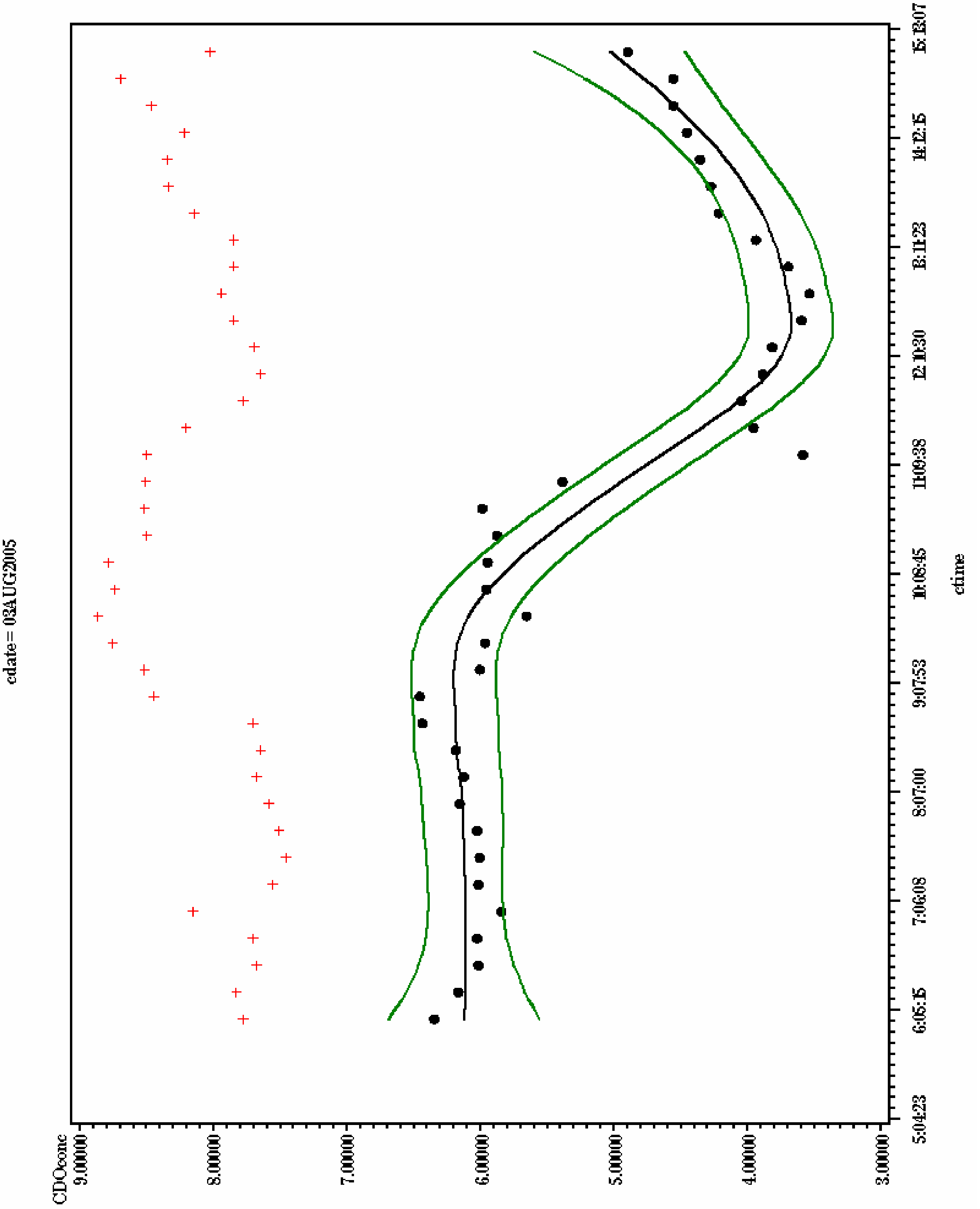
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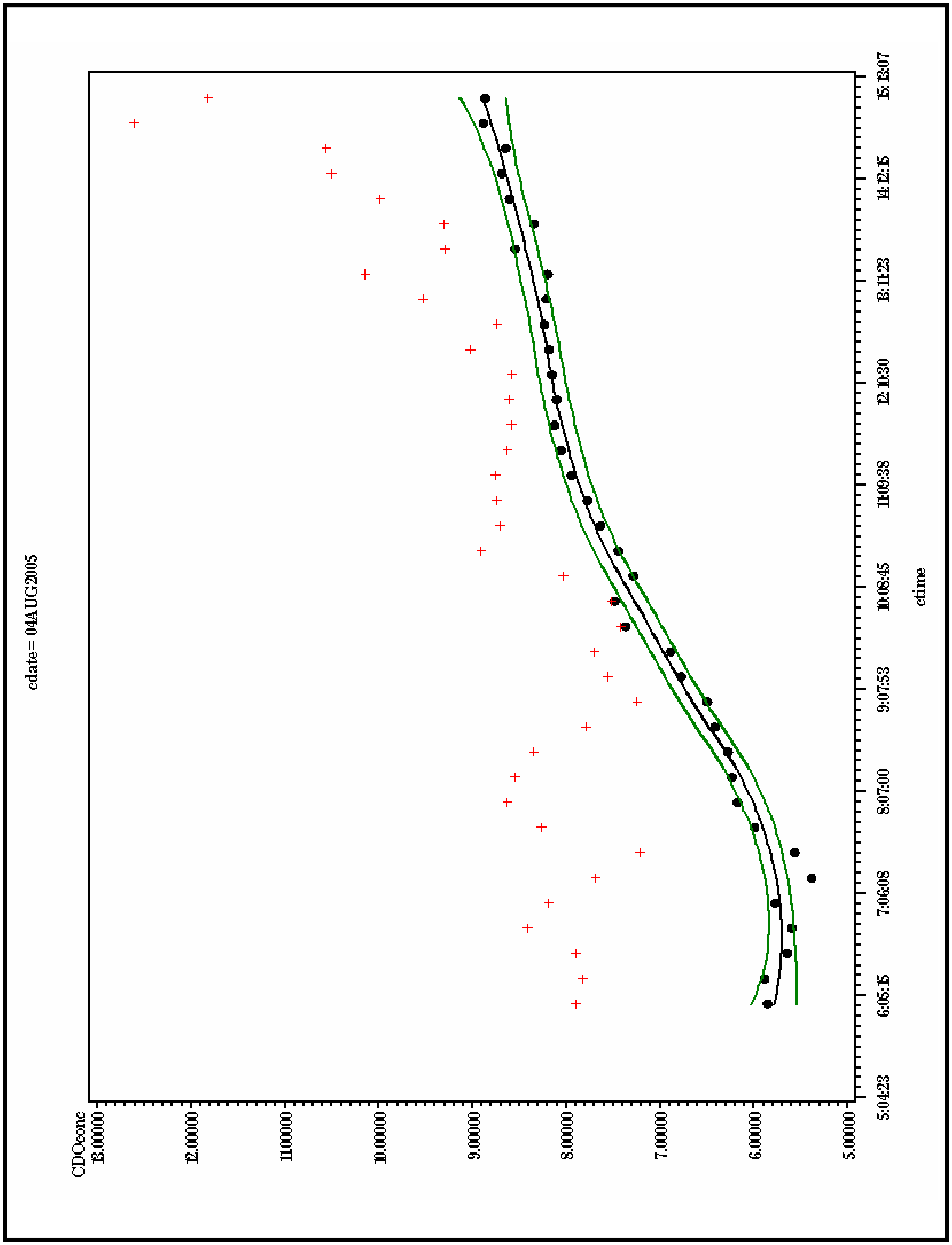
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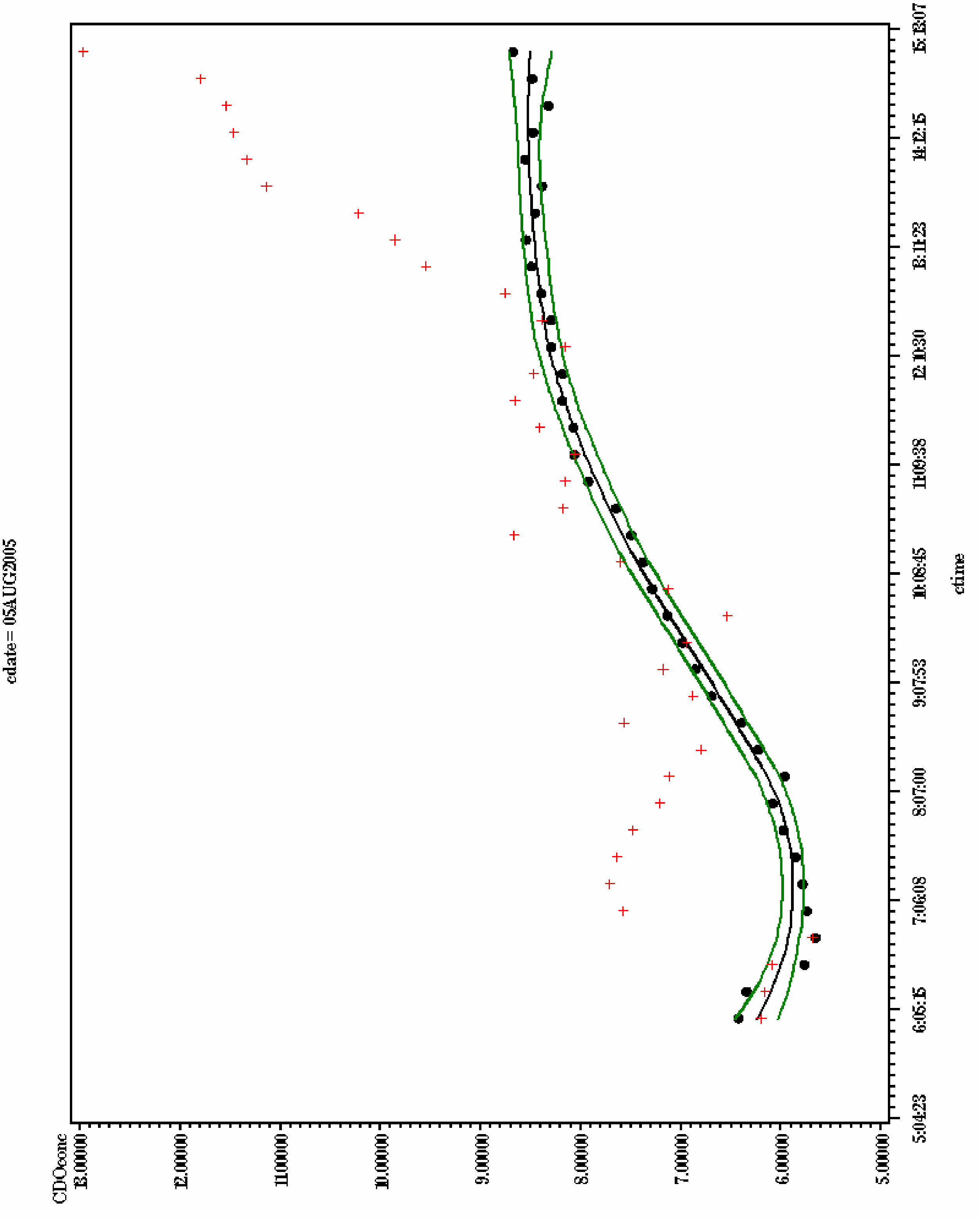
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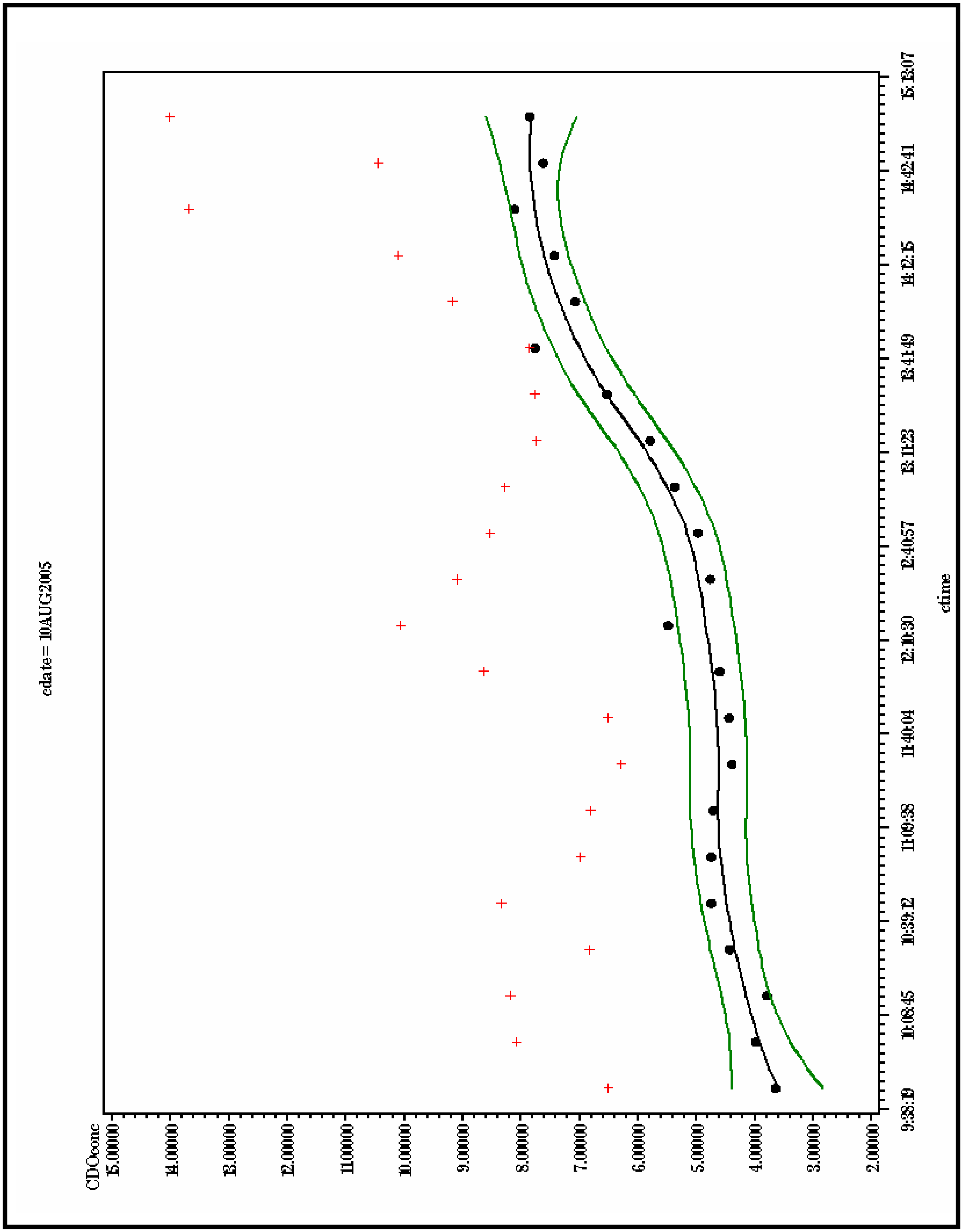
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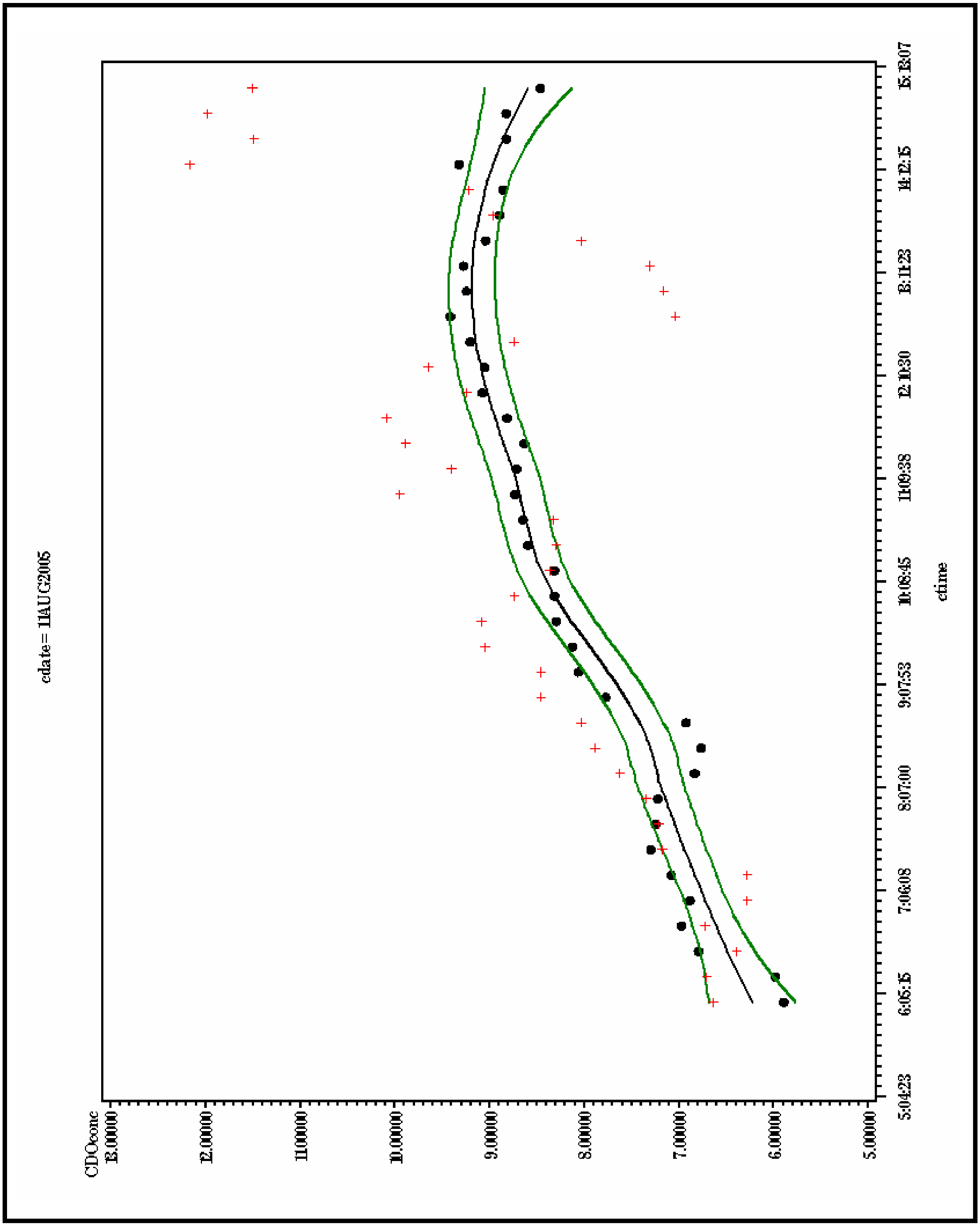
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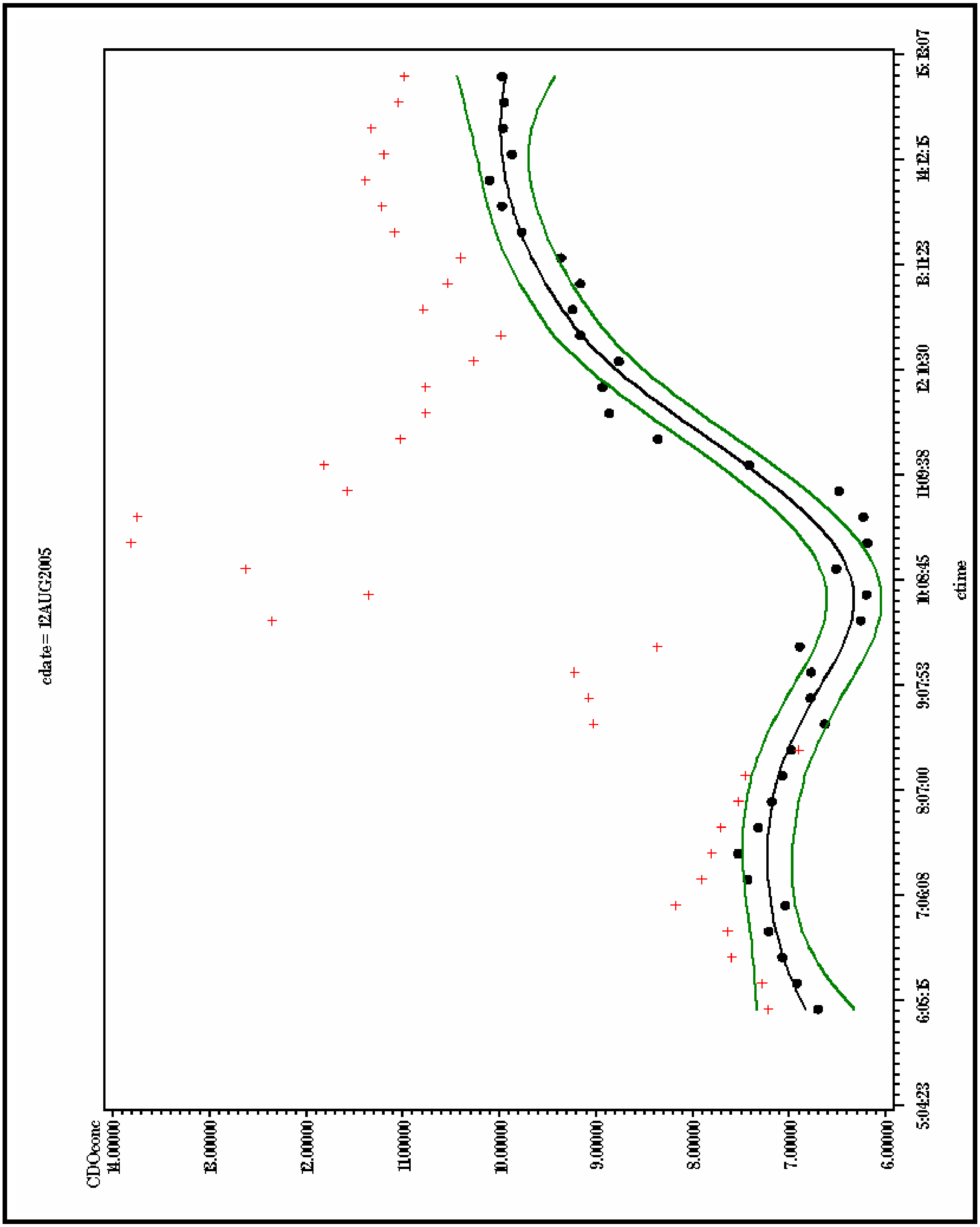
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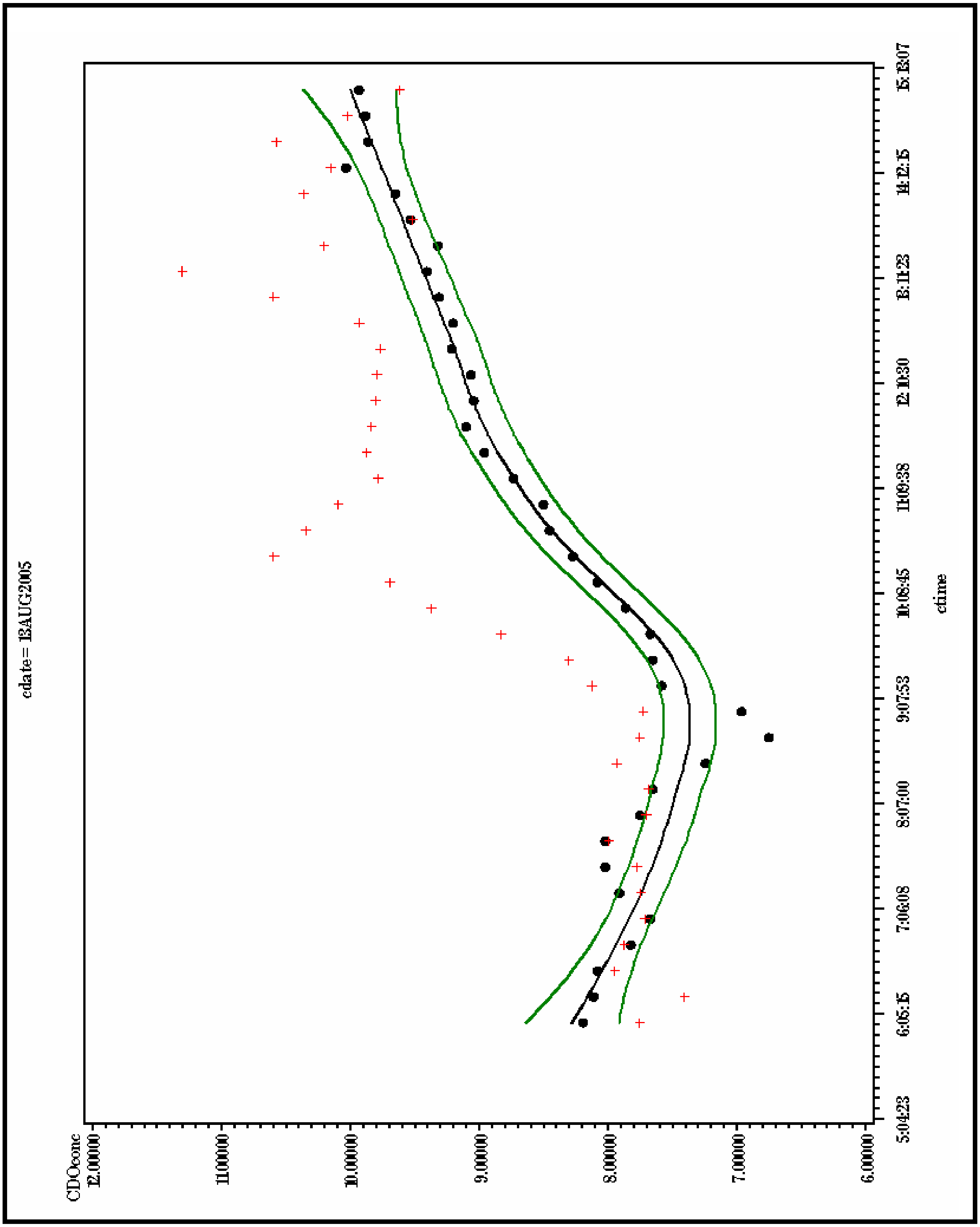
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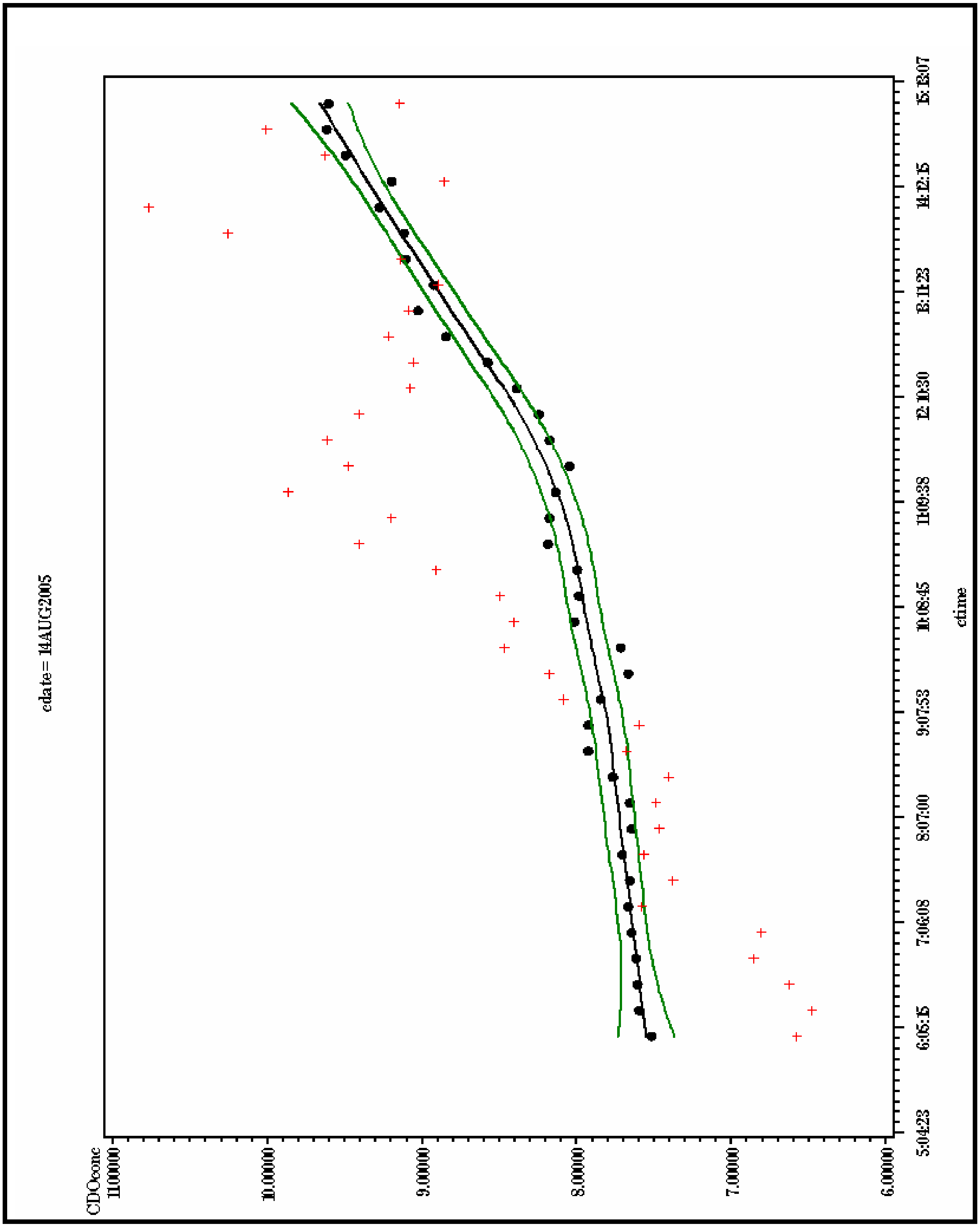
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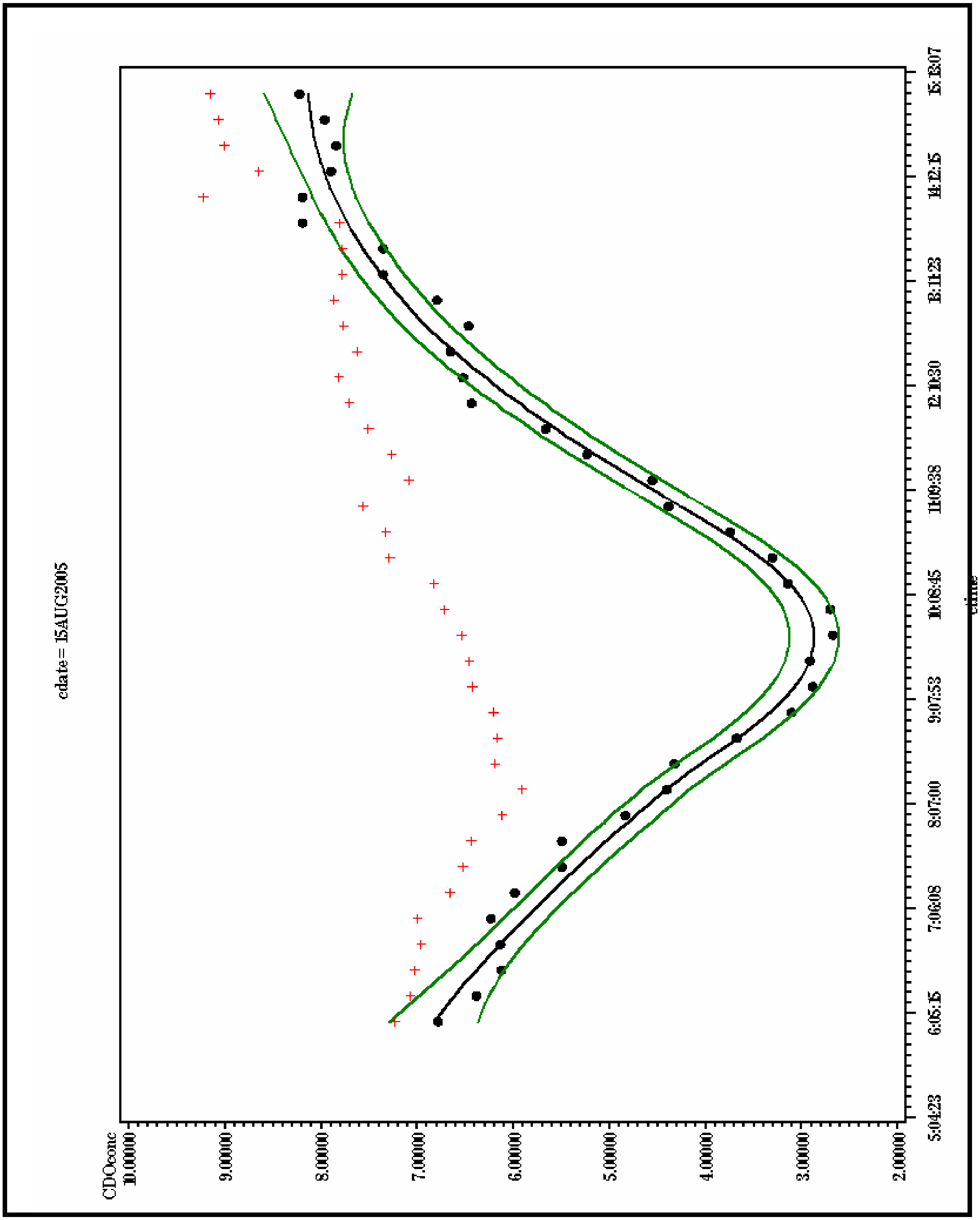
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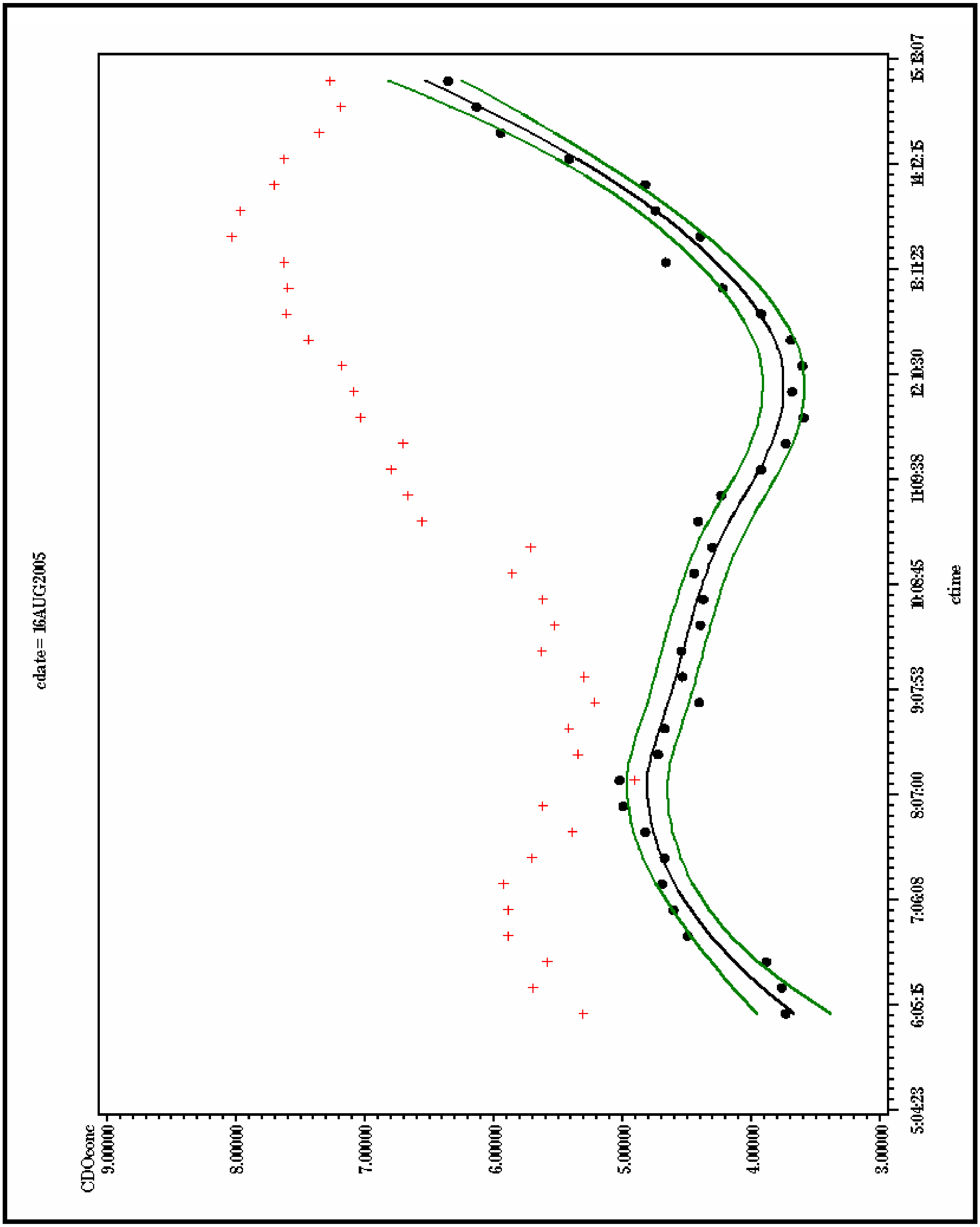
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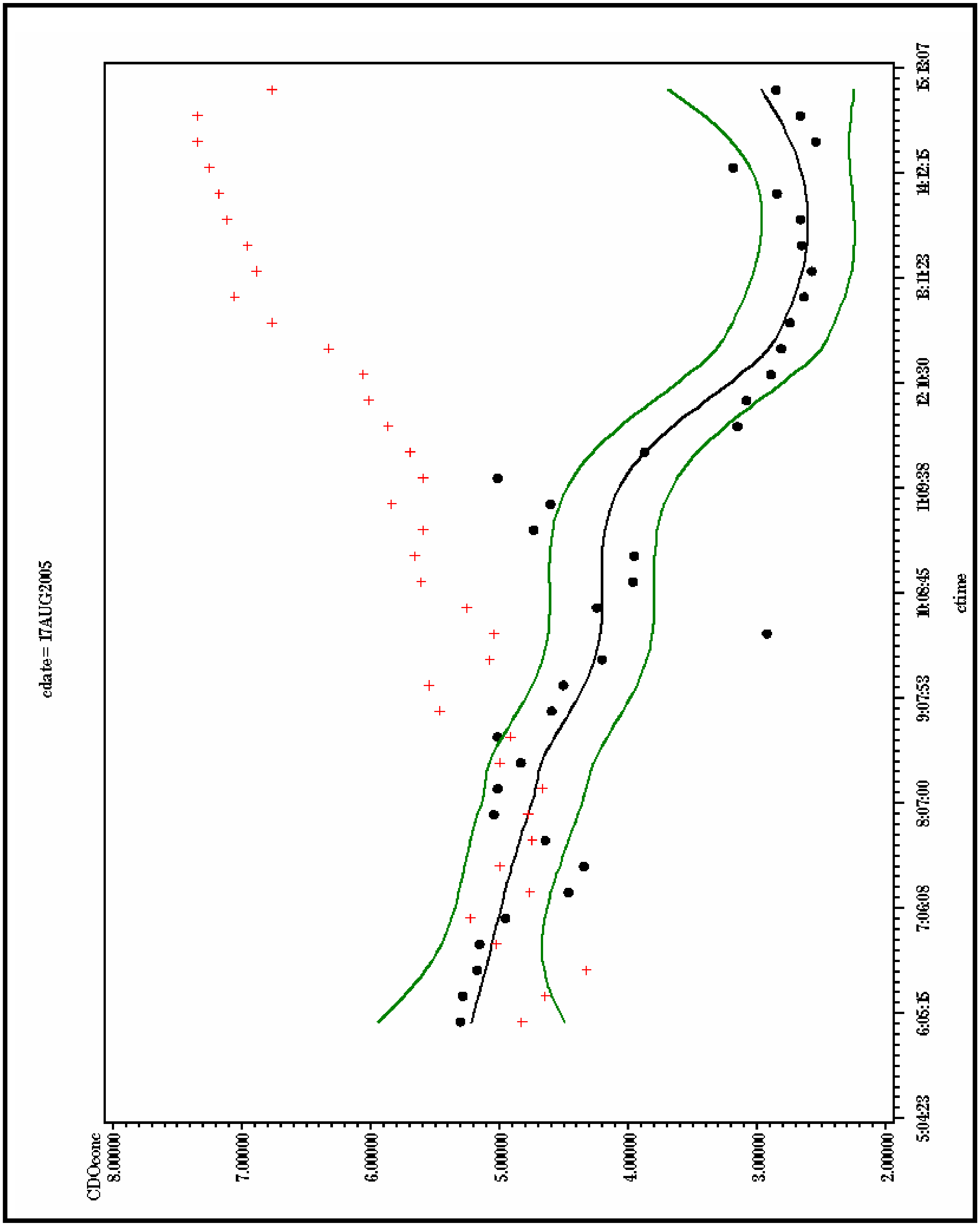
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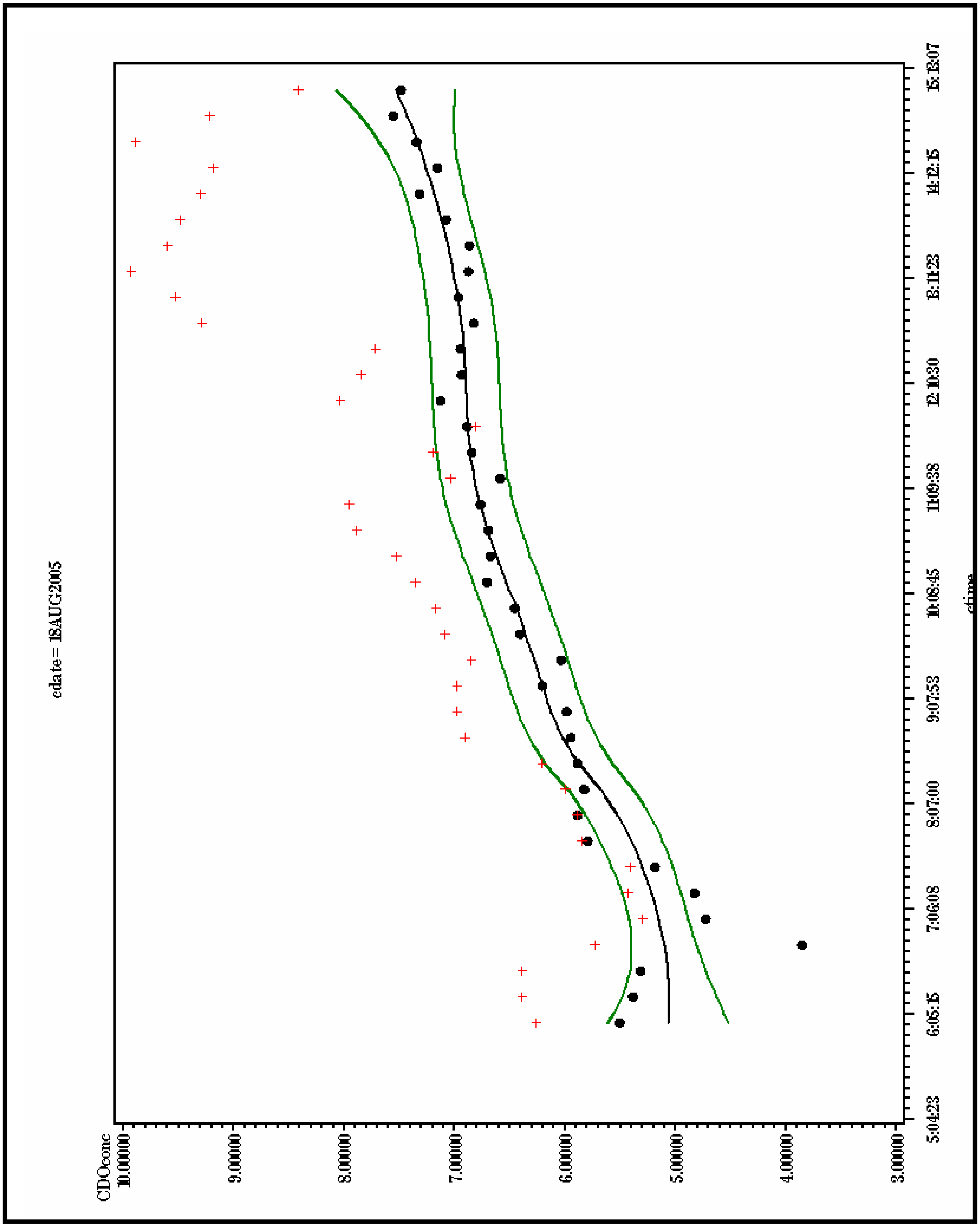
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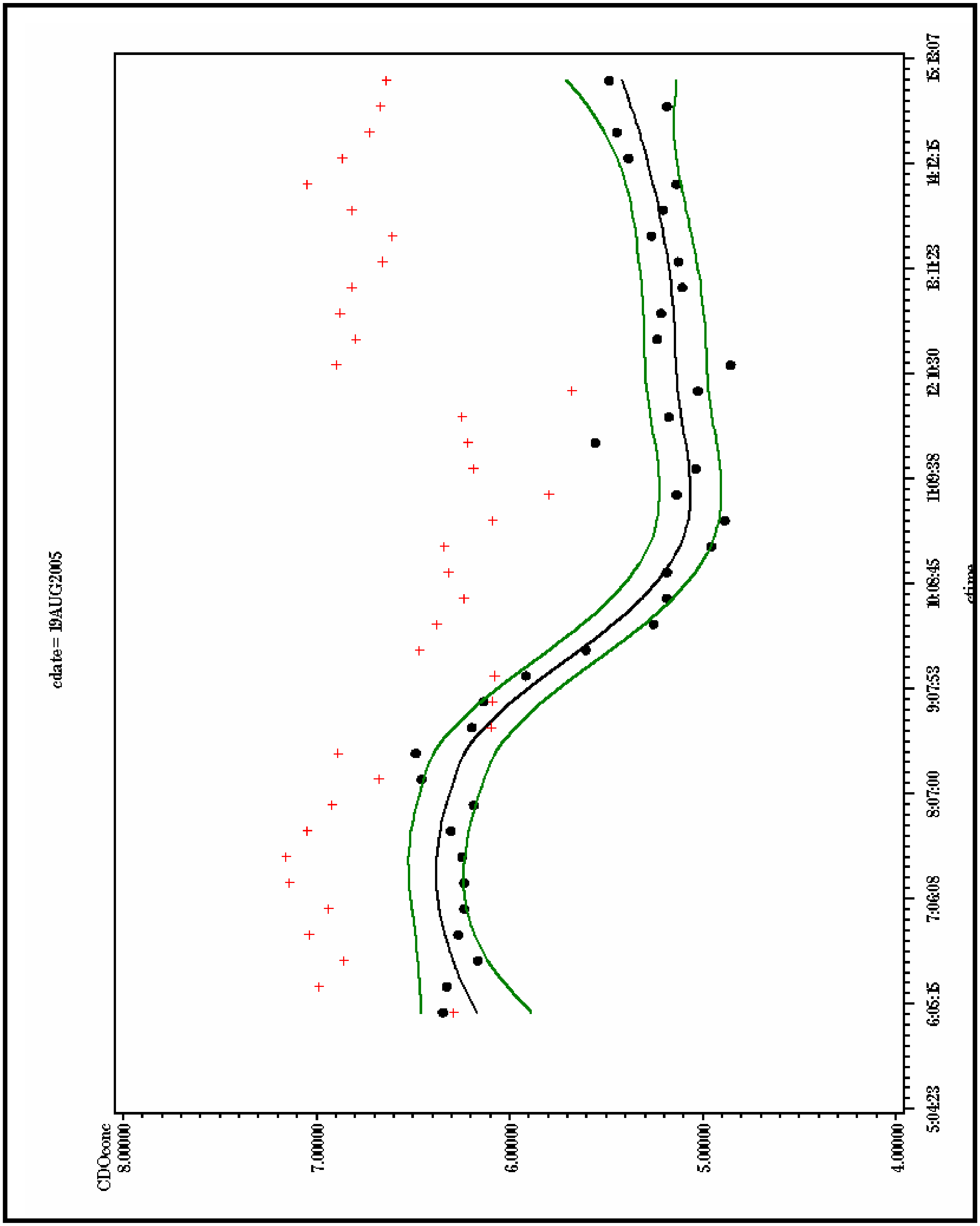
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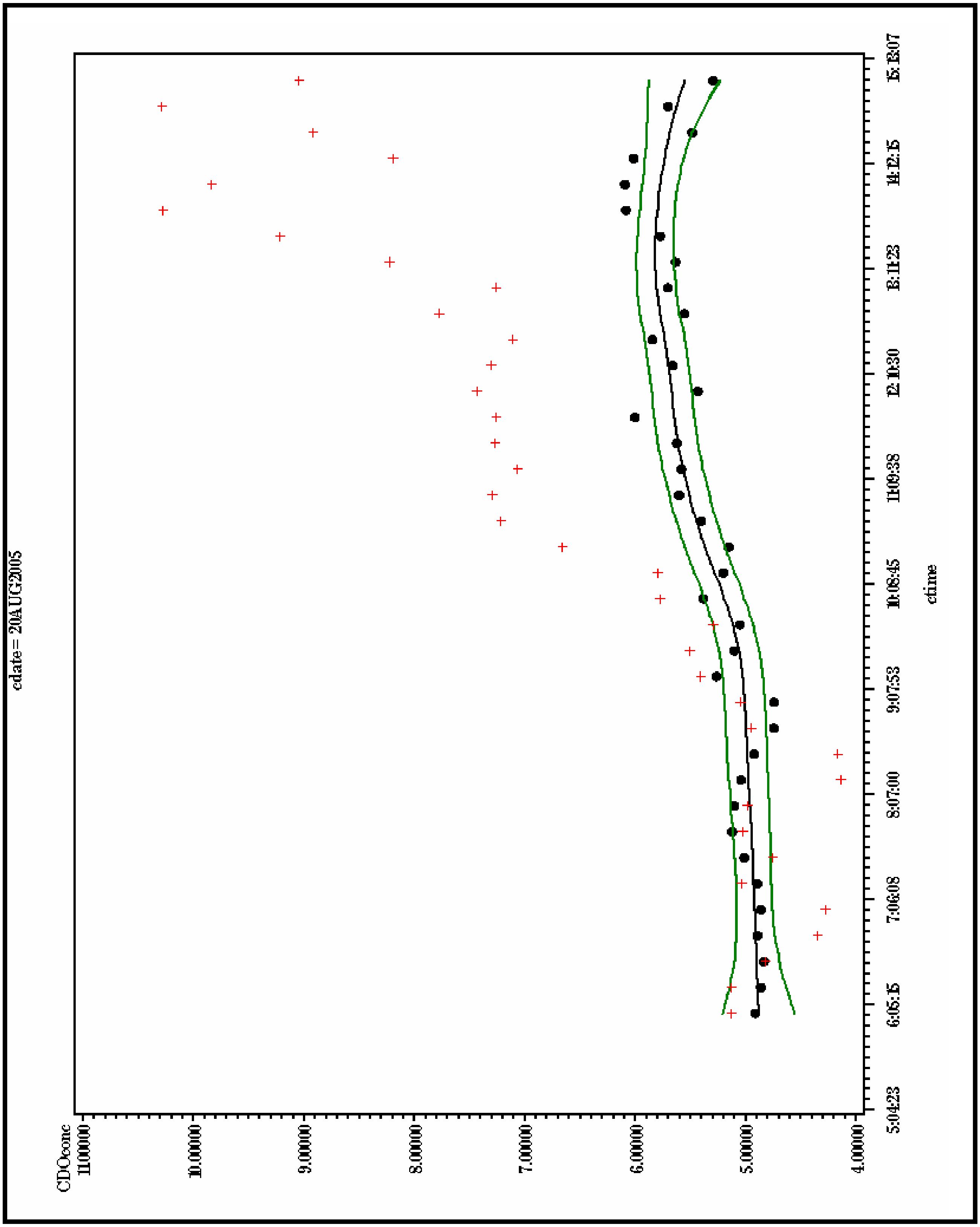
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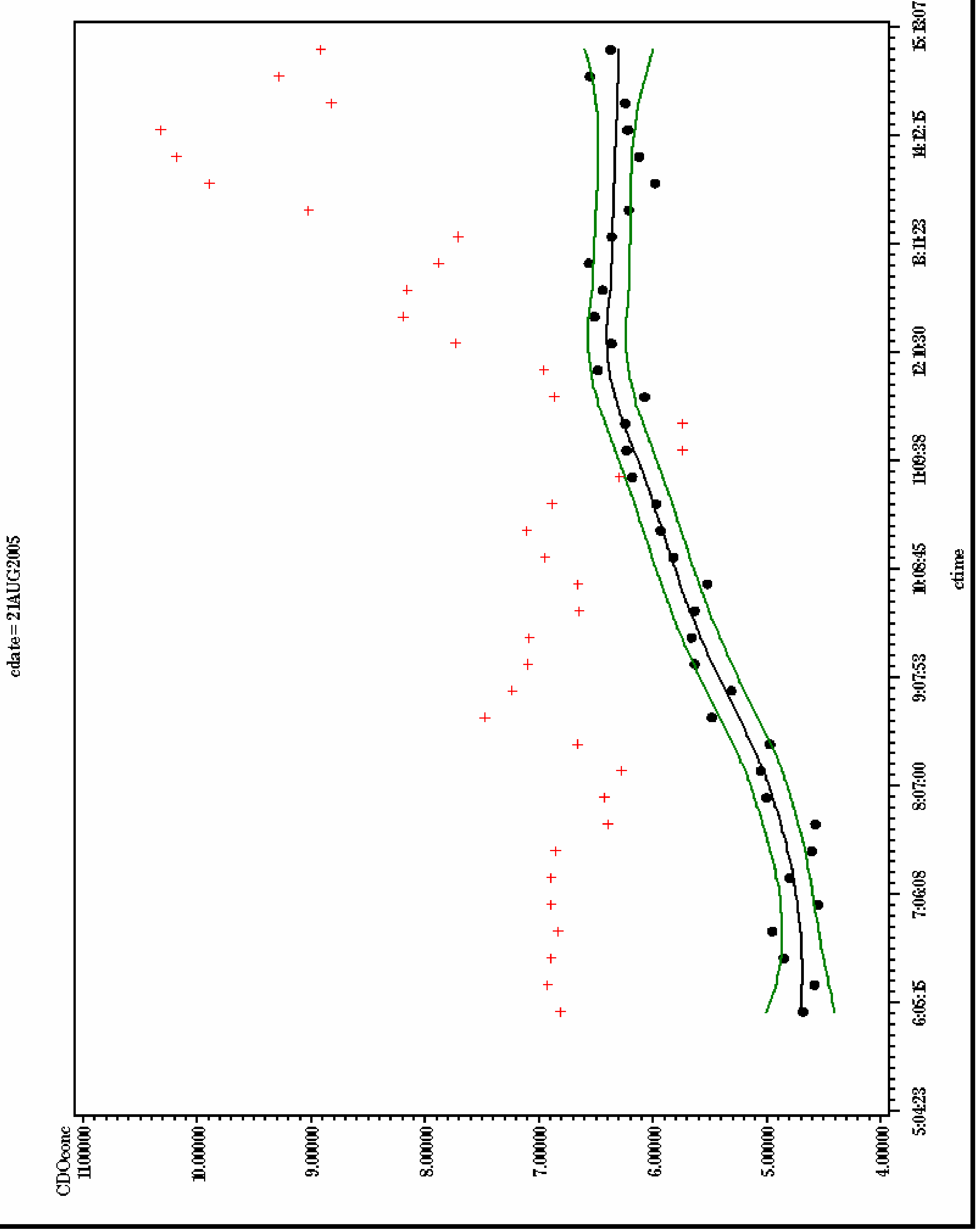
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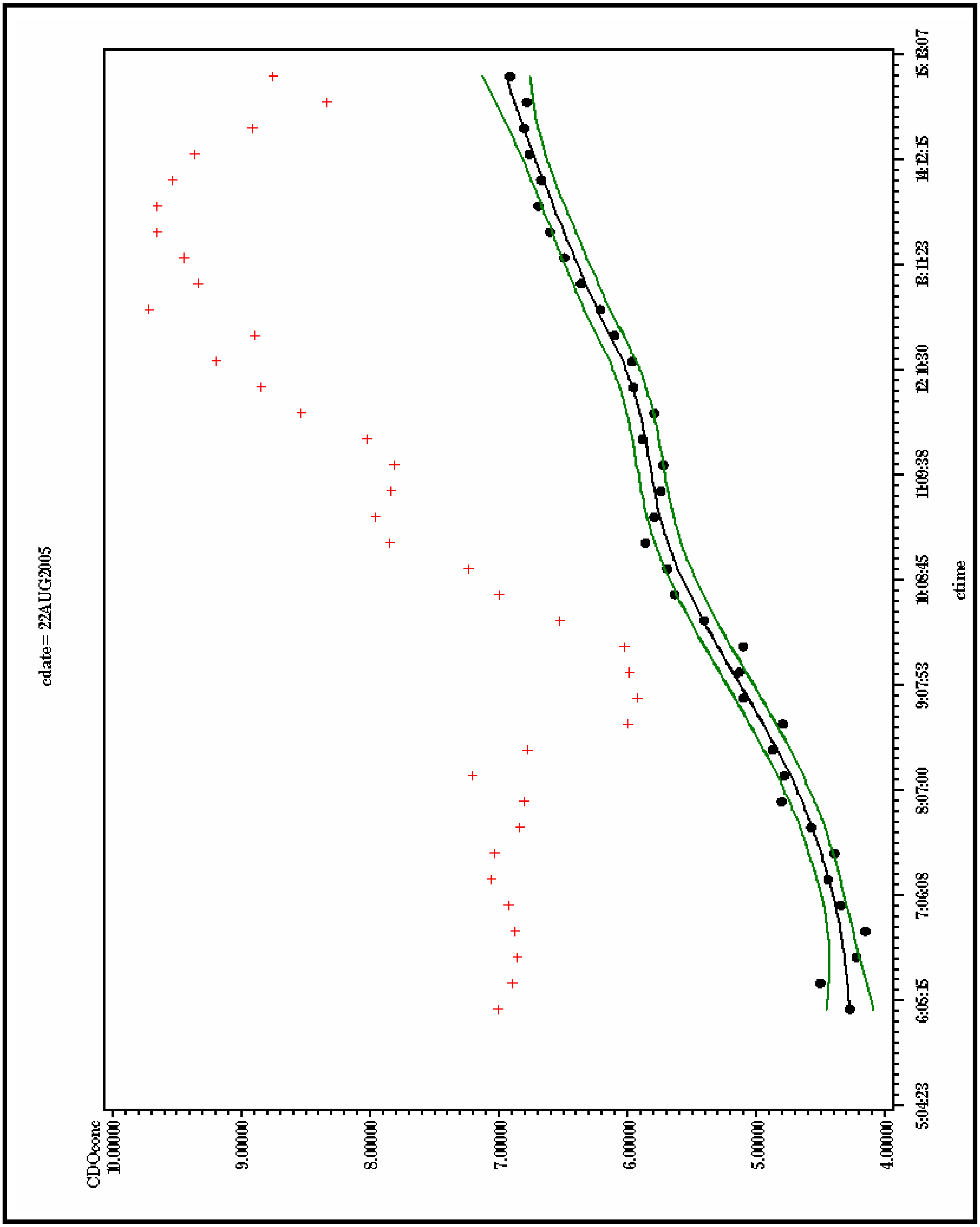
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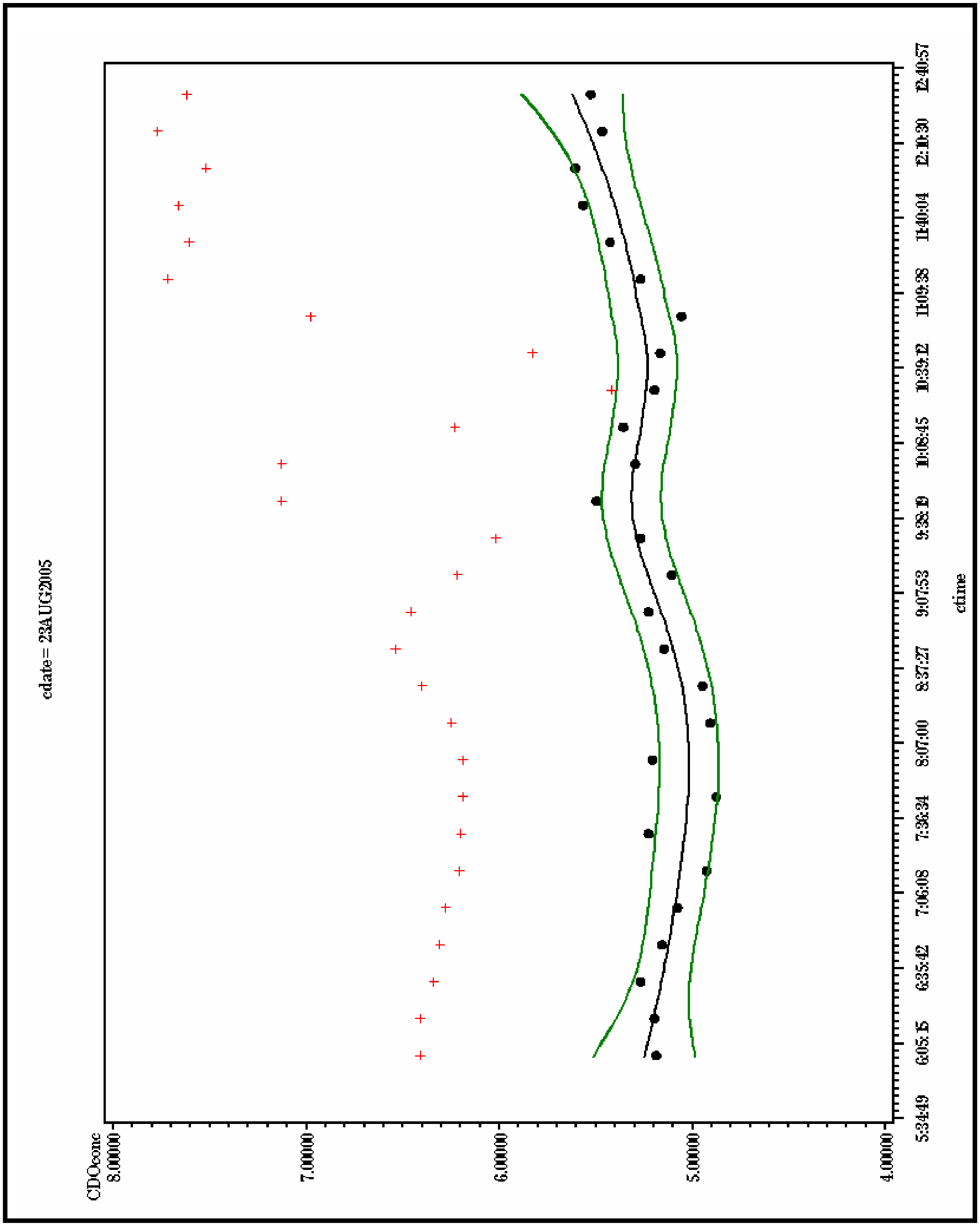
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5.0 Spatially Intensive Shallow Water Quality Monitoring of the Patuxent River: A Multi-Year Analysis

W.R. Boynton, P.W. Smail, R.M. Stankelis, E.M. Bailey, H.L. Soulen, M. Hessey

5.1 Introduction

This chapter includes analyses, based mainly on Patuxent River DATAFLOW data collected between 2003 and 2005, a period that included extremely wet as well as more normal weather conditions. We have emphasized analyses focusing on chlorophyll-a both because it is a central water quality variable with relevance to both SAV (Kemp *et al*. 2005) and hypoxia (Hagy *et al* 2004) and because chlorophyll, as a proxy for algal biomass, is known to be responsive to nutrient loading rates (Boynton and Kemp 2006). Furthermore, we have focused these analyses on the mesohaline region of the Patuxent because this is the region thought to be most sensitive to changes in nutrient supply rates (Testa 2006). We did not address issues related to DATAFLOW calibration of chlorophyll or other DATAFLOW variables as this is the focus of a much larger and comprehensive analysis (conducted by E. Perry and B. Romano). However, we are informed of progress concerning these analyses and will continue to participate in reviewing results of these efforts.

During 2005 we evaluated patterns in surface water quality using the DATAFLOW VI mapping system in the Patuxent River. The monitoring effort of 2005 marked the third year of a three year shallow water monitoring sampling cycle for the Patuxent River estuary. DATAFLOW VI was deployed from a small research vessel and provided high-resolution spatial mapping of surface water quality variables. Our cruise tracks included both shallow (<2.0m) and deeper waters, and sampling was weighted towards the littoral zone that represented habitat critical to Submerged Aquatic Vegetation (SAV) and associated organisms.

Traditional water quality monitoring in Chesapeake Bay, and in tributary estuaries such as the Patuxent, has been conducted almost exclusively in deeper channel waters, and conditions in these areas do not adequately represent water quality conditions in shallow zones. Thus, it was important to collect water quality data in both shallow water and deeper off-shore habitats and to determine the extent of gradients in water quality parameters between these areas of the estuary. The DATAFLOW cruise track covered as much area as possible, in both shallow and deeper portions of the system. The vessel traveled at approximately 20 knots, or 10 meters per second and collected data at 3 second intervals which amounts to about one observation made every 30 meters.

5.2 Methods, Locations and Sampling Frequency

5.2.1 DATAFLOW VI

DATAFLOW VI is a compact, self-contained surface water quality mapping system, suitable for use in a small boat operating at speeds of up to 20 knots. A schematic of this system is shown in Figure 5-1. DATAFLOW VI differed from version 5.5 through the addition of a wireless display and miniature, ruggedized PC data-logger, which eliminated the need for separate depth and YSI data-loggers. Surface water (approximately 0.5m deep depending on vessel speed and angle of plane) was collected through a pipe ("ram") deployed from the transom of the vessel. Assisted by a high-speed pump, water was passed through a hose to a flow meter and then to an inverted flow-through cell to ensure that no air bubbles interfere with sampling or data sonde performance. Finally, the water sample moved to an array of water quality sensors which recorded the water quality variables, time, and geographic position. The total system water volume was approximately 3.0 liters.

DATAFLOW surveys were conducted from a CBL vessel and typically involved two field technicians to perform sampling operations and safe navigation. The DATAFLOW package consisted of a water circulation system that is sampled at a prescribed rate by a Yellow Springs, Inc. 6600 DataSonde combined with a ruggedized minicomputer running data-logging software. This sensor provided data on dissolved oxygen, temperature, conductivity and salinity, as well as turbidity and fluorescence (from which we derived chlorophyll-a concentration).The computer also recorded spatial position and depth data with an accuracy of approximately 10 meters from a Garmin 168 GPS/Depthsounder unit utilizing an NMEA 0183 v. 2.0 data format. Data files were output in a comma and space delimited format. Although the flow rate does not affect any of the sensor readings, decreased flow is an indication of either a partial blockage or an interruption of water flow to the instrument and affects the water turnover rate of the system. An inline flow meter wired to a low-flow alarm alerted the operators of potential problems as they occurred. The low-flow alarm was set to 3.0 liters per minute. A single 1100 gallon per hour "Rule Pro Series" pump provided approximately 20-25 liters per minute of flow to the system on station at idle and 35-40 liters per minute of flow while underway at 20 knots due to additional flow created by the ram effect. During the course of a cruise, the vessel stopped at established, calibration stations located along the cruise track. While anchored, whole water samples were taken from the water circulation system. The Nutrient Analytical Services Laboratory (NASL) at Chesapeake Biological Laboratory (CBL) analyzed this water sample for dissolved nutrient content, concentrations of total suspended and volatile solids, and chlorophyll-*a*. Samples were also taken and analyzed for chlorophyll-*a* by the Maryland Department of Health and Mental Hygiene (MD DHMH), and these data were transmitted directly from MD DHMH to Maryland DNR. The crew also measured turbidity using a Secchi disk, and determined the flux of Photosynthetically Active Radiation (PAR) in the water column using Li-Cor quanta sensors. These calibration stations provided additional enhancement of the high-resolution description of a tributary, and provided laboratory values with which we verified instrument parameter values obtained during the cruise. The data that were collected substantially improved characterization of water quality conditions in the near shore habitats as well as system-wide water quality.

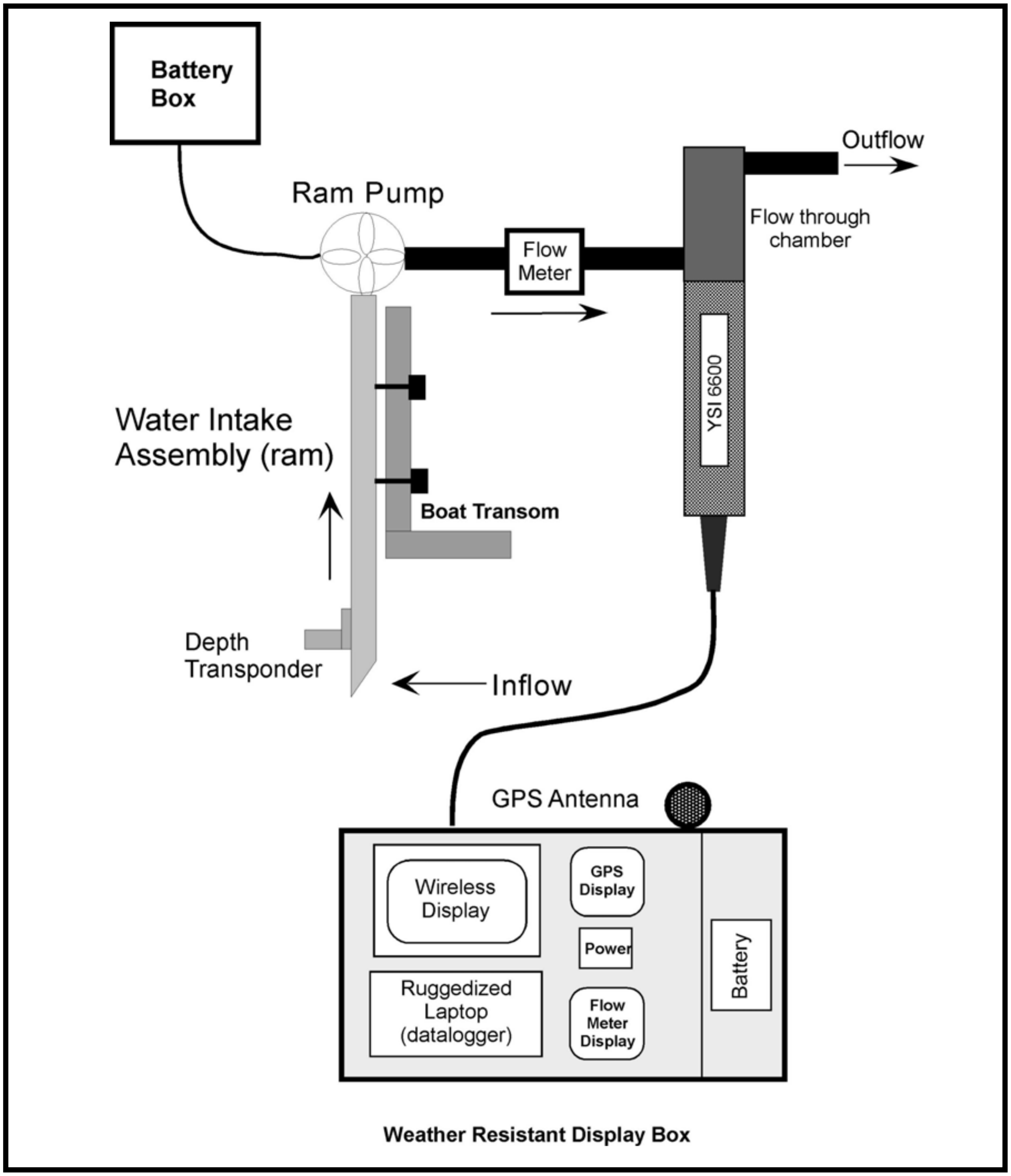


Figure 5-1. Schematic diagram of DATAFLOW VI illustrating the path of water through the instrument. *Seawater is drawn up through the ram behind the transom of the research vessel. A centrifugal pump mounted on the ram (ram pump) boosts the flow. The water flows through a paddle-wheel type flow meter that triggers a horn if the flow rate falls below 3 l min-1, and then to an inverted flow-through chamber where it is sampled by the YSI 6600 datasonde sensors. The inverted mount is used in order to evacuate any air bubbles in the system. After sampling, the water is discharged overboard. The displays for the instruments, including the Wireless Display for the Ruggedized Laptop, Garmin 168 GPS/Depthsounder, and flow meter are located on the instrument platform.*

5.2.2 Sampling locations and frequency

DATAFLOW cruises were performed on a monthly basis on the lower (mesohaline) and upper (tidal fresh and oligohaline) portions of the Patuxent River estuary, for a total of sixteen cruises during 2005. Typically, the lower Patuxent (Cedar Point to Benedict – Mesohaline Region) was sampled on the first day, and the upper Patuxent (Benedict to Jug Bay – Tidal Fresh and Oligohaline Region) on the second, though severe weather or other contingencies occasionally required rescheduling. Two of the cruises (March and November) were truncated, covering an area from Solomons to Broomes Island in order to capture early and late season data for SAV restoration efforts at CBL and Jefferson Patterson Park. The cruise dates are listed in Table 5-1. Cruise tracks were chosen to provide a reasonable coverage of each water body while sampling both near-shore and mid-river waters. A sample cruise track is shown for each region in Figure 5-2. The selection of calibration station locations in each region was made to sample the greatest possible range of water quality conditions found during each cruise and to sample a broad spatial area. Every effort was made to maintain the same location of calibration stations between cruises. The location of several calibration stations were also chosen to correspond to Maryland DNR long-term fixed and continuous monitor water quality monitoring stations within each segment, and these stations were sampled during each cruise. The coordinates for those stations are listed in Table 5-2.

Table 5-1. DATAFLOW cruise dates in 2005.

Region	Spring	Summer	Fall
Patuxent River	3/24, 4/11, 4/12, 5/17, 5/18, 6/27, 6/28	7/12, 7/13, 8/8, 8/9	9/13, 9/14, 10/11, 10/12, 11/8

Table 5-2. Location of DATAFLOW calibration stations.

*coincident with DNR Long-Term Fixed Station water quality monitoring stations †coincident with DNR Continuous Monitoring instrument stations **Coordinates are in NAD 83**.

Region	Station	Latitude (deg mins)	Longitude (deg mins)
Patuxent River	PXNS01	38° 17.046' N	76° 23.274' W
	PXDF10*	38° 18.756' N	76° 25.332' W
	SV09†	38° 19.002' N	76° 27.156' W
	PXDF09*	38° 20.388' N	76° 29.094' W
	PXPO†	38° 24.528' N	76° 31.308' W
	PXDF08*	38° 25.368' N	76° 36.126' W
	PXBD†	38° 30.600' N	76° 40.650' W
	PXDF05*	38° 34.866' N	76° 40.602' W
	PXDF06	38° 31.518' N	76° 39.840' W
	PXDF02	38° 33.630' N	76° 39.630' W
	PXKL†	38° 37.578' N	76° 40.608' W
	PXDF03	38° 41.220' N	76° 41.748' W
	PXDF01	38° 45.426' N	76° 41.958' W

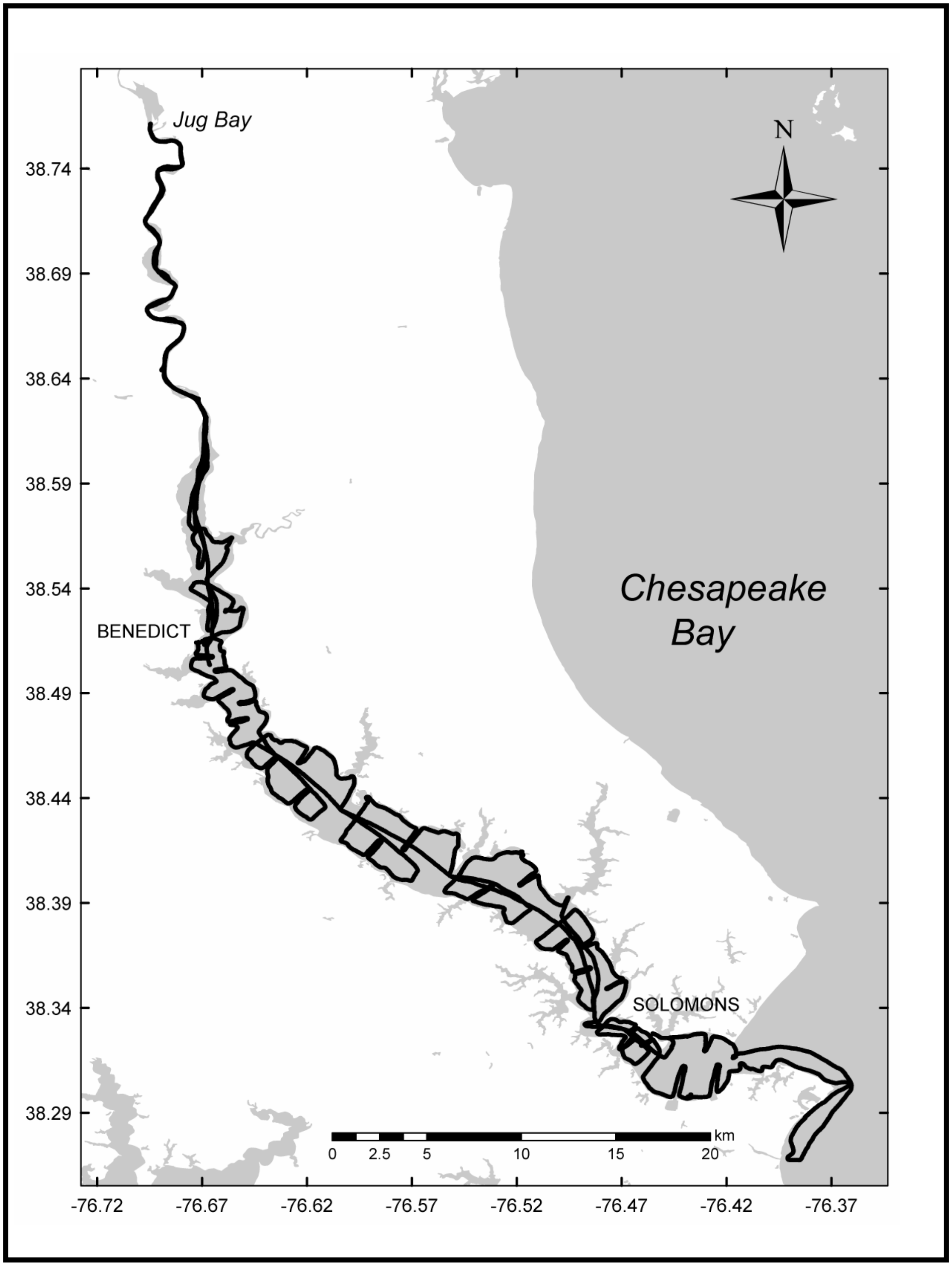


Figure 5-2. Typical DATAFLOW cruise track for the Patuxent River. Mesohaline and Tidal Fresh/Oligohaline portions of the estuary were sampled in consecutive days, circumstances permitting.

5.2.3. Calibration Stations

At each calibration station, a series of measurements were made and whole water samples collected. Locations of the calibration stations are found in Figure 5-3. Secchi depths were recorded and Li-Cor quanta sensors were used to determine the amount of photosynthetically active radiation (PAR) in the water column. These data were used to determine the water-column light attenuation coefficient (Kd), and subsequently, the new “percent light through water” (PLW) parameter for SAV habitat requirements (USEPA, 2000). YSI datasonde turbidity sensor output (NTU) was individually regressed against Secchi depth and Kd. values. Whole water samples were taken, later filtered in the lab, and sent for analysis at NASL at CBL for both total and active chlorophyll-*a* values, as well as total suspended solids (TSS) and total volatile solids (TVS). These chlorophyll-*a* values were compared against chlorophyll sensor output. Water samples were also filtered on station for later NASL analysis to determine concentrations of dissolved nutrients. These nutrients included dissolved inorganic nitrogen (DIN; summation of ammonium [NH_4^+], nitrite [NO_2^-], nitrate [NO_3^-]) and dissolved inorganic phosphorus (DIP). Other nutrients analyzed included Dissolved Organic Carbon (DOC), Particulate Carbon (PC), Particulate Phosphorus (PP), Particulate Inorganic Phosphorus (PIP), Total Dissolved Nitrogen (TDN), Total Dissolved Phosphorus (TDP), and Silicate (SiO_2). A detailed explanation of all field and laboratory procedures is given in the annual CBL QAPP documentation (Smail *et al*. 2005).

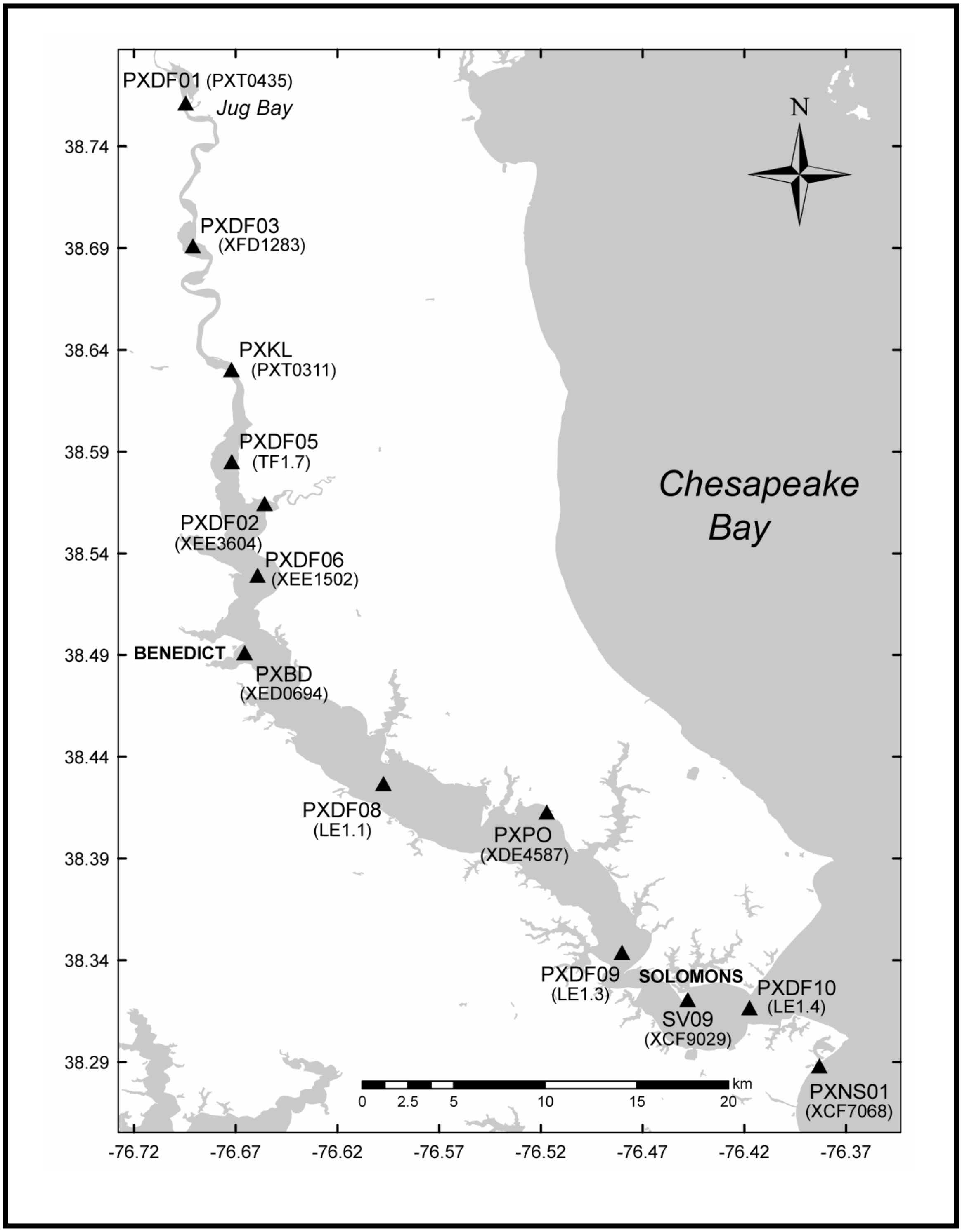


Figure 5-3. DATAFLOW calibration stations on the Patuxent River estuary, 2005.

5.2.4. Data QA/QC Procedures

The data gathered with DATAFLOW underwent QA/QC processes approved by managers and researchers from Maryland and Virginia through Chesapeake Bay Program Tidal Monitoring and Analysis Workgroup meetings (Smail *et al*. 2005). Data files were formatted and checked for erroneous values using a macro developed by Maryland DNR for Microsoft Excel. The QA/QC process ensured that extreme values resulting from data concatenation error (a function of how the instrument data are logged) or turbidity spikes resulting from operating a vessel in shoal areas could be flagged in the proofed dataset. Data are also visually inspected using ArcGIS where specific values can be compared with calibration data and the cruise log in order to eliminate obvious erroneous values as described above. Combined datasets from the entire sampling season were also plotted in order to reveal extreme values or other temporal patterns.

5.2.4 Contour Maps

Contour maps were generated using the ESRI ArcGIS 8.3 software suite to assist in the interpretation of spatial patterns of different water quality parameters. Examples of these maps are found in this report. Interpolation was accomplished using the Ordinary Kriging routine in the Geostatistical Analyst extension within the ArcGIS software. Interpolation technique is subject to much discussion regarding effectiveness and veracity of representation, so these maps are provided to illustrate only one method used to visualize patterns found in the chosen dataset. Datasets were also plotted using the ArcGIS software to reveal route events during individual cruises. Since each sample from the DATAFLOW system is recorded as a discrete point in space and time, this proved to be a useful quality assurance tool to remove erroneous data (e.g., extreme turbidity values due to vessel grounding or propeller induced wash). Each map was interpolated from discrete measurements taken during each DATAFLOW cruise. If multiple datapoints were spatially indistinguishable, the interpolation routine would use the average of these coincidental points.

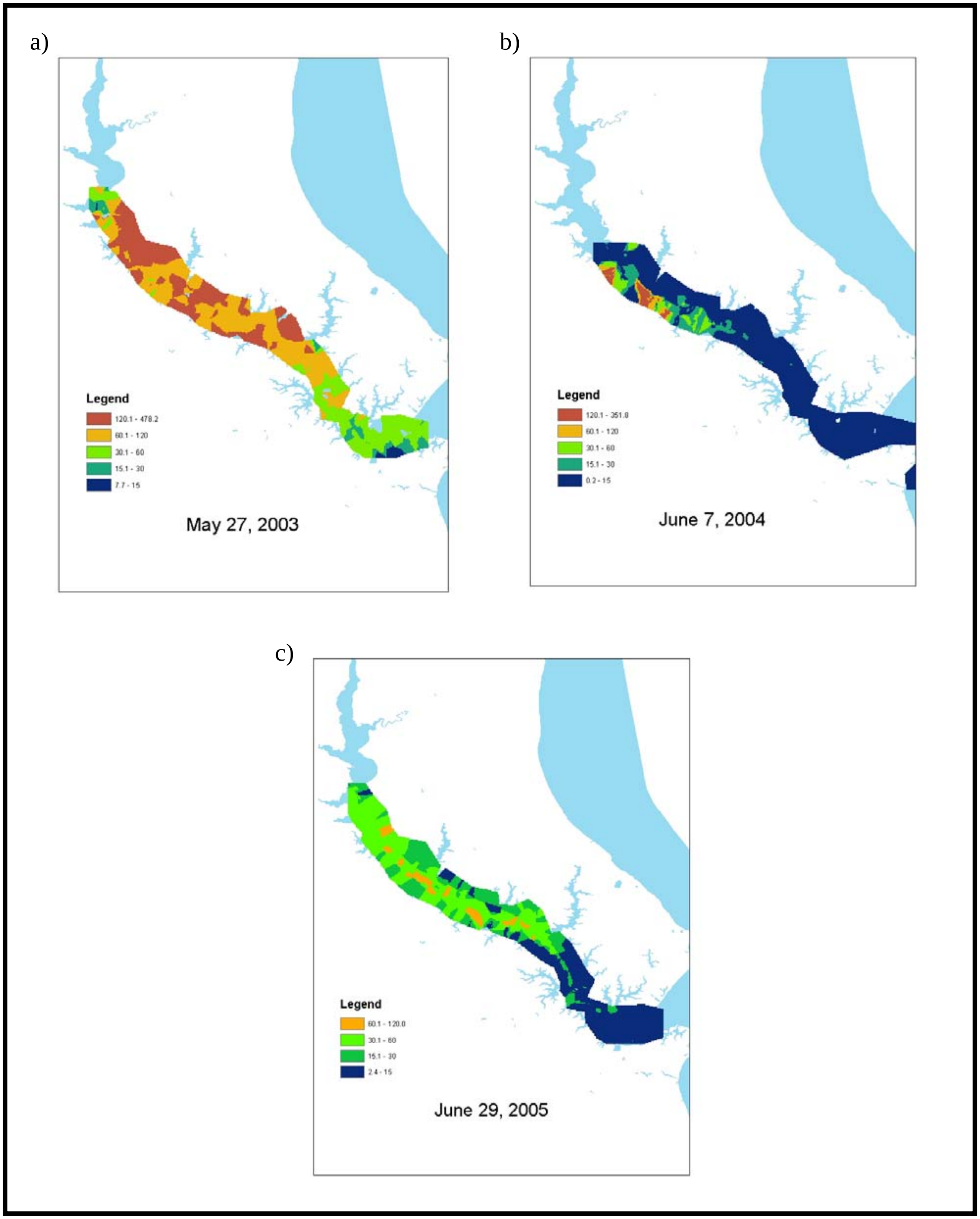
The usefulness of linear regressions to accurately translate YSI sensor output to universally recognized standards requires that a sufficient range of data be present in order to obtain a high correlation between variables. This can be accomplished by using data collected from a single cruise, or by combining data from multiple cruises, and locations. The rationale for using data from a single cruise comes from the assumption that the specific components leading to water column light attenuation (or species if measuring chlorophyll) will be more similar within a single cruise compared to data collected over the entire season, resulting in a better fit of the data. In contrast, when data are combined over a whole season, or from different locations, there is a greater chance that the relationship between the two measurement variables will vary among cruises, thus leading to an overall lower correlation. However in circumstances where the observed gradient (turbidity or chlorophyll) within a single cruise is relatively small compared to the resolution and accuracy of the instruments, a higher correlation may be achieved by combining the data from multiple cruises. We present examples of these issues below.

5.3 Results and Discussion

5.3.1 DATAFLOW Chlorophyll-a Distributions: Inter-Annual Variations

During the period 2003-2005 we conducted 21 DATAFLOW mapping cruises on the Patuxent River estuary beginning at the mouth and extending upstream to Jug Bay in the tidal freshwater portion of the system. In all cases, this mapping effort took two days with the lower estuary (estuary mouth to Benedict, MD) being mapped on one day and the upper estuary being mapped on the next day. All DATAFLOW data files were sent to MD DNR as specified in our contract as were all calibration and profiling station data sets. Mapping cruises were conducted monthly from April through October of each year (extended to March – November in some years). There were a total of 13 calibration/profiling stations sampled during each cruise. To put the intensity of DATAFLOW data collections in some perspective, about 16,000 observations of each variable were made during each cruise, including both sectors of the estuary. Routine, long-term monitoring collects 13 surface water samples during each cruise. This comparison is not intended to indicate that one system of measurement is better than the other but rather to indicate the very large increase in measurement intensity for surface water properties using the DATAFLOW approach.

We have selected one DATAFLOW cruise date for each year to emphasize the inter-annual variability associated with these systems. In this case chlorophyll was selected, mainly because it is known to be responsive to nutrient loading rates in this estuary and because of the role chlorophyll plays in SAV light requirements (Figure 5-4). We have indicated earlier in this report that the period 2003 – 2005 was characterized by very wet (2003), average (2004) and dry (2005) conditions. While we did not conduct DATAFLOW cruises during 2002, river flow data indicate that 2002 was an exceptionally dry year. Thus, within a short period of time the estuary was exposed to widely varying conditions of river flow and we know that this can have many effects on estuarine water quality conditions (Boynton and Kemp 2000). These maps suggest several points. First, there is a clear and dramatic response to nutrient loading rates. Chlorophyll concentrations in surface waters were very large during spring 2003 (Fig. 5-4a) throughout most of the mesohaline estuary with much of the estuary having concentrations above 60 µg/l and about 20% of the mesohaline estuary with concentrations in excess of 120 µg/l. During 2004 and 2005 concentrations were much lower in general, especially during 2004 when, even during the period of maximum chlorophyll concentration, much of the mesohaline region was below that required for SAV (chlorophyll < 15 µg/l). In addition, the position of the chlorophyll maximums appear related to river flow. During the very high flow year relatively high chlorophyll was present throughout the mesohaline estuary. During average or lower flow conditions (2004 and 2005; Figs. 5-4b and 5-4c), high chlorophyll values were observed towards the up-stream end of the mesohaline region rather than throughout the system. Second, in all three years maximum chlorophyll concentrations occurred during mid to late spring as has been observed in the mainstem Chesapeake Bay (Kemp *et al* 2005). Our interpretation of this is that this chlorophyll mass is supported by "new nitrogen" inputs, mainly coming from the Patuxent watershed. This emphasizes the need for reductions in later winter and spring nutrient inputs from the land. In another portion of this report (Chapter 2.0) we made calculations that indicate that during winter-spring new inputs of nutrients play a large role in supporting primary production and algal biomass accumulation while during the summer and fall internal recycling of nutrients that entered the system during winter-spring is more important. Thus, a key restoration idea is to reduce sharply late winter-spring nutrient loads. Summer and fall loads are already relatively small and further reductions will likely have smaller impacts. Third, there does not seem to be any strong and consistent signal regarding chlorophyll accumulation in channel versus shoal areas. For example, during the high chlorophyll year (2003) very high concentrations were seen in both shoal and channel areas. In contrast, during the average flow year (2004) highest concentrations were restricted to the upper mesohaline area and were largely associated with the southern shore. During the drier year (2005) high chlorophyll concentrations were relatively rare but were associated with the channel in the upper half of the mesohaline region. We had anticipated observing highest chlorophyll concentrations in shallower areas because of both less likelihood of algal cells sinking beneath the pycnocline and hence out of the euphotic zone and because of better linkage between sediment nutrient sources and euphotic waters. However, at least in this analysis of maximum chlorophyll concentrations, a clear shoal versus channel pattern did not emerge. Fourth, there does not appear to be much in the way of “nutrient memory” in this ecosystem. We have commented on this issue in previous reports and papers (e.g., Boynton and Kemp 2000; Kemp *et al*. 2005). In this case chlorophyll values in spring 2003 were very high and we have argued this was in response to elevated winter-spring nutrient loading rates. Chlorophyll values were much reduced during 2004 when nutrient loading rates were much lower (see Chapter 2.0 and next section of this Chapter). If there was a significant nutrient storage in the system, presumably in the sediments, we would not expect to see very large decreases in chlorophyll in the year following an exceptionally wet year. In fact, that is exactly what we did observe. Boynton *et al* (1982) assembled a time-series of chlorophyll data for the mainstem Chesapeake Bay for a time period before and after the Tropical Storm Agnes event in 1972 and found that chlorophyll was elevated during the year (1973) following this event but that even this huge signal was lost quickly (by 1974). The message here seems to be that attention should be paid to current loading conditions largely independent of previous loading rates except in cases where previous loads were extremely high, as in the Agnes event. Fifth, the DATAFLOW methodology provides us with previously unattainable levels of spatial detail of water quality in surface waters. However, we do not have, at least with the DATAFLOW methodology, similar resolution of temporal patterns. In the current program DATAFLOW cruises are on a monthly basis and we are left with less certainty about the persistence of observed patterns. We do have two means of improving understanding of temporal patterns. First, the traditional monitoring program samples twice a month and examination of these data can provide some hints as to the persistence of spatial pattern, but only in a very general fashion because of low sample size. Second, ConMon data collection is at very high frequency (96/day) and could also provide some indications of persistence of large spatial features. However, ConMon sites are fixed in space and are located in shallow areas so there are important limitations here as well. There are also a few buoys moored in deeper water with high frequency measurement capabilities (e.g. ACT buoy in Patuxent) and these would also aid in assessing spatial persistence of patterns. However, we suggest that it would be useful to conduct DATAFLOW cruises covering more limited areas of targeted estuaries on a more frequent measurement schedule to gain some additional insight regarding persistence of spatial patterns. Perhaps on a seasonal basis a portion of a mesohaline reach could be assessed with DATAFLOW on a daily basis for a week, then once per week, bi-weekly and then with the routine monthly sampling. Some plan for assessing the fidelity of DATAFLOW seems needed because of the importance of DATAFLOW data in assessing water quality conditions.


a)
Legend
🟥 120.1 - 478.2
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May 27, 2003
b)
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🟥 120.1 - 351.0
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🟩 30.1 - 60
🟩 15.1 - 30
🟦 0.2 - 15
June 7, 2004
c)
Legend
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June 29, 2005

Figure 5-4. Interpolated maps of surface water chlorophyll concentrations for a) 2003, b) 2004 and c) 2005 from the mesohaline portion of the Patuxent River estuary. DATAFLOW cruise dates were selected based on these dates having the highest chlorophyll concentrations for each year.

5.3.2 Comparisons of DATAFLOW and Traditional Monitoring Data: chlorophyll in the mesohaline estuary

We have summarized monthly (April through October) surface water chlorophyll concentrations collected with DATAFLOW methodology (Table 5-3) and with conventional bi-weekly, fixed station monitoring methodology (LTBM, Table 5-4) for 2003, 2004 and 2005. Average monthly area-weighted concentrations for the entire mesohaline portion of the estuary (mouth to Benedict, MD) were generated using Ordinary Kriging interpolation with special care given to avoidance of interpolation over land masses extending into the estuary. Area weighted concentrations based on LTBM (Long-Term Biomonitoring) data were computed by assuming equal weighting of areas between LTBM stations in the mesohaline estuary. Area weighted chlorophyll concentrations ranged from 2.1 µg/l (May 2004) to 107.2 µg/l (May 2003) during the measurement period. In all years highest concentrations occurred in May or June. The general pattern of area weighted chlorophyll concentration for the mesohaline estuary was similar based on LTBM data. Chlorophyll concentrations ranged from 5.5 µg/l (April 2004) to 127.0 µg/l (May 2003). We have also constructed a scatter plot of DATAFLOW versus LTBM area weighted chlorophyll concentrations on a monthly basis using data from all years (Fig. 5-6) and on an annual basis for three years (Fig. 5-7).

Both plots suggest strong relationships at the "whole-estuary" spatial scale with regard to chlorophyll concentrations. Specifically, concentrations by month, and on an annual scale, were higher during 2003 than in other years. This simple analysis suggests that we obtain the same basic pattern, again at large spatial scales (whole mesohaline estuary), with either measurement system. Using data from either measurement system we find that high flow years produce large accumulations of chlorophyll during spring and, during the subsequent summer, poor water quality conditions. These data were also averaged to semi-annual time scales (April-October; SAV growing season) and the same pattern emerges, as expected (See Table 5-3).

Finally, in both scatter plots of LTBM versus DATAFLOW chlorophyll concentrations (month and annual) for the mesohaline Patuxent there was a noticeable bias towards higher LTBM compared to DATAFLOW measurements. For example, at annual time scales (April-October) LTBM concentrations were higher than DATAFLOW values for the same year (Fig 5-7 and Tables 5-5a and 5-5b). Month-based comparisons showed a similar pattern (Fig. 5-6). These consistent differences could have arisen for several reasons including the fact that two different measurement systems were employed in making measurements (LTBM uses lab-based chlorophyll extraction while DATAFLOW uses in-situ fluorometry) and two different interpolation schemes were used. It appears to us unlikely that the bias is based mainly on differences in chlorophyll measurements. We often have excellent calibration curves relating DATAFLOW to lab-based chlorophyll measurements. Rather, it seems more likely that the crude scheme used to develop LTBM-based, area-weighted chlorophyll concentrations for the mesohaline estuary is the issue. We could use a more sophisticated method and this would have the effect of decreasing whole-estuary estimates of chlorophyll concentration based on LTBM data. At this point that effort does not seem warranted because we get the same story from both data sets; the estuary responds rapidly (seasonal time scale) to increases and decreases in nutrient loading rates.

Year	April	May	June	July	August	September	October
2003	23.8	107.2	53.1	18.8	12.8	4.8	7.9
2004	5.1	2.1	15.6	9.4	11.9	15.4	10.4
2005	5.2	7.3	27.3	No Data	23.7	8.7	3.7

Table 5-3. Interpolated mesohaline area average monthly surface water chlorophyll concentrations measured on Patuxent River estuary DATAFLOW cruises during 2003-2005. Chlorophyll values were measured using a YSI Data sonde 6600. There was a single sampling cruise per month.

Year	April	May	June	July	August	September	October
2003	46.0	127.0	45.5	37.0	39.5	12.4	14.0
2004	5.5	17.5	14.0	11.6	19.0	30.0	15.5
2005	15.5	25.6	11.0	18.0	23.0	12.0	12.0

Table 5-4. A summary of area weighted monthly surface water chlorophyll concentrations measured on Patuxent River estuary at long-term water quality monitoring stations during 2003-2005. Monthly averages were based on two sampling cruises per month.

a)

Year	Average-DF
2003	32.6 µg/l
2004	10.0 µg/l
2005	12.7 µg/l

b)

Year	Average-LTBM
2003	42.9 µg/l
2004	16.2 µg/l
2005	16.7 µg/l

Table 5-5. Interpolated area average annual (April – October) chlorophyll concentrations in surface waters of the mesohaline region of the Patuxent River estuary for the three year sample period (2003-2005). The DF (a) designation indicates data collected via DATAFLOW sampling scheme; LTBM (b) designation indicates data collected via Long-Term Biomonitoring sampling scheme.

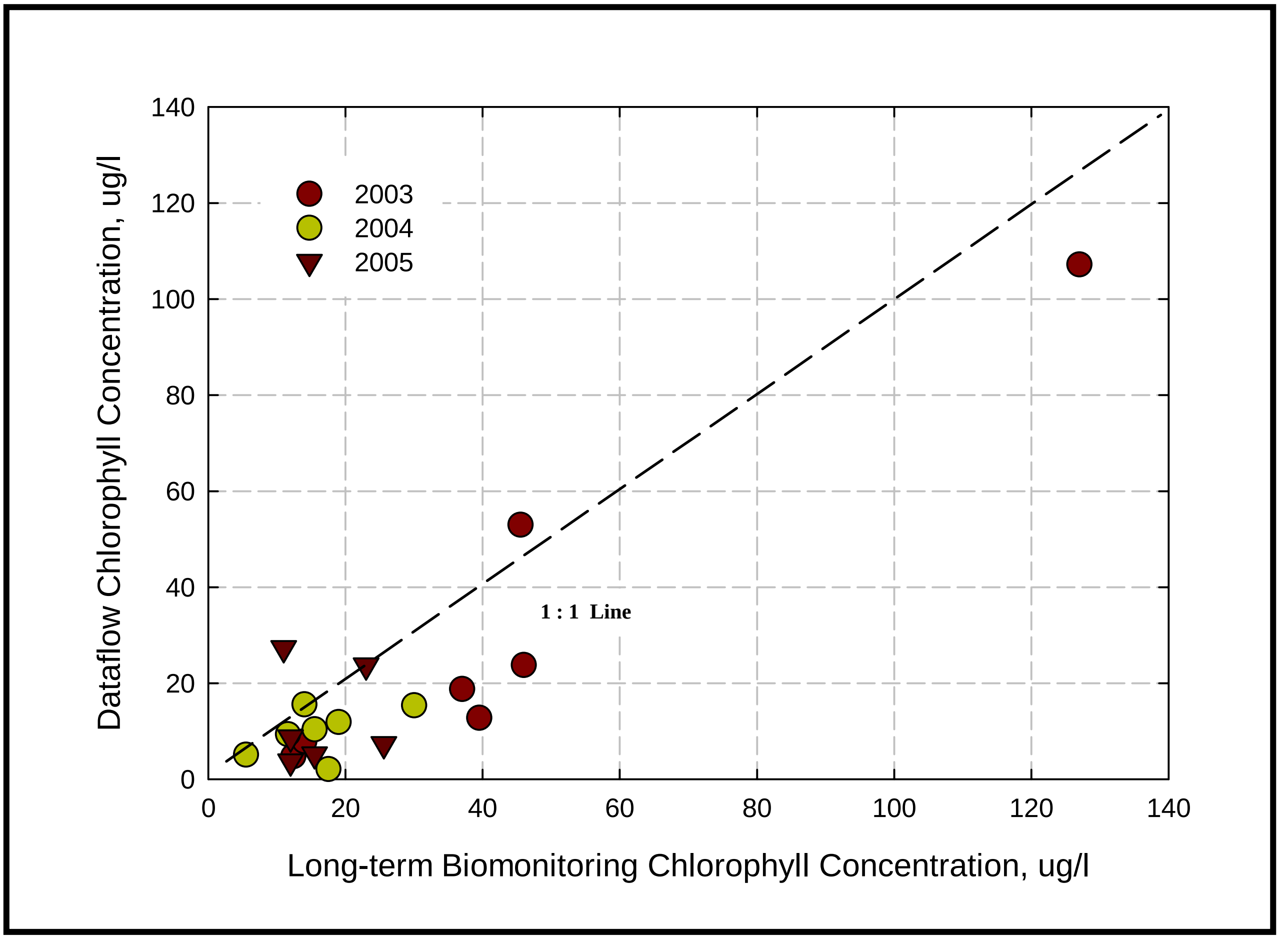

Figure 5-6. Scatter plot of monthly average (April – October) surface water chlorophyll concentrations for the mesohaline region of the Patuxent River estuary. Data were collected during 2003, 2004 and 2005. Chlorophyll concentrations on the X-axis were computed based on data collected via the Long Term Biomonitoring Program (LTBM); Y-axis data were collected via the DATAFLOW measurement program. Both sets of chlorophyll data were interpolated to the full mesohaline region as specified in the text.

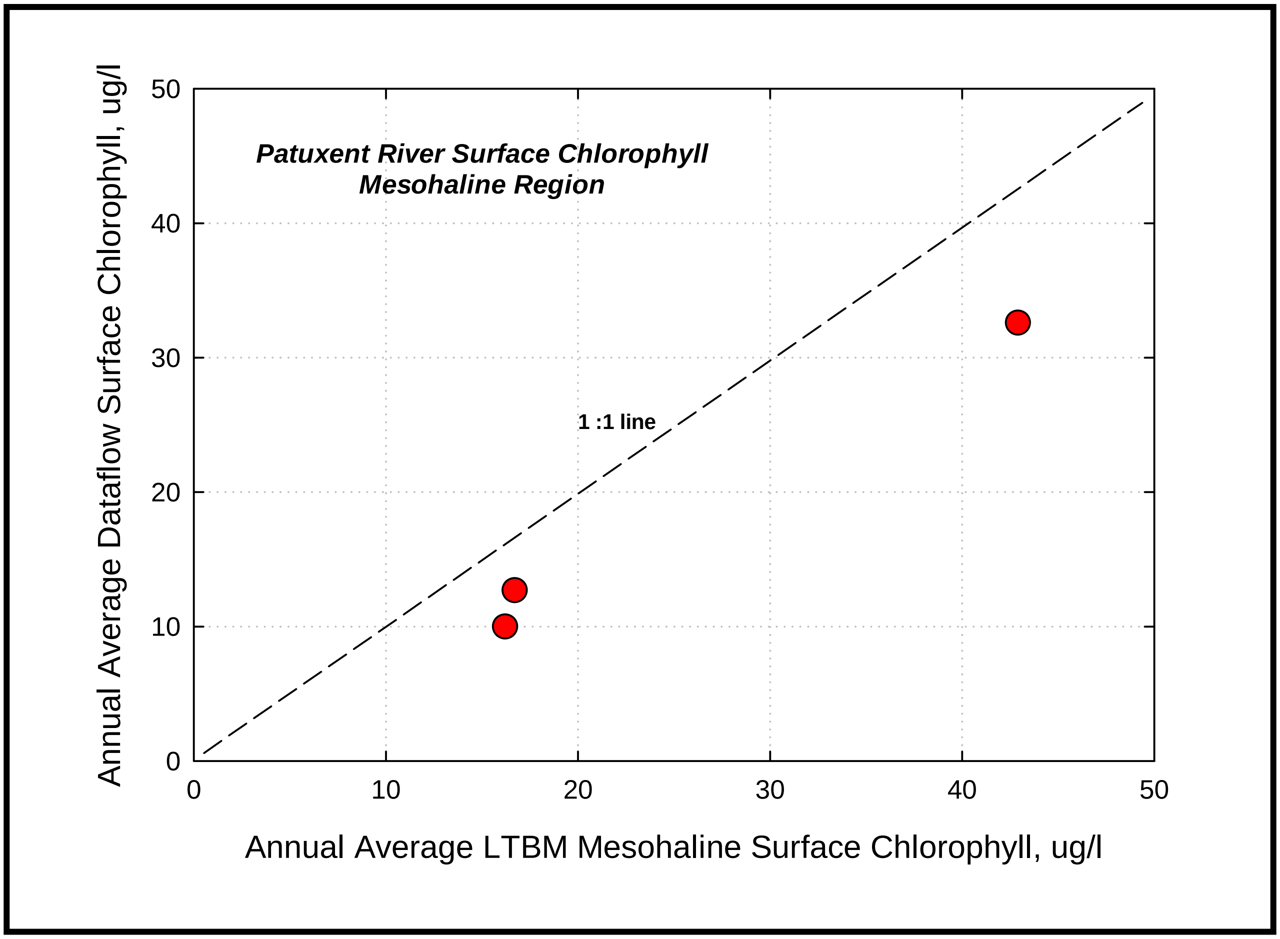

Figure 5-7. A very limited scatter plot of annual average (April – October) surface water chlorophyll concentrations for the mesohaline region of the Patuxent River estuary. Data were collected during 2003, 2004 and 2005. Chlorophyll concentrations on the X-axis were computed based on data collected via the Long Term Biomonitoring Program (LTBM); Y-axis data were collected via the DATAFLOW measurement program.

5.3.3 DATAFLOW chlorophyll-a distribution in deep versus shallow water environments: Implications for SAV success in the mesohaline estuary

One of the prime justifications for utilizing DATAFLOW methodologies in the Chesapeake Bay Biomonitoring Program is to obtain far more detailed spatial descriptions of water quality conditions than was possible using conventional, center-channel monitoring approaches. By way of example, traditional sampling of the Patuxent River estuary produces about 13 surface water measurements (of many parameters) during a single cruise. In contrast, about 4,000 to 9,000 measurements (of far fewer parameters and only in surface waters) are typically made in the mesohaline portion of the Patuxent during a routine DATAFLOW cruise. This comparison does not lessen the value of traditional monitoring but it does show that the spatial resolution possible with DATAFLOW methods is greatly enhanced.

In particular, there is the need to assess current and anticipate future water quality conditions and scales of variability (seasonal to inter-annual) in flank and shallow water habitats. These shallow areas are places where SAV communities formerly existed (e.g., Kemp *et al* 2006; Stankelis *et al* 2004) and where there is high interest in restoring these communities. Thus, detailed spatial patterns of water quality variables related to SAV failure or success are of prime importance in assessing areas that may be candidates for re-introduction of SAV. In addition, there is the need to better understand whatever linkages may exist between shallower and deeper water portions of Chesapeake Bay tributary ecosystems. For example, it is possible (but rarely quantified) that some portion of algal biomass produced in near-shore areas is transported off-shore into deeper and stratified portions of the estuary where it sinks below the pycnocline and further exacerbates hypoxic or anoxic conditions via decomposition of phytoplanktonic organic matter. There is evidence of this in the mesohaline Patuxent River estuary where data collected at a ConMon site indicated surface water chlorophyll concentrations substantially greater than those recorded off-shore at the ACT buoy site. So, DATAFLOW collections can have important utility in both determining if certain areas meet habitat criteria for SAV as well as find application in better understanding relationships between shallow and deep portions of an estuary.

In this section we examined DATAFLOW-based chlorophyll distributions in the mesohaline Patuxent River estuary for a three year period (2003, 2004 and 2005). We chose to examine chlorophyll for several reasons rather than other variables associated with DATAFLOW methodologies. First, there is now ample evidence to show that chlorophyll levels are strongly related to nutrient loading rates (e.g. Boynton and Kemp 2000; Kemp *et al*. 2005). Since reduction of nutrient loads is of prime importance to management agencies this relationship to chlorophyll is of special importance. During the three year examination of the Patuxent River estuary a very wet, close to average and a dry year occurred. Since much of the nutrient load to the Patuxent is diffuse, climate plays a central role in determining seasonal, annual and inter-annual loading rates. Thus, we have an opportunity to again examine links between nutrient loads over a large range and estuarine chlorophyll responses based on spatially intensive data sets. Second, criteria for SAV have been developed (chlorophyll concentration < 15 µg/l for mesohaline species of SAV) and DATAFLOW data can be readily used to see if habitat criteria are met. Finally, epiphytic growth on and subsequent shading of SAV leaves is an issue also involving chlorophyll and provides further justification for selecting this variable for examination. Further investigation of epiphytic chlorophyll accumulation rates on SAV is the focus on another chapter in this report.

5.3.4 Deep versus Shallow Water Chlorophyll Distributions

We have organized DATAFLOW surface water chlorophyll concentration measurements made in the mesohaline portion of the Patuxent River estuary during SAV growing seasons (April – October) in 2003, 2004 and 2005. These data were sorted into those observations collected in shallow, near-shore waters (<2 m depth) and those collected in waters deeper than 2 m and averaged by cruise date (Table 5-6; Fig 5-8 and Fig 5-9). Data used was the transponder depth from QA/QC'd data so any erroneous depth data were eliminated from the distributions.

Surface water chlorophyll concentrations throughout the mesohaline portion of the Patuxent River estuary ranged from 3.7 to 135 µg/l in shallow waters and between 2.3 and 80 µg/l in deep waters. While the highest concentrations occurred in shallow waters, during most cruises there were small differences between deep and shallow concentrations (Fig. 5-8). There was considerable variability concerning the months during which highest chlorophyll concentrations occurred (Table 5-6). For example, during the wet year of 2003 highest concentrations occurred during April-June in both deep and shallow portions of the estuary with highest concentrations favoring shallow areas. During 2004, a year of near-average river flow, peak concentrations were much reduced in all mesohaline areas and peak concentrations occurred in June-July in shoal areas but not until August-September in deeper zones of the estuary. During 2005, a dry year, highest concentrations occurred during June-August at both deep and shallow sites. From the point of view of enhancing SAV survival, water quality conditions were more favorable for growth during both spring and fall and less favorable during summer periods. Increased water residence time along shorelines due to bottom friction or topographic features may play a role in promoting near-shore biomass accumulation.

On an annual basis (SAV growing season; April-October) chlorophyll concentrations in shallow waters averaged 34.1, 10.8 and 11.9 µg/l during 2003, 2004 and 2005, respectively. In deeper waters these concentrations for the same years were 27.3, 10.1 and 12.8. Thus, there is close correspondence in inter-annual chlorophyll patterns in shallow and deep waters and these patterns reflect the general pattern of nutrient loading rates.

We had expected to see generally higher chlorophyll concentrations in shallow waters but this pattern did not emerge in this evaluation of the mesohaline Patuxent River estuary (Figs 5-8 and 5-9). Higher concentrations seemed likely in shallow waters for a number of reasons: 1) due to bottom friction and local shoreline topography water residence times would be longer in shallow areas and this longer residence time would favor algal biomass accumulation; 2) shallow waters are entirely within the euphotic zone and hence light limitation of algal growth would be less likely and it is not possible for algal cells to sink out of the euphotic zone, again likely promoting algal biomass accumulation; 3) sediments serve as an important source of N and P needed for algal biomass accumulation. In shallow sites there is a direct and intimate coupling of a sediment nutrient source and euphotic waters not separated by a pyconocline. Clearly, while these processes are likely active they were not sufficient to generally favor high biomass in shallow waters. It was true that the highest concentrations were observed in shallow waters. However, this was not generally the case. Specifically, shallow water chlorophyll concentrations were higher than in deep waters on 9 of 20 cruises in the mesohaline Patuxent River estuary. However, during 10 of 20 cruises deep and shallow water chlorophyll concentrations differed by less than 2 µg/l.

Finally, the mesohaline portion of the Patuxent River estuary often exhibits shallow water surface water chlorophyll concentrations in excess of SAV criteria (<15 µg/l). Eight cruises during 2003-2005 concentrations exceeded this guideline concentration. Exceedences were most severe during the wet year of 2003 when peak concentrations reached 134 µg/l and criteria were exceeded during 4 of 7 cruises. During 2004 and 2005 SAV chlorophyll criteria exceedance was not as severe with one and two cruises exhibiting high chlorophyll concentrations during these years (Table 5-6).

		< 2m		**> 2m**		
Year	**Date of Cruise**	**Cruise Average Chl Conc (ug/l)**	**Number of Observations Depth <2m**	**Cruise Average Chl Conc (ug/l)**	**Number of Observations Depth >2m**	**Ratio of Observations (< 2m/>2m; %)**
2003	4/28/2003	23.2	570	24.6	3657	16
	5/27/2003	134.5	509	80.1	3078	17
	6/17/2003	26.7	1206	42.6	3161	38
	7/29/2003	27.9	1059	17.8	3420	31
	8/26/2003	12.4	2659	13.0	3016	88
	9/25/2003	5.6	3641	5.2	2986	122
	10/16/2003	8.5	2617	7.8	2864	91
2004	4/12/2004	4.9	2773	5.4	5770	48
	5/10/2004	3.7	758	2.3	1970	38
	6/7/2004	15.0	1589	10.6	6435	25
	7/13/2004	19.5	2034	10.6	8019	25
	8/10/2004	10.1	2279	16.3	7206	32
	9/14/2004	13.9	2857	15.6	6389	45
	10/6/2004	8.6	2858	10.2	6457	44
2005	4/11/2005	4.9	2569	6.7	6552	39
	5/17/2005	11.2	1436	8.3	6617	22
	6/29/2005	17.0	1051	23.0	6798	15
	7/12/2005	No Data	440.0	No Data	2257.0	19
	8/8/2005	26.1	1511	26.5	6707	23
	9/16/2005	8.2	204	9.3	399	51
	10/13/2005	3.7	241	3.1	3761	6
	Averages	**19.3**	**1660**	**17.0**	**4644**	**39.8**

Table 5-6. DATAFLOW chlorophyll measurements in surface waters of the mesohaline Patuxent River estuary. Chlorophyll concentrations were sorted into two depth zones (<2m and >2m) and averaged for each cruise. A reduced number of measurements were available for summer/fall 2005 because of problems with probe performance. The <2m/>2m ratio indicates the percent of observations in SAV habitat.

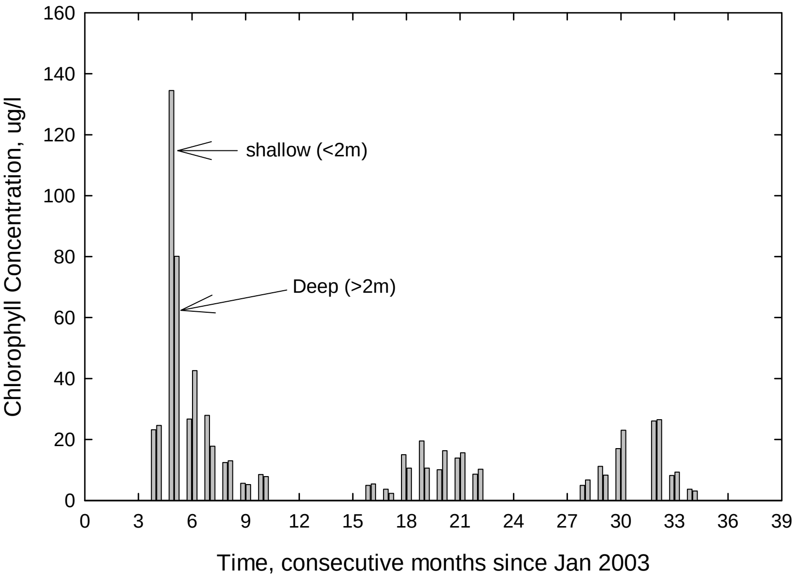

Figure 5-8. Monthly average surface water chlorophyll concentrations for the mesohaline region of the Patuxent River estuary collected with DATAFLOW methodology. Data were sorted into depth bins of <2m and >2m.

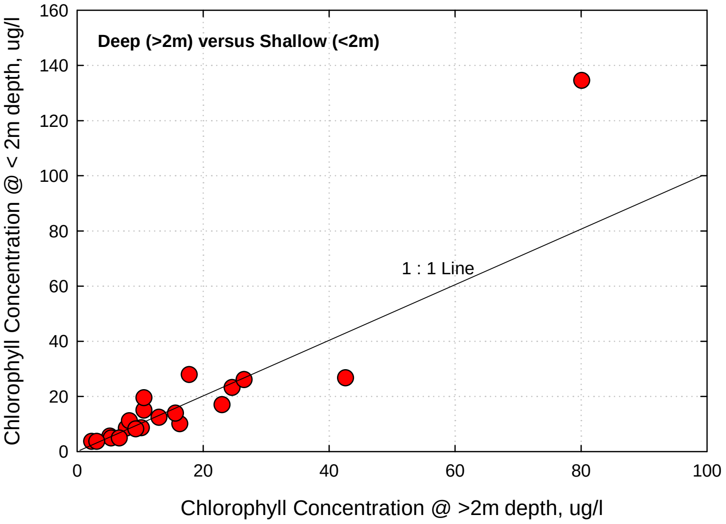

Figure 5-9. Scatter plot of surface water chlorophyll measured in deeper (>2 m) versus shallow (<2 m) water in the mesohaline region of the Patuxent River estuary during 20 cruises conducted during 2003-2005. Data were collected using the DATAFLOW methodology.

5.3.5 SAV Habitat Criteria and Shoreline Length

For purposes of examining habitat conditions for SAV in the mesohaline region of the Patuxent River estuary we assembled DATAFLOW cruise data for chlorophyll and plotted DATAFLOW cruise tracks for late spring periods during 2003, 2004 and 2005 (Fig 5-10(a),(b),(c)).

Portions of cruise tracks in blue indicate surface water chlorophyll concentrations less than 15 µg/l; portions of cruise tracks in brown indicate concentrations in excess of the SAV criteria. Note that in all maps, some chlorophyll concentrations reached very high values.

Several useful patterns emerged from inspection of these maps. First, in years of especially strong river flow (and nutrient loading rates) much of the estuary, at least during some portions of the SAV growing period, have chlorophyll concentrations in excess of SAV criteria. In 2003, for example, both shallow and deep waters throughout the mesohaline estuary had chlorophyll concentrations at generally high levels during June. Exceptions to this include small portions of the river shoreline in the vicinity of St. Leonards Creek. However, the clear message here is one wherein chlorophyll concentrations were well beyond SAV habitat criteria during a wet year. In lower flow years (2004 and 2005) quite a different pattern emerged wherein chlorophyll concentrations in portions of the mesohaline estuary are below SAV criteria values and the portions in compliance tend to be in the high-mesohaline and on the northern shore of the estuary. This suggests that upland sources of nutrients supporting chlorophyll accumulation are a dominant driver in this system. We bring attention to this last observation because recent box modeling studies by Testa (2006) reported a 20 year trend in gradually increasing DIN flux from the mainstem Chesapeake Bay to the Patuxent. If, during the DATAFLOW surveys mapped in Fig. 5-10, deep Chesapeake Bay water was the dominant source of nutrients supporting biomass accumulation we would expect to see a chlorophyll pattern opposite the one documented (e.g., highest concentrations in the vicinity of the Bay rather than highest concentrations in the upper mesohaline estuary). Testa (2006) has noted that the import of DIN from the Bay to the river tends to be s summer event and thus it is likely that the maps we developed did not capture this effect. However, we have compared the DIN import fluxes of DIN computed by Testa (2006) with full ecosystem nitrogen budgets (see last Chapter, this report) and found that these import fluxes constituted about 20-25% of the total N entering the mesohaline estuary during an average year. Thus, these import fluxes do not dominate the mesohaline but they certainly are not a good pattern to be observing relative to water quality restoration efforts and they are large enough to influence ecosystem properties and processes (including SAV restoration) in the portion of the Patuxent downstream of Point Patience. We note that Stankelis *et al*. 2003 and Boynton and Stankelis 2005) noted that several SAV restoration techniques (seed dispersal and transplanting of whole plants) were repeated unsuccessful for more than 1.5 years in this portion of the Patuxent. These studies suggested that severe epiphytic fouling of SAV leaves, probably induced by both relatively clear water and possibly by enhanced supply rates of DIN from the Bay, was the prime cause of failures.

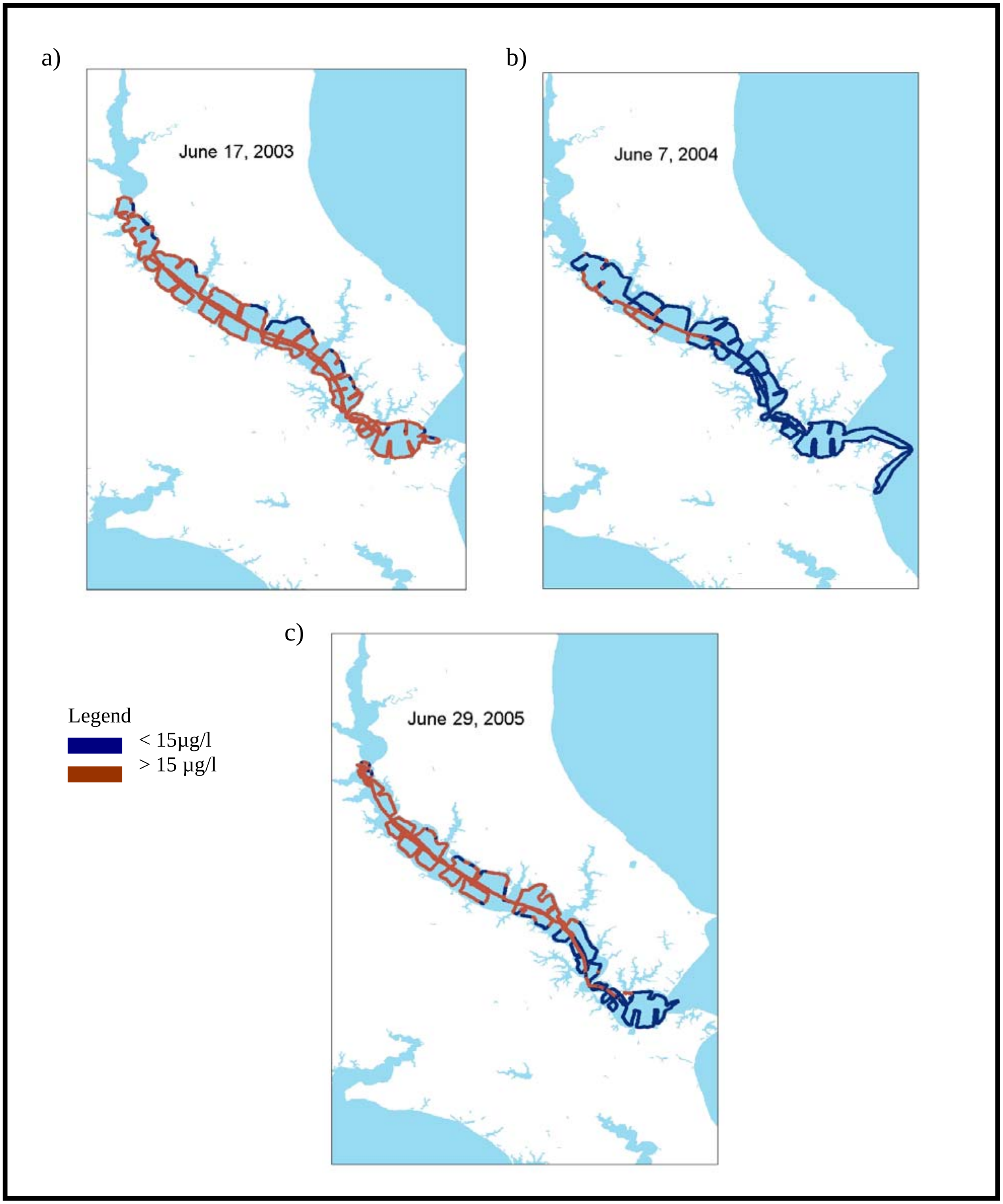

Figure 5-10. DATAFLOW-based maps of surface water chlorophyll concentrations above and below SAV habitat criteria (< 15 µg/l) for selected late spring dates during a) 2003, b) 2004 and c) 2005 in the mesohaline region of the Patuxent River estuary. Portions of cruise tracks in blue indicate surface water chlorophyll concentrations less than 15 µg/l; portions of cruise tracks in brown indicate concentrations in excess of the SAV criteria.

One of the weaknesses of the DATAFLOW program is that temporal resolution is poor. Sampling frequency is once per month at most sites. However, some of the variables nicely measured with DATAFLOW methodology operate at time scales considerably shorter than the cruise frequency. For example, near-shore water clarity can be strongly influnced by wind-induced wave action and these events occur on time scales of hours to several days. Algal blooms can develop and die-off on time scales of days to a week or slightly more. The point here is that we do not as yet have a clear understanding of the fidelity of DATAFLOW maps. Do they adequately represent conditions during a day, several days, or a few weeks? We recognize that no one approach to water quality characterization will be efficiently capable of doing everything needed in terms of time, space and variables measured. It does seem prudent to continue current efforts to assess the temporal fidelity of DATAFLOW characterizations using ConMon sites, other available buoys and by considering some trials wherein selected areas are mapped at higher frequencies to assess temporal variability. Despite these issues, DATAFLOW maps provide spatial resolution to asses habitat that was never before possible.

We have also made numerical estimates of the length of shoreline (total shoreline of mesohaline estimated to be 75.2 km) exceeding SAV chlorophyll criteria and these are summarized in Table 5-7 and in Figure 5-11. During 2003-2005 we conducted a total of 21 DATAFLOW cruises and all but one (July 2005) yielded useful chlorophyll distributions in depth zones of < 2m. The range in shoreline length exceeding criteria ranged from zero or near-zero (5 of 20 cruises) to very considerable (>25% of shoreline during 7 of 20 cruises). During the high flow year of 2003 about 85% of mesohaline shoreline had chlorophyll concentrations above criteria values during May and during April – June, 2003 at least 68% of mesohaline shoreline did not meet criteria. During this high flow year the early spring SAV growing period was likely very compromised by high chlorophyll concentrations. However, during this year the percent of shoreline not meeting criteria rapidly dropped for the rest of the growing season. This “high flow” pattern was not evident in 2004 and 2005, both years with normal or below average flow. In these years there were no prolonged periods when substantial shoreline did not meet criteria and the period when criteria were least achieved was during summer, a period when some SAV species (e.g. eelgrass) do not grow a great deal or lose much of their above-ground biomass. Thus, there appear to be a range of conditions related to river flow that change both the magnitude and seasonal pattern of shoreline habitat quality relative to SAV growth and survival.

Cruise Date	Mesohaline Shoreline Length with Surface Chlorophyll > 15 ug/l (km)	Percent of Total Shoreline Length with Chloro >15 ug/l (%)
4/28/2003	53.9	71.7
5/27/2003	63.6	84.6
6/17/2003	50.8	67.6
7/29/2003	19.0	25.3
8/26/2003	14.1	18.8
9/25/2003	0.1	0.1
10/16/2003	5.1	6.8
4/12/2004	0.0	0.0
5/10/2004	0.0	0.0
6/7/2004	6.2	8.2
7/13/2004	7.5	10.0
8/10/2004	10.0	13.3
9/14/2004	24.6	32.7
10/6/2004	1.7	2.3
4/11/2005	0.0	0.0
5/17/2005	6.4	8.5
6/29/2005	32.2	42.8
7/12/2005	No Data	
8/8/2005	54.7	72.7
9/16/2005	3.1	4.1
10/13/2005	0.0	0.0

Table 5-7. Shoreline length and percent of total shoreline length in the mesohaline Patuxent River estuary exhibiting surface water chlorophyll concentrations in excess of SAV criteria (>15 µg/l) during SAV growing seasons of 2003, 2004 and 2005. Data were collected using DATAFLOW methodology.

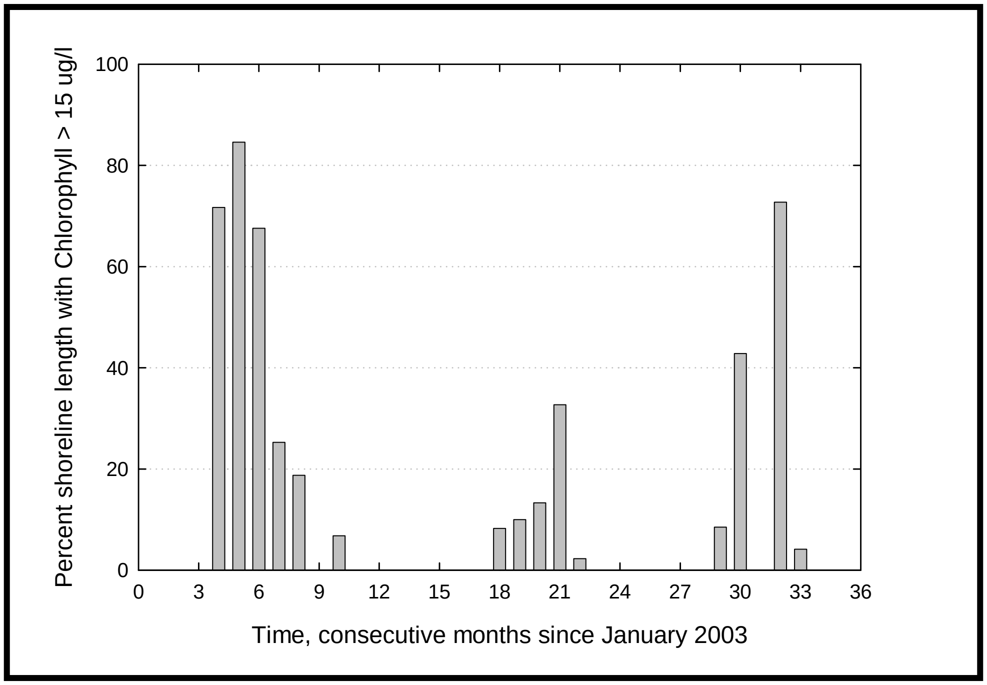

Figure 5-11. Percent of mesohaline Patuxent River estuary shoreline with surface water chlorophyll concentrations in excess of SAV criteria (<15 µg/l) during SAV growing seasons of 2003, 2004 and 2005. No data were collected during months of Nov-Dec and Jan-Mar of each year.

5.3.6 Relationships between nitrogen loading rate and mesohaline chlorophyll concentrations

We have compiled reports of statistical models developed to relate primary production or algal biomass to nitrogen loading rates or nitrogen concentration (“Table 1”). In a system like the Patuxent there is ample evidence that nitrogen is a key variable regulating rates of primary production and algal biomass accumulation (D”Elia *et al*. 1986; Fisher *et al*. 1999; Testa 2006). However, we could ask “Is this normal for estuarine ecosystems or is the Patuxent a special case?” As we shall see below, it appears that nitrogen is a frequent “master variable” controlling estuarine phytoplanktonic primary production.

All but one of the statistical models summarized in Table 1 has been generated during the last two decades, and the models take a variety of forms, for example, using N concentration or loading rate as an independent variable. Most models were computed on annual time scales, and for several it was unclear how temporal and spatial variability was taken into account. Sample size used to develop these models also varied widely, and some are based on multi-system comparisons while others were based on multi-year data collected for one system. Given the myriad factors known to influence production and algal biomass accumulation, it is impressive that N alone was able to account for a large portion of the variability of phytoplankton production. This, we believe, is the primary “take-home” message from these efforts. Serious reductions in N loading rates will cause reductions in algal biomass accumulation, rates of primary production and associated poor water quality and habitat conditions.

There are, of course, some limitations with these analyses. These are basically correlations and thus do not demonstrate causation; results may be related to some other co-variate. More important is that other possible explanations of production or biomass variability were not always thoroughly examined. For example, in some of these papers it seemed like N was assumed, a priori, to be the key explanatory variable and others, such as phosphorus or light availability, were not examined with equal rigor. One could make the case that sufficient data are now available to initiate a more comprehensive, comparative synthesis of estuarine primary production (both pelagic and benthic) that considers a wider selection of independent variables and uses dimensional scaling to the extent needed to ensure adequate comparability among different estuarine locations. In short, estuarine ecologists need to take a lesson from the limnologists who began doing just that some 30 years ago (e.g., Volleinweider 1976) and developed tools useful for both scientific understanding and for lake management.

Table 1. A summary of statistical models relating phytoplankton primary productivity or biomass to nitrogen (concentration or loading rates) or other variables. Abbreviations B, Zp, I_0, Z and R_{time} refer to phytoplankton biomass (as chlorophyll), euphotic depth, incident radiation, average system depth, and water residence time, respectively.

Location	Independent Variable, X (units)	Dependent Variable, Y (units)	Predictive Equation	r^2 / n	Reference
Multiple estuaries	TN-loading (g N m^{-2} y^{-1})	Phytoplk Prod (g C m^{-2} y^{-1})	Y = 25 + 13X	0.60 / 14	Boynton et al. 1982
Multiple estuaries and Univ RI MERL	DIN-loading (mol N m^{-2} y^{-1})	Phytoplk Prod (g C m^{-2} y^{-1})	logY = 0.44log (X) + 2.33	0.93 / 19	Nixon et al. 1996
Multiple estuaries	TN-loading (g N m^{-2} y^{-1})	Phytoplk Prod (g C m^{-2} y^{-1})	Y = 244 + 175log(X)	0.36 / 51	Borum and Sand-Jensen 1996
Waquoit Bay estuarine system, MA	Annual average DIN conc (µM)	Phytoplk Prod (g C m^{-2} y^{-1})	Y = 60.9 + 13.96X	0.61 / 12	Valiela et al. 2001
San Francisco Bay other estuaries	Composite parameter X = f(B, Z_p, I_0)	Phytoplk Prod (mg C m^{-2} y^{-1})	Y = 15 + 0.73X	0.82 / 211	Cole and Cloern 1987
Chesapeake Bay					
Narragansett Bay and Univ RI MERL	Composite parameter X = f(B, Z_p, I_0)	Phytoplk Prod (g C m^{-2} y^{-1})	Y = 220 + 0.70X	0.82 / 1010	Keller 1988
Boston Harbor	Composite parameter X = f(B, Z_p, I_0)	Phytoplk Prod (mg C m^{-2} y^{-1})	Y = 285 + 0.79X	0.66 / 12	Kelly and Doering 1997
Multiple estuaries	DIN (mM m^{-3}); tidal range	Phytoplk Biomass	not provided; positive slope indicated	na / 163	Monbet 1992
Multiple ecosystems and MERL	DIN input (mmol m^{-3} y^{-1})	Phytoplk Biomass	not provided; positive slope indicated	na / 34	Nixon 1992
Chesapeake Bay mesohaline region	River flow (m^3 d^{-1}) (proxy for N-load)	Phytoplk Biomass	not provided; positive slope indicated	0.70 / 34	Harding et al. 1992
Maryland lagoons	TN load (gN m^{-2} y^{-1})	Phytoplk Biomass	Y = 16.9 + 0.70X	0.96 / 9	Boynton et al. 1996
Danish coastal waters	TN concentration (ug l^{-1})	Phytoplk Biomass (July)	not provided	0.64 / 168	Borum 1996
Canadian estuaries	TN concentration (ug l^{-1})	Phytoplk Biomass	log Chl-a = -4.06 + 1.78 log TN	0.72 / 15	Meeuwig 1999
Chesapeake Bay and Tributaries	Scaled TN load (mg N m^{-2} yr^{-1}) (R_{time}, yrs)$^{-1}$	Phytoplk Biomass	y = 18.9 + 0.078X	0.82 / 17	Boynton and Kemp 2000
Danish estuaries and coastal waters	TN concentration	Phytoplk Biomass	Ln(Chl) = 0.96 Ln (TN) - 4.19	0.30 / 162	Neilsen et al. 2002

Surface water chlorophyll-a concentrations collected during 2002 (drought year) through 2005 at long-term biomonitoring stations between Benedict, MD and the mouth of the Patuxent River estuary were organized and area-weighted monthly and annual mean concentrations computed. Concentrations are provided in Table 5-8 as are estimates of nitrogen loading at the USGS station at Bowie, MD and at Benedict, MD.

Year	Sav Ann Avgs (April-Oct) (ug Chloro/l)	Annual Averages (ug Chloro/l)	Average Annual Load at Bowie kg TN/day	4 k above Benedict Annual Average TN kg/d
2002	9.87	10.85	1094	1449
2003	42.86	34.22	3385	5095
2004	16.20	17.12	2063	3238
2005	16.72	15.53	1307	2000

Table 5-8. A summary of average SAV growing season and annual surface water chlorophyll-a concentrations in the mesohaline region (Benedict, MD to mouth) of the Patuxent River estuary. Annual average total nitrogen (TN) loads (kgN/day) at the fall line (Bowie, MD) and at at estuarine cross-section 4 km above Benedict, MD are also included.

Several important points emerge from this summary. First, there is a very substantial range in both SAV growing season and annual average chlorophyll-a concentration in surface waters. During the low flow year of 2002 concentrations were close to 10 µg/l for both computations. However, concentrations increased by about 400% during the very wet year of 2003, especially so for the SAV growing season average. During the most recent years concentrations were between 15 and 17 µg/l. Thus, the levels of interannual variability were large. In addition, during the drought year of 2002 chlorophyll-a concentration was below the Bay Program SAV criteria of 15 µg/l for the mesohaline Patuxent. During the wet year of 2003, concentration was far in excess of the criteria concentration and during more average flow conditions only slightly higher than criteria conditions. Considering only the chlorophyll-a criteria it appears that most of the mesohaline area would meet SAV chlorophyll-a criteria during dry and average flow years if chlorophyll-a concentrations were reduced by relatively small amounts.

To examine the issue of factors controlling chlorophyll-a concentration in surface waters of the mesohaline Patuxent we assembled nutrient loading (TN) data from two sources and these data are summarized in Table 5-8. As indicated above, there is ample reason to relate nitrogen load to algal biomass. The first set of loading numbers comes from the River Input Monitoring Program site at Bowie, MD. This site has been maintained by USGS since 1978 and provides an excellent time-series of inputs near the head of tide. However, most of the Patuxent basin and the largest single sewage treatment plant discharge is located downstream of this gauging station so there is uncertainty about just how well loading data from this site represents TN loads to the mesohaline estuary. However, Testa (2006) has recently completed a box-modeling computation and has provided us with TN transport estimates for an estuarine cross-section just upstream of Benedict (Table 2). Loads at this point in the estuary are about 1.6 times the loads at the fall line station and this is to be expected since so much of the basin drains into the Patuxent downstream of the fall line. Fortunately, there is a very strong relationship between loads measured at these two sites (R2 = 0.99; n=4; years 2002-2005). So, while the magnitudes are different, the fall line load remains a useful index of nutrient load to the lower, mesohaline estuary.

To examine surface chlorophyll-a responses to nutrient loads we produced a scatter plot of average annual surface water cholorophyll-a as a function of annual TN loading rate both for the Bowie and Benedict sites. As expected, both TN loads were very significant predictors of surface water chlorophyll-a in the mesohaline estuary.

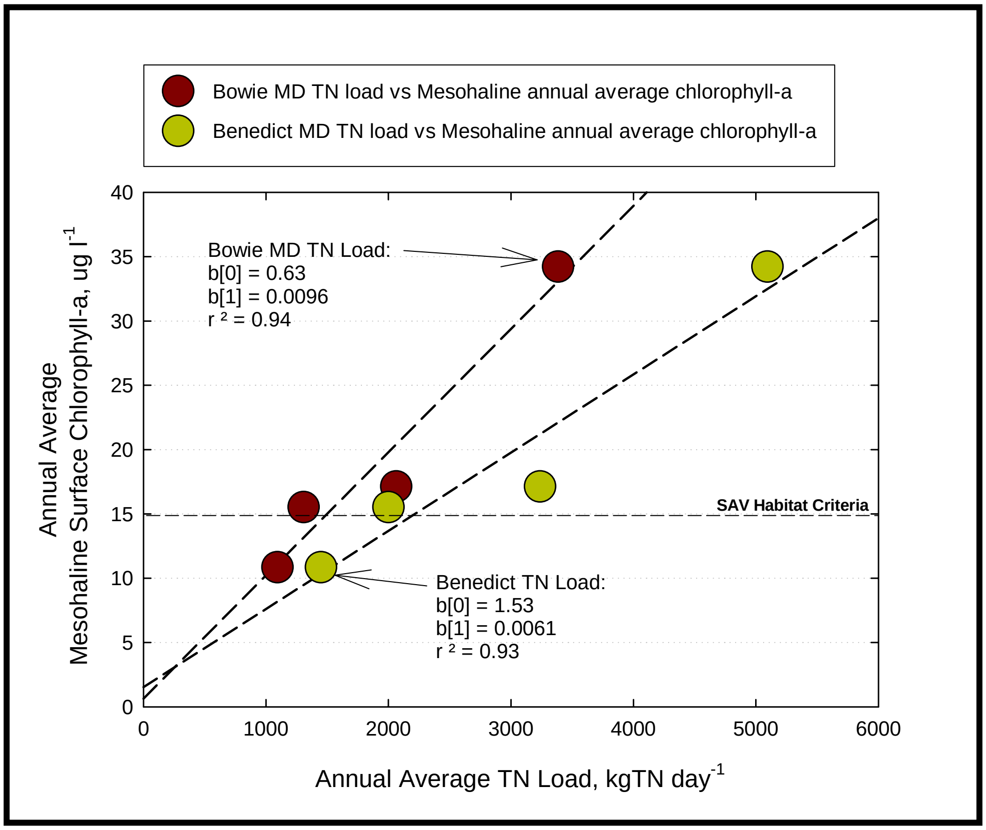

Figure 5-12. Scatter plots of annual average surface water chlorophyll-a concentration as a function of TN loading rates estimated at the USGS station at Bowie, MD and from box model computations at Benedict, MD. The horizontal dashed line represents the Chesapeake Bay Program chlorophyll-a criteria for SAV.

In Figure 5-12 the slopes of the two curves differ and that is simply because nutrient loads are larger at Benedict than at Bowie. Goodness of fit parameters were virtually identical at both sites. Several useful points emerge from this relatively simple analysis. First, the mesohaline estuary appears to be quite responsive to nutrient loading rate. In this small selection of data, nutrient loads differed by a factor of about 3.5 between wet and dry years. Surface water chlorophyll varied by a factor of 3.1 between wet and dry years. Second, when nutrient loading rates dropped substantially following the very wet year of 2003, so did chlorophyll concentrations and concentrations dropped again during 2005 when TN loads again decreased by a small amount. This suggests that there is little multi-year nutrient memory in these heavily enriched ecosystems. If substantial amounts of N or P were stored in these systems from one year to the next we would not find simple linear relationships between within year loads and chlorophyll concentrations. Finally, in dry and even in years of average hydrology, chlorophyll concentration in the mesohaline region of the estuary was slightly below or slightly above SAV criteria (Fig. 5-12). While we recognize that factors other than water column chlorophyll (e.g., turbidity, nutrient conditions, exposure to waves, grazing by swans and other herbivores) impact SAV survival, these data suggest that at the low end of contemporary TN loading rates chlorophyll levels are close to being consistent with SAV success. This further suggests that modest reductions in nutrient loading rates might well produce some ecosystem changes that would be positive, such as SAV re-invasion of the mesohaline estuary.

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6.0 Submerged Aquatic Vegetation (SAV) Habitat Evaluation

E.M. Bailey, P.W. Smail, M. Hessey, R.M. Stankelis, H. Soulen, and W.R. Boynton

6.1 Introduction

It is generally agreed that light availability is the most critical resource limiting the extent and distribution of SAV populations (e.g. Duarte, 1991). For example, a number of studies have demonstrated that SAV epiphytes can substantially reduce the amount of available light reaching the leaf surface (e.g., Burt *et al*., 1995; Stankelis *et al*., 1999; Brush and Nixon, 2002; Stankelis *et al*., 2003). However, epiphyte loads can be modified to a great extent by a variety of factors including epiphyte grazer density (e.g. Neckles *et al*., 1993; Williams and Ruckelshaus, 1993), water column light availability (Stankelis *et al*., 2003), nutrient availability (Kemp *et al*., 1983; Burt *et al*., 1995), wave action, and leaf turnover rates. As a result of this inherent complexity, field monitoring remains an important tool for understanding why SAV thrives, survives or declines at specific locations. In Chesapeake Bay, field monitoring is particularly important because of the large range of conditions found within the Bay and its tributaries. For example, in some Chesapeake Bay tributaries, modest reductions in nutrient loading has been achieved in recent years resulting in improved water quality conditions (e.g. Boynton *et al*., 1995). Yet, many of these tributaries, including the extensive mesohaline portion of the Patuxent River that was historically populated with SAV has not shown significant recovery (VIMS, 2002).

In 1997, the EPC began an ambitious and diversified study of the near-shore water quality conditions important to SAV growth and survival. The primary goal of the near-shore water quality evaluation was to measure a suite of water quality parameters in the shallow near-shore habitat to assess compliance with established SAV habitat requirements (Batuik *et al*., 1992; Batuik *et al*., 2000; Kemp *et al*., 2004) and to directly measure epiphyte fouling rates using artificial substrates. Annual studies have been conducted in the Patuxent estuary, with varying scope and extent since 1997, and provide a time series of data that has become quite unique. In 1998, a study was conducted to compare epiphyte fouling rates on live SAV to fouling on artificial substrates (Mylar® strips). Results of this study suggested that Mylar® strips could be used as an acceptable surrogate for live plants in order to estimate light attenuation from epiphytic fouling (Stankelis *et al*. 1999). Despite some potential limitations, artificial substrates can be used effectively to compare the effects of differing water quality conditions on epiphyte accumulation rates and light attenuation when live plants are not available (e.g., Burt *et al*., 1995, Stankelis *et al*., 1999). In addition, artificial substrates can be standardized between sites, and provide a quick assessment of epiphyte growth potential at SAV restoration sites.

In the 2005 field season, the EPC measured water quality conditions and epiphyte fouling rates at two locations in the lower Patuxent River Estuary. These locations, CBL (SV09) and Pin Oak (PXPO), were monitored for 4 consecutive weeks each, in the spring, summer and fall of 2005. These sites are under active consideration for large-scale SAV restoration.

6.2 Methods

6.2.1 Station Locations and Sampling Frequency

In 2005, 2 stations were monitored in the lower Patuxent River estuary (Fig 6-1, Table 6-1). Both of these stations have been studied since 1997, and have been the location of SAV restoration activities. Sampling was conducted for 4 consecutive weeks each in the spring, summer and fall months. During each sampling block, three weekly epiphyte samples were collected for a total of 9 weekly measurements (Table 6-1). This sampling schedule was designed to measure seasonal variation in epiphyte fouling rates in a cost effective manner.

Table 6-1 Station codes, grid location, DNR station names, and sampling dates for Patuxent River epiphyte sampling in 2005.

Geographic Location Name	**Station Codes & Bottle Numbers**	**Geographic Coordinates (NAD 83)**		**DNR CONMON Station name**	**Sampling Dates (retrieval)**
		Latitude	Longitude		
CBL	SV09 (600)	38º 19.016	76º 27.119	XCF9029	Spring 5/24, 5/31, 6/08 Summer 8/01, 8/08, 8/15 Fall 9/27, 10/03, 10/10
Pin Oak	PXPO (611)	38° 24.625	76° 31.351	XED4587	Spring 5/23, 5/31, 6/08 Summer 8/01, 8/08, 8/15 Fall 9/27, 10/03, 10/10

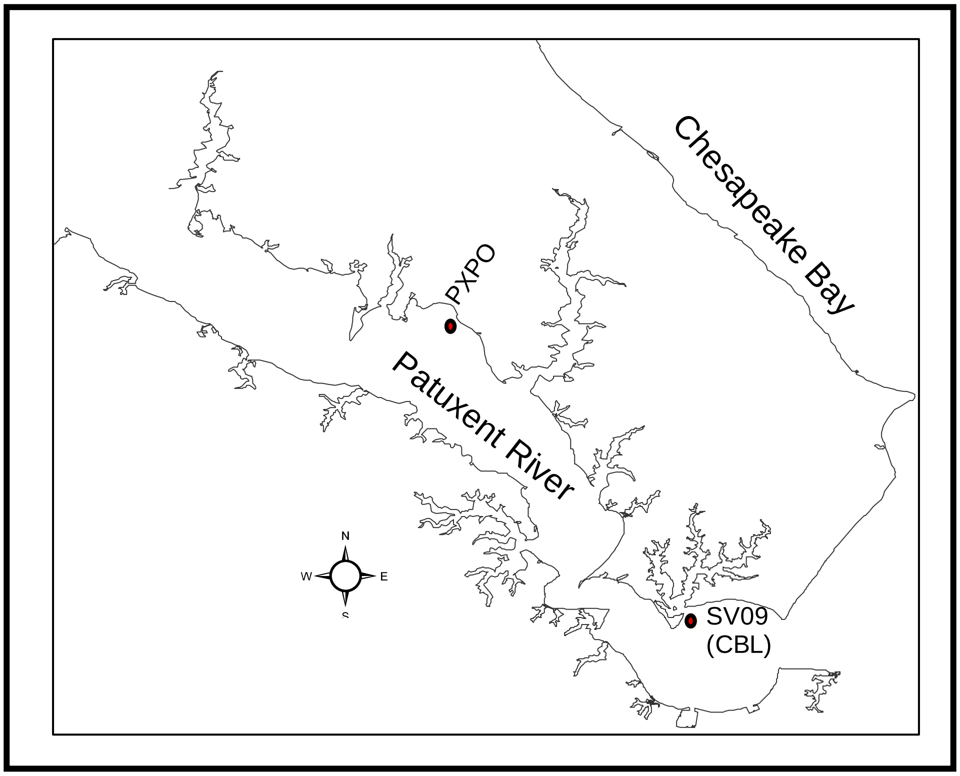

Figure 6-1. Location of Submerged Aquatic Vegetation (SAV) monitoring stations in the Patuxent Estuary: PXPO (611) and SV09 (600).

6.2.2 Field Methods

6.2.2.1 Water Quality

Temperature, salinity, conductivity, and dissolved oxygen measurements were made with a Yellow Springs International (YSI) 600R, YSI 6920 or YSI 6600 multi-parameter water quality monitor suspended at 0.5 meters below the water surface. Water column turbidity was estimated with a secchi disk where possible, while water column light flux in the photosynthetically active range (PAR) was measured with a *Li-Cor* LI-192SA under-water quantum sensor and LI-190 deck sensor. When possible, measurements were collected at a minimum of three discrete water depths in order to calculate water column light attenuation (Kd). Weather and sea-state conditions, such as air temperature, percent cloud cover, approximate wind speed and direction, total water depth, and wave height, were also recorded.

Whole water samples were collected at approximately 0.5 meters below the water surface by using a hand held bilge pump, the outflow from the DATAFLOW intake, or by dipping a sample bottle in the water. The whole water samples were placed in coolers for transport back to the laboratory for further processing. In the laboratory, a portion was filtered for dissolved nutrient concentrations with a 25mm, 0.7 µm (GF/F) glass fiber filter. The filtered portion was analyzed by the Nutrient Analytical Services Laboratory (NASL) for ammonium (NH_4^+), nitrate (NO_3^-), nitrite plus nitrate ($NO_2^- + NO_3^-$) and phosphate (PO_4^{-3}). Whole water portions were also filtered in the laboratory using 47 mm, 0.7 µm (GF/F) glass fiber filters and were transferred to NASL for analysis of total suspended solids (TSS), total volatile solids (TVS), total and active chlorophyll-*a* concentration. Total chlorophyll-*a* also includes chlorophyll-*a* plus breakdown products.

6.2.2.2 Epiphyte Growth Measurement Method

In order to assess the light attenuation potential of epiphytic growth on the leaves of submerged aquatic vegetation (SAV) artificial substrata, thin strips of Mylar® polyester plastic, were deployed at each sampling location for a period of 6 to 8 days. Each collector array (Figure X-2) consisted of a square PVC frame with a vertical PVC shaft in the center of the square. A line with a small surface float that allows for easy location of the collector was attached to the shaft. Each collector array held up to six strips per deployment. Mylar® strips (2.5 cm wide x 51 cm long and 0.7 mil thick) were attached to the frame so that the top was allowed to move freely in the water column. Small foam floats (~3.5 x 3.3 cm) were attached to the top of each strip to help maintain a vertical position in the water column at all times.

On each sampling date, six replicate Mylar® strips were collected. Three were analyzed for chlorophyll-*a* mass, and three for total dry mass/inorganic dry mass. While suspended in the water, Mylar® strips were gently removed from the array and cut with scissors to remove the middle 1/3 marked section (64.5 cm^2, Figure 6-2). This section was once again cut in half, and placed in a 60 ml plastic centrifuge tube which was placed in a cooler for transport back to the laboratory. The samples were immediately frozen upon arrival at the laboratory prior to further processing.

Upon thawing, the Mylar® strip sections collected for dry mass/inorganic mass analysis were scraped of all material and rinsed with distilled water. Scraped material and rinse water were diluted to a fixed volume (300 - 500 ml). The solution was mixed as thoroughly as possible on a stir plate until homogenized. A small aliquot (10 to 50 ml) was then extracted with a glass pipette and filtered through a 47 mm, 0.7 µm (GF/F) glass fiber filter. Once filtered, the pads were immediately frozen and delivered to NASL for analysis. Samples collected for epiphyte chlorophyll-a concentrations did not require further processing because chlorophyll-a was extracted directly off the Mylar® surface via a method similar to Strickland and Parsons (1972) and Parsons *et al*. (1984). A comparison using this method to the more traditional method of scraping and filtering the epiphyte material found no statistical difference (Stankelis *et al*., 1999).

6.2.3 Chemical Analysis Methodology

Methods for the determination of dissolved nutrients were as follows: ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate ($NO_2^- + NO_3^-$), and dissolved inorganic phosphorus (DIP or PO_4^-) were measured using the automated method of EPA (1979). Methods of Strickland and Parsons (1972) and Parsons *et al.* (1984) were followed for chlorophyll-*a* analysis. Total suspended solids (TSS) and total volatile solids (TVS) were measured with a gravimetric method.

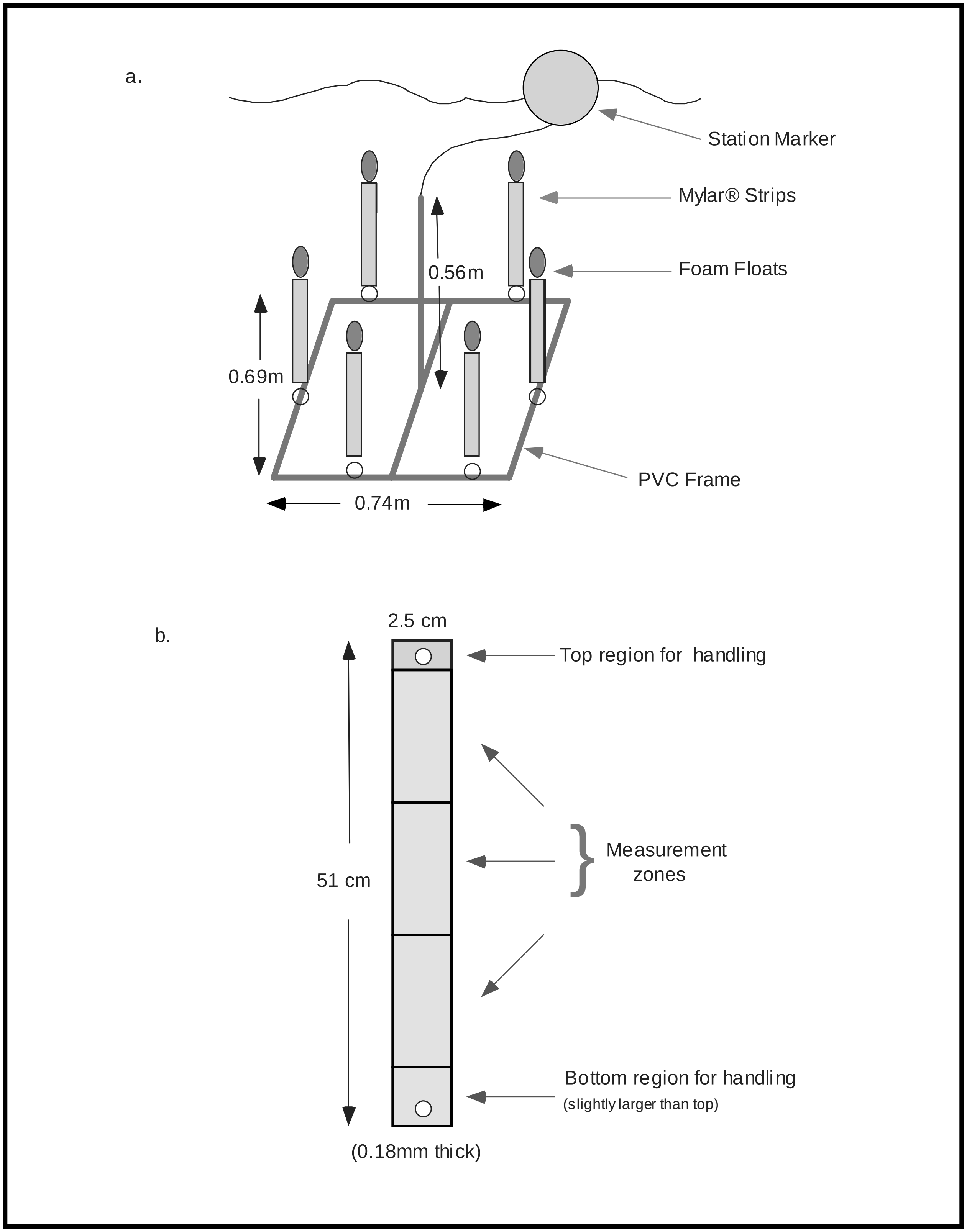

Figure 6-2. Diagram of SAV Epiphyte Collector Array.
a. Epiphyte Collector Array
b. Mylar® strips

6.2.4 Estimating light Epiphyte Light Attenuation

Estimates of epiphyte light attenuation were calculated using epiphyte dry mass and the existing relationships between dry mass and light attenuation (Fig. 6-3 a,b). These relationships were developed using direct measurements of epiphyte light attenuation and dry mass accumulated on Mylar® strips deployed at a number of locations from 1997 to 1999 (Boynton *et al*. 1998; Stankelis *et al*., 1999; Boynton *et al*., 2000). These estimates along with corresponding measurements of water column light attenuation (Kd) allow us to calculate the percent of surface light reaching the depth of the SAV blade through the water column (PLW) and the percent surface light reaching the blade of SAV through the epiphyte layer at the leaf surface (PLL). Calculations of these metrics defined by the Chesapeake Bay Program (Batuik et. al, 2000) are shown below in Table 6-2.

Table 6-2. Calculation of % surface light reaching the depth of the SAV blade (PLW) and % surface light reaching leaf surface (PLL).

$PLW = (I_Z/I_0)*100 = 100*[e^{-kd*Z}]$

$PLL = [e^{-kd*Z}][1-LA/100]$

Where: Iz = Light flux (PAR) at depth

I_0 = Light flux (PAR) at surface

LA = Epiphyte light attenuation

Z = Observation depth (m)

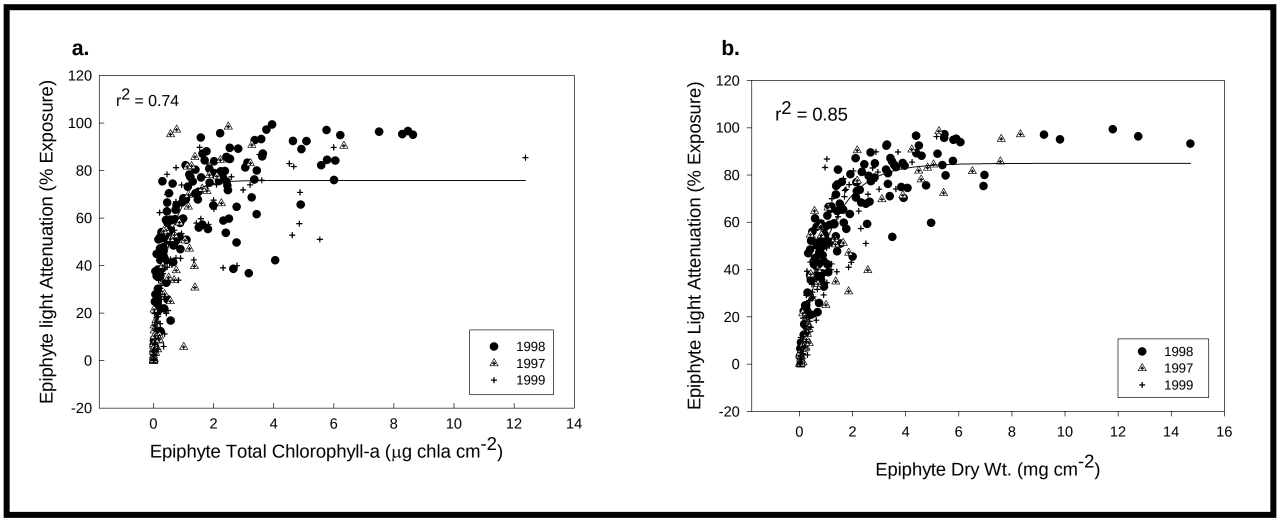

Figure 6-3. (a) Epiphyte light attenuation vs. epiphyte chlorophyll-a, where light attenuation = $77.36*(1-e^{-2.082 * \text{Epi Chla}})$ and (b) epiphyte light attenuation vs. epiphyte dry mass where Light Attenuation = $84.634*(1-e^{-0.963 * \text{Epi drywt}})$.

6.3 Results

6.3.1 Water Quality conditions

Growing season water column light attenuation (Kd) in the Patuxent River during 2005 continued the trend seen in 2004 with greatest water clarity in the spring (Figure 6-4) at both sites. During the summer, water clarity at both sites frequently fell near or below the recommended habitat limit.

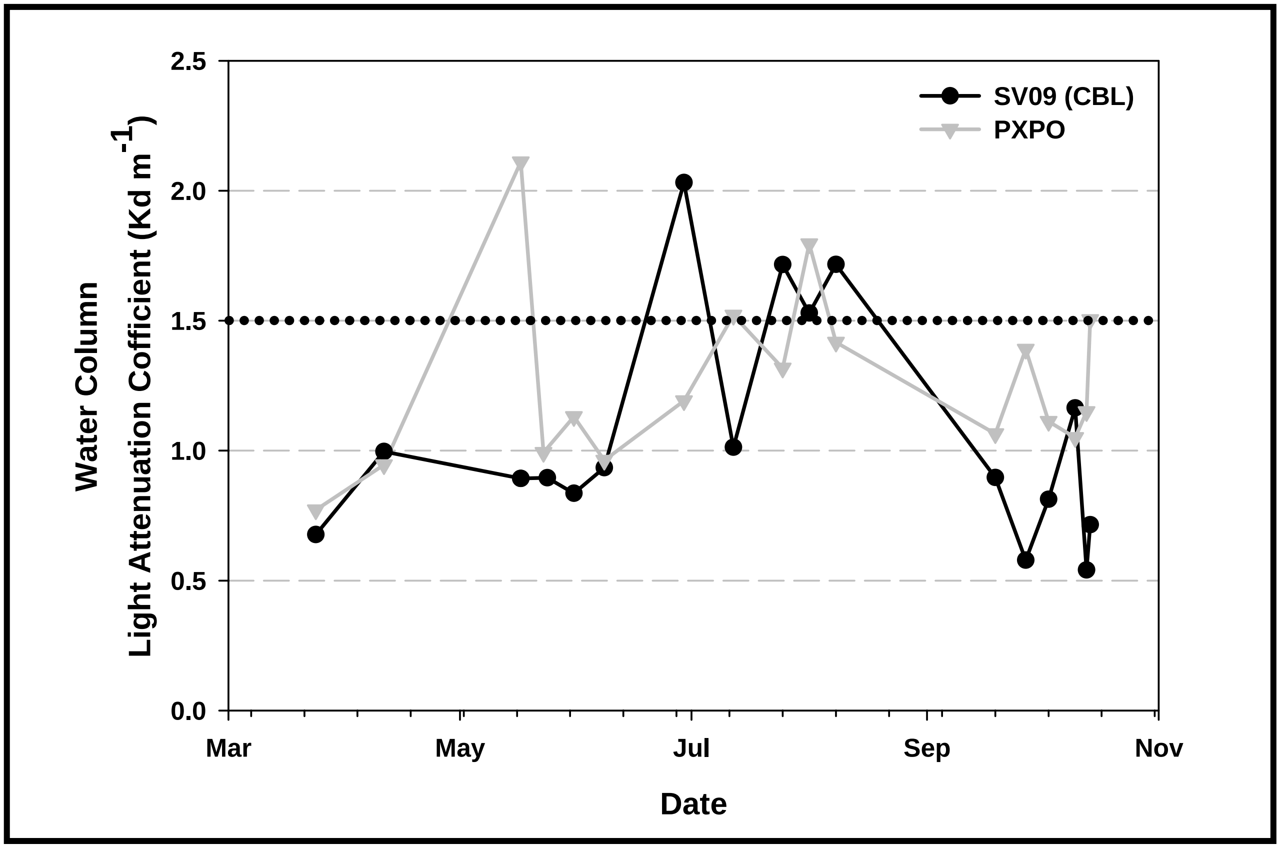

Figure 6-4. Patuxent River light attenuation coefficient (Kd) vs. date. ***Dotted line represents mesohaline SAV habitat criteria.***

Growing season median water column light attenuation (Kd) values were 0.90 m^{-1} at CBL, and 1.15 m^{-1} at Pin Oak (Fig. 6-4). Both were below recommended mesohaline habitat limits (Batuik, *et al*., 2000), and were very similar to values measured in 2004 (Figure 6-5).

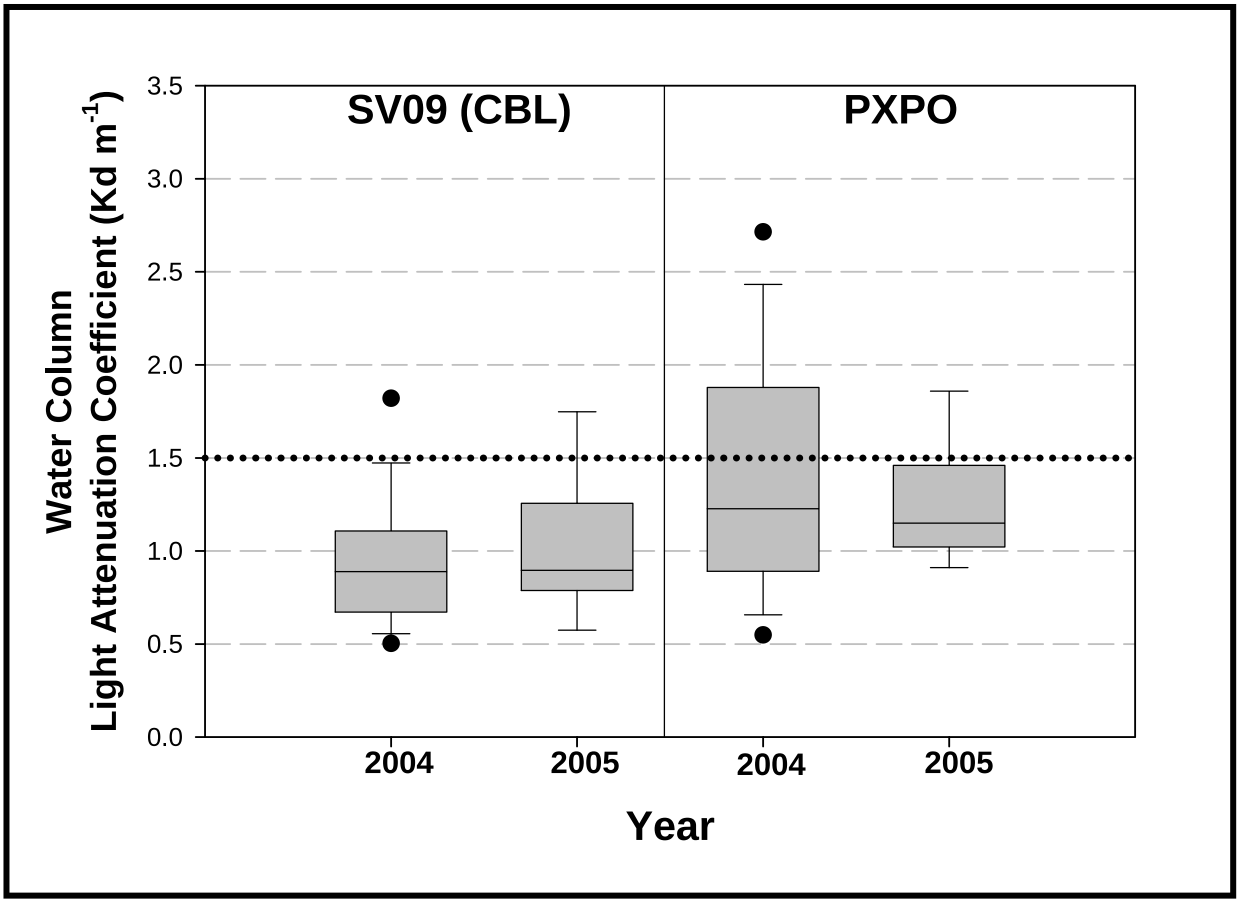

Figure 6-5. Patuxent River light attenuation coefficient (Kd) from March through November 2004 and 2005. ***Box ends represent 25th and 75th percentiles, lines represent median values, whiskers are 10th and 90th percentiles and dots are 5th and 95th percentiles. Dotted line represents mesohaline SAV habitat criteria.***

Note that 2005 was a relatively dry year; Patuxent River annual average river flow at Bowie, MD was around 12 m^3 sec^{-1} (see Chapter 2.0 in this report).

6.3.2 Epiphyte Fouling

The temporal patterns of epiphyte fouling in 2005 were similar to those seen in previous years, with rapidly increasing fouling rates as water temperatures exceed 20°C in the spring (Fig. 6-6). Summer and fall dry mass accumulation rates were high at both stations, averaging over 4 mg cm^{-2} week^{-1} during the summer at CBL(SV09) and just under 2 mg cm^{-2} week^{-1} at PXPO. Despite lower than normal river flow (and associated inputs of nutrients and sediments) in 2005, Patuxent River dry mass fouling rates were higher than those found in 2003 (high flow) and 2004 (average flow) during summer and fall. At CBL summer and fall accumulations showed a strong trend of increasing dry mass fouling since 2003. This may be in part due to a change in DIN supply sources to the mesohaline estuary. Testa (2006) found that from 1985 to 1993 most of the time there was a net transport of DIN from the Patuxent River to the mainstem of the Chesapeake Bay. From 1993 through 2004, 20% of the DIN inputs into the mesohaline Patuxent were found to come from the Chesapeake Bay and most of this transport occurred during the summer months. This source could be providing DIN to epiphytes at the CBL site and then later available to those at the PXPO site as bay water moves father up river from the mouth during a dry summer.

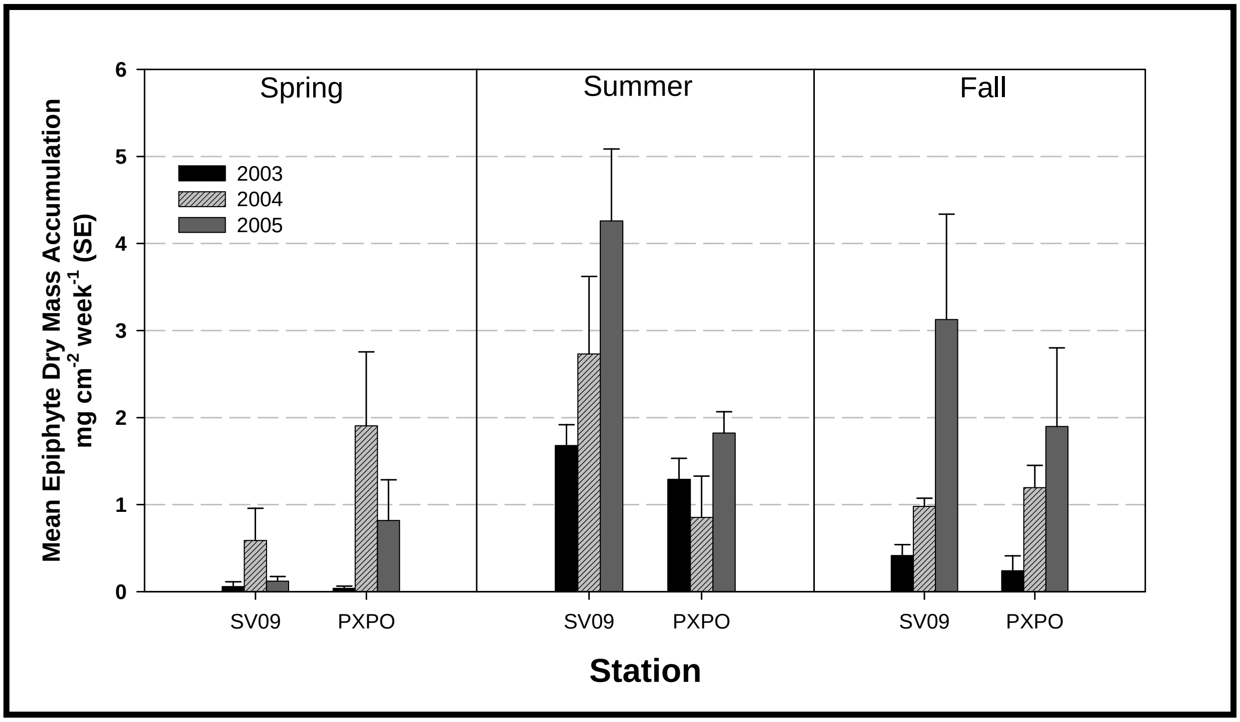

Figure 6-6. Seasonal mean epiphyte dry mass accumulation rates at DNR Patuxent River stations SV09 (CBL) and PXPO (Pin Oak) in 2003, 2004 and 2005.

Epiphyte total chlorophyll-*a* accumulation rates continued to show a strong link to nutrient availability (Figure 6-7). Summer rates were high averaging over 4.5 µg cm^{-2} week^{-1} at CBL and over 2.5 µg cm^{-2} week^{-1} at PXPO. As seen previously, the CBL station had higher summer and fall rates than the PXPO station.

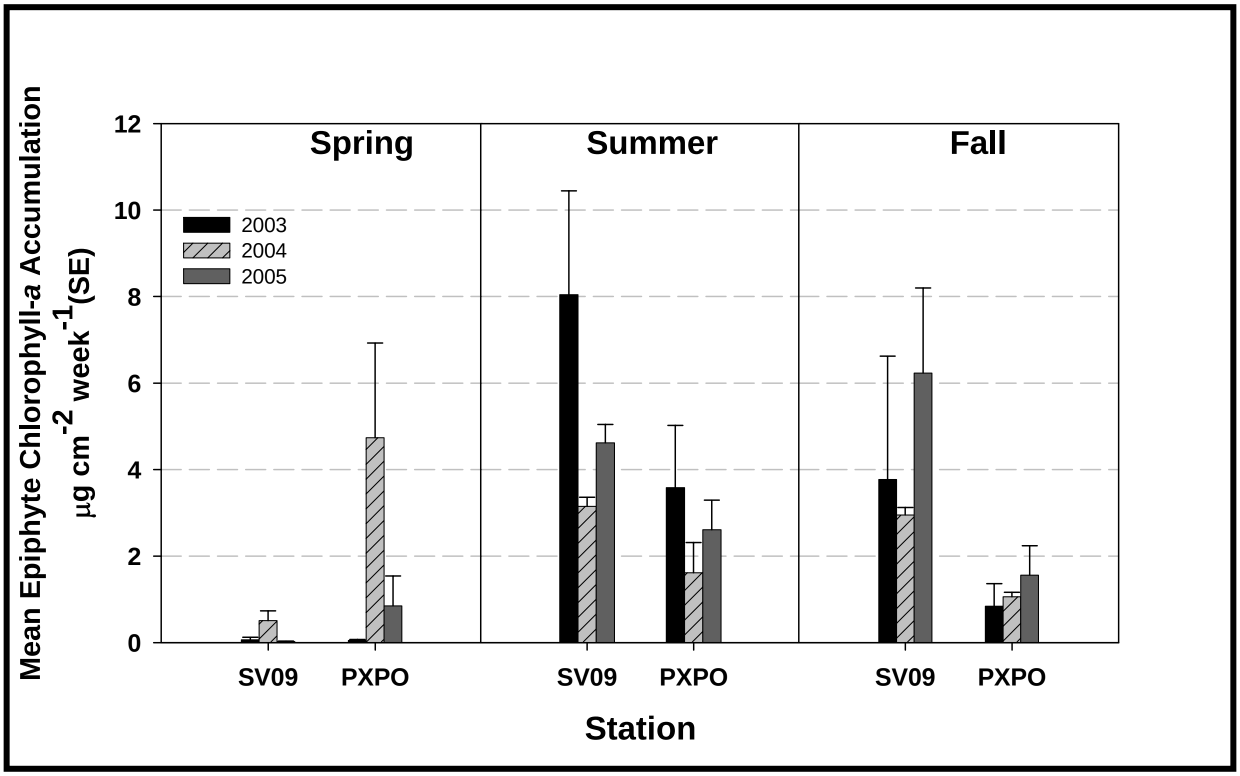

Figure 6-7. Seasonal mean epiphyte total chlorophyll-*a* accumulation rates at DNR Patuxent River stations SV09 (CBL) and PXPO (Pin Oak) in 2003, 2004 and 2005.

6.4 Discussion

The long term record in both water clarity and epiphyte fouling at Pin Oak and CBL reflect an ecosystem that responds dramatically to changes in nutrient loading rates and probably other input factors as well. From 1998 to 2005, median water clarity or PLW (calculated from the blocked sampling design) has varied dramatically. For example, in 2002, one of the driest years on record, median PLW at CBL was 48%. In contrast, in 1998, during a slightly higher than average flow year, median PLW at CBL was 26% (Fig X-5). Similar patterns were seen at Pin Oak with median PLW ranging from 39% in 2002 to 14% in 2004 and back up to 30% in 2005. Moreover, median epiphyte fouling rates have also varied substantially between years. When epiphyte fouling and water clarity are converted to PLL values, available light has also varied dramatically among years. At CBL, median PLL values have ranged from 25% in 2003 (a very high flow year), to 4% in 1998 (Fig 6-8). While at Pin Oak, median PLL values ranged from 22% in 2002, to 4% in 1998. Throughout this record, median PLL values appear to fluctuate around the recommended minimum PLL value of 15%, where in some years water quality conditions (plus fouling) appear adequate for SAV survival, and in others extremely poor. In 2005 (a dry year) PLW was high at both CBL (42%) and Pin Oak (30%), while light reaching the leaf surface was low (~8%) and substantially lower than the recommended 15% minimum.

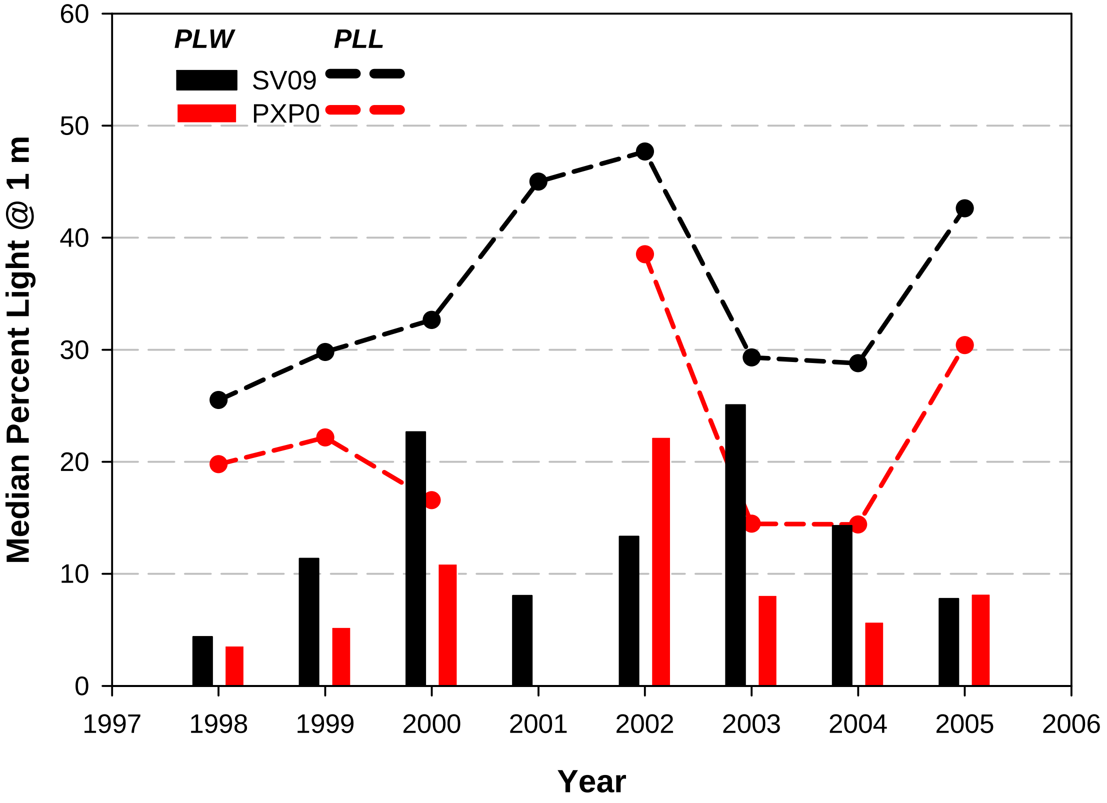

Figure 6-8. Median percent light reaching to 1 m depth (PLW) and to the leaf surface (PLL) at long-term stations SV09 (CBL) and PXPO (Pin Oak) in the lower Patuxent River Estuary in 2005.

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Nutrient Budgets and Management Actions in the Patuxent River Estuary, Maryland

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Introduction

During the past several decades global use of phosphorus (P) and nitrogen (N) has increased at an alarming rate and is expected to further accelerate in some parts of the world. The quantitative extent of nutrient production **(Vitousek et al. 1997)** and use has been determined for many areas of the globe **(e.g., Zheng et al. 2002; van Egmond et al. 2002)** and estimates are now available concerning the magnitude of nutrient discharges to estuarine and coastal ecosystems at global **(Kroeze and Seitzinger 1998)**, national **(Howarth et al. 2002)** and regional scales **(Van Breemen et al. 2002**). The detrimental ecological effects of nutrient enrichment have also been examined for a variety of coastal ecosystems (**Carpenter et al. 1998; Conley 2000; Rabalais 2002).** A report by the **National Research Council (2000)** found nutrient over-enrichment to be the greatest pollution threat faced by coastal marine environments. A NOAA assessment concluded that some 40% of coastal waters of the USA exhibited advanced indications of nutrient stress (**Bricker et al. 1999**). While there is a rapidly accumulating body of knowledge concerning nutrients in estuarine and coastal marine waters, most of this information tends to be focused on particular issues rather than integrated at the ecosystem level where the relative importance of many processes can be compared, evaluated, better understood and used in management desisions.

A decade ago we used whole-system nutrient budgets as a quantitative framework to examine N and P in the nutrient-enriched Patuxent River estuary, a major tributary of Chesapeake Bay. Our goal was to examine the magnitude of nutrient sources, internal nutrient storages and losses and nutrient export from the estuary (**Boynton et al. 1995).** Results indicated that the Patuxent had moderate and high N and P loads, respectively, compared to other coastal and estuarine systems. Further, we found that relatively little N (~25%) and virtually no P passed out the mouth of the estuary and most of the N export was in dissolved or particulate organic forms rather than as compounds directly available to plant communities. Denitrification in sub-tidal sediments and long-term sediment burial of particulate N and P were important internal loss terms, the former a common feature of many estuaries but the later important only in sediment-rich coastal plain ecosystems such as the Patuxent (**Nixon et al. 1996; Boynton and Kemp 2005**).

Some portions of the budget were better evaluated than others and several potentially important items were either neglected, because little or no data existed, or were entirely excluded because our biases and conceptual model of how things worked at the time did not include these processes. For example, we used input data from only two relatively dry years; there was no assessment of interannual variability because sufficient data were not available. The entire tidal estuary (e.g., tidal fresh, oligohaline and mesohaline regions) was treated as a single unit so there was no spatial resolution. The budgets also considered only total nitrogen and total phosphorus, nutrient exchanges with the Chesapeake Bay were estimated by difference (i.e., land plus atmospheric inputs minus internal losses), and the extensive tidal marshes of the Patuxent were considered to be neutral with regard to nutrient processes.

In the intervening years several things have led us to re-examine nutrient budgets for this estuary. First, there is now a substantial time-series of nutrient inputs from point, diffuse and atmospheric sources and this record includes wet, average and dry years. Associated with this input record are measurements of water column nutrient stocks, phytoplankton primary production and biomass, zooplankton and benthic invertebrate biomass and sediment nutrient releases. Many of these measurements were made at monthly or finer time scales. Seasonal, as well as interannual, variability can now be examined. Second, several new data sets have been developed; burial rates of N and P in sub-tidal areas and intertidal marshes have been estimated **(Merrill 1999; Greene 2005a**) and denitrification rates have been measured in marsh and sub-tidal estuarine sediments using a more reliable technique (**Kana et al. 1994, 1998**). Third, the net flux of N and P between the oligohaline and mesohaline portions of the estuary and at the junction of the Patuxent with the Chesapeake Bay have been estimated using a box-model (**Hagy et al. 2000**) thus making it possible to have an estuarine nutrient budget with independent measurements for all major input and output terms (**Nixon et al. 1996**). Finally, during a decade long period, a nutrient management plan, focused on point source nutrient reductions, was implemented in the basin. During the mid-1980's phosphorus was removed at all major sewage treatment plants and by 1993 nitrogen was also being removed, only during warm seasons, at all the major treatment plants (**D'Elia et al. 2003**). Thus, this estuary was subjected to a major, system level management action.

The overall objective of this work is to produce a more thoroughly evaluated budget for N and P in this estuarine system. We have the relatively rare opportunity to assess how well we did the first time around. We also have the opportunity to examine issues related to interannual variability in nutrient inputs to an estuarine system and the manner in which estuarine processes respond to these variations in inputs. Finally, we can examine the effects of major management actions on the N and P budgets of a large coastal plain estuary.

Description of the Patuxent Basin and Estuary

The Patuxent River basin encompasses 2264 km^2 of land, 133 km^2 of tidal waters and 29 km^2 of tidal marshes (**Table 1; Fig. 1**). The Patuxent ranks sixth in drainage basin size, sixth in estuarine volume and seventh in freshwater inflow among the tributaries of the Chesapeake system (**Cronin and Pritchard 1975**). While it is far smaller than several other tributaries, it is still among the largest of the 60 tributaries that are part of the Chesapeake Bay complex and it is among the better known and studied because of a long history of management debate, court cases and eventual management actions aimed at water quality and habitat restoration (**Malone et al. 1993**; **D'Elia et al. 2003; Kemp et al. 2005**).

Several large land use changes occurred in this basin during the 370 years since European settlement and these are summarized here because they played a prominent role in the current nutrient ecology of the estuary. During the late 1600's, land use changes began in the Patuxent basin to support agricultural activities, especially tobacco production. Until the mid-1700's, traditional "hill and hoe" type agriculture remained dominant, a form of farming that was characterized by low erosion rates, retention of soil fertility and rotation between short production periods (6-8 years) followed by long (20 years) fallow periods (**Walsh 2001**). However, after 1780 agricultural practices shifted from traditional methods to newer "high farming" techniques developed in Europe and embraced by many large landowners in the United States. Land was plowed deeper, stumps and roots removed, fallow periods reduced, marginal lands brought into production and plowing mainly directed down contours, rather than across, to ease the strain on plow animals (**Walsh 2001**). By the early 1800's some 40% of Southern Maryland land was cleared and by the late 1800's up to 80% of the land had been cleared (**Cooper 1995**). **Earle and Hoffman (2001**) vividly described agricultural changes in the Patuxent basin and the huge effects these had on land fertility, drainage patterns, rural economics and soil erosion rates.

Direct measurements of ecological conditions in the Patuxent watershed and estuary during these early periods do not exist, but other sources provide useful information. One of the earliest observations concerns filling of tidal river channels with soils eroded from surrounding lands associated with changes in farming practices. As early as 1780 some of the small, upper estuary ports of the Chesapeake had shoaled to the point where commercial vessels could not operate. **Middleton (1953**) lists Mattawoman Creek and Port Tobacco on the Potomac River, Elkridge on the Patapsco and Upper Marlboro on the Patuxent as among those affected. These ports had water depths of about 6m at settlement but these were reduced to less than 1 m by the late 1700's. Until 1815 a customs office operated at the Port of Queenstown on the Patuxent (river km 79; adjacent to the present town of Upper Marlboro, MD) where ships of 300 tons and drafts of 3.5 m came to trade. During the War of 1812, British war ships operated in the Patuxent as far upstream as the current town of Nottingham (river km 64; **Khan and Brush, 1994**) and until the 1730's barges operated 32 km upstream of Queenstown in support of an iron works (Donald Shomette, pers comm.). Since 1850 forest re-growth was a major ecological feature of the basin, a pattern that persisted until about 1985, when forested lands again started to decline as land was converted to urban and residential uses.

We also have limited descriptions of water quality from a century before direct measurements were initiated. Mr. J. Hungerford, a Baltimore lawyer, owned a plantation that bordered the lower Patuxent estuary. Escaping from a cholera epidemic in Baltimore during summer 1832, Hungerford spent time at the plantation and published a book that contained the following descriptions of the mesohaline estuary (**Hungerford 1859**):

"Of all the bright rivers that flow into it (Chesapeake Bay) there is not one which excels the Clearwater (Patuxent) in the purity of its waters"

and

"So transparent are its waters that far out from shore you may see, in the openings of the sea-weed forest, on its bottom the flashing sides of the finny tribes as they glide over the pearly sands"

While such descriptions are qualitative, the message is evident; the estuary was clearer than it has been in recent decades (**Stankelis et al 2003**).

Two paleoecological studies have also been conducted in the Patuxent and these provide more quantitative indications of past ecological conditions. **Brush and Davis (1984**) examined sediment cores collected from the tidal-fresh, oligohaline and mesohaline portions of the estuary and concluded there was little compositional change in diatom and macrophyte community composition for 300-1600 years prior to European settlement. During the post-settlement period, when land was being rapidly cleared, turbidity-intolerant diatom and macrophyte species disappeared from the upper portions of the estuary, but similar changes were not as evident in mesohaline areas. However, following increased fertilizer use and sewage treatment plant discharges, submerged macrophyte communities also disappeared from the mesohaline portion of the estuary during the late 1960's (**Stankelis et al. 2003**).

In a more recent study, **Khan and Brush (1994**) obtained several cores from the tidal-fresh estuary and adjacent marshes (river km 73). Analyses of these cores indicated that the estuary in this region was deep enough for ocean-going vessels during the 1600's but began filling following initial land clearance. Erosion rates were very high during the mid to late 1800's (7-8 times the pre-settlement rates), during the period 1890-1910 and again during rapid urbanization of the upper basin (1960-1980). An important conclusion from this work was that the marsh edges adjacent to the tidal river were only about 100 years old. Supporting this conclusion, **Flemer et al (1971**) earlier examined US Geological Survey and Maryland Geological Survey maps of the upper Patuxent from 1904, 1938 and 1949 and found a high degree of consistency in the areal extent of marshes (~19 km^2) during this half-century period. **McCormick and Somes (1982**) reported very similar areas of tidal wetlands for more recent times. Thus, these marshes appear to have been an extension of the channel filling processes that occurred during the previous two centuries. We have emphasized at some length land use and sedimentation patterns in this estuary because tidal marshes and abundant supplies of fine-grained sediments play central roles in the contemporary nutrient dynamics of this estuary.

Human population in the Patuxent basin was about 30,000 (13 people km^{-2}) in 1900. The basin remained very rural until about 1960 when rapid population growth began, a trend that continues to the present (536,000; 235 people km^{-2}; **Table 1**). During a recent 10 year period (1985-1995) population increased by 36, 14 and 50% in the upper, mid and lower basins, respectively. Population density in 1995 was highest in the upper basin (356 people km $^{-2}$) and less than half that in the mid (154 people km $^{-2}$) and lower (157 people km $^{-2}$) basins. Population density in mid-Atlantic basins averaged 317 people km $^{-2}$, very similar to the upper portion of the Patuxent basin, but much higher than the mid and lower basins (**Basta et al. 1990**).

The dominant land use in the Patuxent basin remains forested lands (44%) and the percentage of forested lands decreases from the lower to upper basin. Urban and agricultural lands occupy about the same proportions in the upper and middle sub-basins (20-30%) while agricultural lands represent a smaller proportion of land use in the lower basin. Recent land use assessments have indicated that forested and agricultural lands are currently decreasing and are being converted mainly to residential and urban uses (**Costanza et al. 1995**).

The Patuxent River and estuary are about 170 km in total length and the lower 95 km are tidal (**Fig. 1**). The upper portion of the tidal estuary (rkm 40 -95) is narrow (50 – 300m), very turbid (Kd =3.0), vertically well-mixed with a tidal range of 0.5 - 1.0m and average depth of 1.1 m. In addition, this portion of the estuary is flanked by extensive tidal freshwater and salt marshes with ratios of marsh area to river distance ranging from 0.4 to 0.8 km^2 km^{-1} of river. The lower estuary (rkm 40 to mouth at Chesapeake Bay) is much wider (1 – 5 km), deeper (z = 5.4 m), clearer (Kd = 0.9) and seasonally stratified.

Conceptual Framework for Nutrient Budgets

In an earlier evaluation of nutrients for the Patuxent River estuary, a conceptual model was used to guide development of N and P budgets (**Boynton et al. 1995).** A more detailed conceptual model was developed for this evaluation but still represents a compromise between current understanding of major inputs, exports, storages, internal losses and cycling of N and P and the temporal and spatial availability of data with which to evaluate model terms (Fig. 2).

The drainage basin was treated as three distinct units (upper, middle and lower basins), with the upper basin draining into the upper estuary but having no estuarine waters within that unit of the model. The estuarine area of the basin was divided into upper and lower portions corresponding to the tidal fresh/oligohaline and mesohaline zones, respectively (**Fig. 1**). This model considers four classes of nutrient inputs, five loss terms for N and three for P, eight storage categories, three nutrient cycling pathways and two net nutrient transport terms.

The four classes of nutrient inputs, shown along the left and top of the diagram, include point, diffuse, septic and atmospheric sources. The atmospheric term only includes deposition of N and P to surface waters of the upper and lower estuary; atmospheric deposition of N and P to the watershed is included in the diffuse source terms. Point sources were all municipal sewage discharges. Diffuse sources were estimated at the head of tide (junction of upper and middle basin) based on extensive monitoring of river flow and nutrient concentrations; diffuse sources from the middle and lower basins were estimated using a land-use model. Septic sources were estimated separately based on population living in non-sewered homes. Nitrogen fixation was not directly evaluated in this budget but was probably a small source, as seems to be the case in most nutrient-rich, temperate zone estuarine systems (**Howarth et al. 1988**).

Loss terms in both upper and lower estuarine segments include burial of N and P in sub-tidal and tidal marsh sediments, denitrification in sub-tidal and marsh sediments, fisheries harvests (recreational and commercial yields) and net transport of N and P at the downstream boundary of the two estuarine segments. We recognize that the fisheries harvest term is incomplete; this term should include accumulation of N and P in fish that migrate into the estuary when individuals are small, grow rapidly during summer and then migrate from the system in the fall. However, satisfactory estimates of fish stocks and migrations were not available to attempt this calculation.

Major nutrient pools and several nutrient cycling processes were included in this analysis to allow estimates of turnover times and evaluation of the relative importance of "new" versus "recycled" nutrients. The evaluation of nutrient cycling terms is not complete because activities of water column bacteria, microzooplankton and soft-bodied zooplankton were not included, again because data were not available.

The conceptual model of the nutrient budget can also be expressed as differential equations for TN and TP as follows;

$$dTN/dt_{upper} = (I_{up} + I_{ud} + I_{ma} + I_{mp} + I_{md} + I_{ms}) - (L_{umb} + L_{umdn} + L_{ub} + L_{udn} + L_{uf}) - T_{ul}$$

$$dTN/dt_{lower} = T_{ul} + (I_{la} + I_{lp} + I_{ld} + I_{ls}) - (L_{lmb} + L_{lmdn} + L_{lb} + L_{ldn} + L_{lf}) - T_{lb}$$

$$dTP/dt_{upper} = (I_{up} + I_{ud} + I_{ma} + I_{mp} + I_{md}) - (L_{umb} + L_{ub} + L_{uf}) - T_{ul}$$
$$dTP/dt_{lower} = T_{ul} + (I_{la} + I_{lp} + I_{ld}) - (L_{lmb} + L_{lb} + L_{lf}) - T_{lb}$$

where: I's are input terms; L's are loss terms and T's are transport terms. The specific input, loss and transport terms are defined in **Figure 2**. In this analysis dTN/dt and dTP/dt were assumed to equal zero when averaged over several years.

Data Sources, Methods, and Computations

Nutrient Sources

Inputs of N and P included atmospheric deposition directly to surface waters of the estuary, point, diffuse and septic sources. Input data, in most cases, were available on a monthly basis from 1985 – 2000. In some instances the input record ended in 1997.

Atmospheric Deposition: Estimates of wet nitrogen loading to the surface waters of the estuary utilized data collected at the Wye, MD sample site (38^{o} 54' 47", 76^{o} 09' 09") of the National Atmospheric Deposition Program (**NADP 2001**). NADP reported monthly volume weighted mean concentrations of NH_4 and NO_3 and monthly total precipitation (cm). Concentrations of organic nitrogen in rainfall collected at two locations in the Chesapeake Bay region ranged from an average of 9.1 µM to 21 µM (**Scudlark et al. 1998; Jordan et al. 1995**). Insufficient data were available to compute seasonal deposition estimates; annual average concentration and average rainfall (~100 cm) were used to produce annual wet fall organic N. Estimates of HNO_3/NO_3 dry deposition were from the 1993-1997 Wye, MD AirMoNs dry study (**NADP 2001**). These data were modified in two ways. First, the HNO_3 deposition velocity over soil was reduced by a factor of three to represent over-water deposition velocity. This modification resulted in over-water deposition velocity that was similar to those reported by **Valigura (1995**). Second, the original data were reported for one to three week intervals. These data were linearly interpolated to daily loads and then summed to monthly loads. Ammonia dry fluxes were based on data collected locally between March, 1997 and May, 1999. Generally there were 1 to 3 observations per month (**Larsen et al. 2001**). Atmospheric deposition of P is not nearly as important as it is for N. Accordingly, we put less effort into making estimates and it also appears that there are fewer estimates to consider. In the previous nutrient budget P inputs from the atmosphere were estimated to be 1.3 and 5.3 mg P m-2 month $^{-1}$, for inorganic and total P, respectively (**Boynton et al. 1995**) and these were based on estimates reported by **Smullen et al.(1982) and Wies and O'Melia (1989). Hu et al. (1998**) reported P concentrations in rainwater collected from Long Island Sound to range from below detection to 43 ug l^{-1}. The latter value is comparable to those reported by **Smullen et al (1982**) and we used the older values.

Point Sources: Estimates of point source N and P inputs were obtained from the **Chesapeake Bay Program (2001)** and details concerning these data are contained in **Wiedeman and Cosgrove (1998**). In brief, all major point source discharges to the Patuxent were from municipal sewage treatment plants. Of the 34 plants discharging to the Patuxent, ten had daily discharges in excess of 1 million gallons per day (3800 m^3 d^{-1}) and were classified as major discharges. These discharges represented 97.2% of the total point source flow. Nine of the major plants were located above the head of tide (HoT) and one, the largest, was located just below HoT. Monthly data were available from 1985 – 1999 and included flow (m^3 s^{-1}) and loads (kg d^{-1}) of ammonium, nitrite, nitrate, total nitrogen, dissolved inorganic P and total P.

Diffuse Sources: Diffuse source loads of N (ammonium, nitrite, nitrate, organic nitrogen and total nitrogen), P (dissolved inorganic phosphorus, organic phosphorus and total phosphorus) and total suspended sediments (TSS) were estimated by the Chesapeake Bay Program using Hydrologic Simulation Program-Fortran (FSPF), a widely used watershed model. The simulation time-step in the model was hourly but data used in this analysis were summed to monthly time intervals and covered the period 1985-1997. Details concerning the development and current configuration of this model are provided in a series of technical papers and reports (e.g., **Donigian et al. 1994; Linker et al 1996; Linker et al 1999; Linker et al 2001; Shenk and Linker 2001**). In brief, HSPF is a continuous, physically-based, lumped parameter model that simulates hydrology, sediments and nutrients (or other pollutants) in soils and streams. The version of the model used by the Chesapeake Bay Program has nine different land-uses, including conventional-tilled cropland, conservation-tilled cropland, cropland in hay, pasture, pervious urban land, impervious urban land, mixed open space, forest and animal waste areas. Each land use has its own unit model which is simulated as a single acre unit and the results multiplied by the number of acres of that type of land use draining into a specific river segment. In the case of the Patuxent, diffuse source loads were estimated for three basin segments including: 1) the basin above HoT; 2) the coastal plain portion between the head of tide and Benedict, MD, an area that includes the upper estuary and almost all of the tidal marshes; 3) the smaller lower basin which surrounds the main mesohaline portion of the estuary. The USGS has maintained a flow and water quality monitoring station at the head of tide since 1978 (**Langland et al. 2001**). While the watershed model produced load estimates for the upper basin, we chose to use the USGS estimates because they were a more direct estimate of loads. Finally, nutrients derived from septic systems were not included in the watershed model. Septic system derived P was considered to be negligible. Nitrogen was computed based on the fraction of the population in the middle and lower basin served by septic systems, the average N excreted per person and the amount of N that actually reaches a stream segment (estimated at 40%; Shenk, pers comm.; **Maizel et al. 1997**).

Nutrient Transport between Estuarine Zones and with Chesapeake Bay

Physical exchanges of TN and TP between the upper and lower estuary, and between the lower estuary and Chesapeake Bay, were computed using a salt-and-water balance model (**Hagy et al. 2000).** This model computes advective and dispersive transport of water and salt from a system of equations describing continuity of each for defined regions of the estuary. Assuming that the dissolved and suspended particulate N and P are transported in the same manner as salt, the fluxes of N and P can be computed as the products of physical transport and corresponding constituent concentrations (**Hagy 1996**). Physical exchange between the tidal fresh river and the upper estuary is dominated by seaward advection, but also includes a diffusive exchange flux. Thus, the net flux from the river to the upper estuary can be computed as

$$Q_r c_0 - E_{1,0}\left(c_1 - c_0\right)$$

where Q_r is the freshwater input from the tidal fresh river to the upper estuary, $E_{1,0}$ is the diffusive exchange between the upper estuary and the tidal fresh river, and c_0 and c_1 are the concentrations of N or P in the tidal fresh river and upper estuary, respectively. An identical advection and diffusion equation was applied to exchange between the upper estuary and lower estuary (**Hagy et al. 2000**). Two-layer gravitational circulation dominates the net horizontal transport within the lower estuary and between the lower estuary and Chesapeake Bay (**Hagy et al. 2000**). Therefore, the net exchange between Patuxent River and Chesapeake Bay was computed as the difference between the landward and seaward advective transport. This is

$$Q_6 c_6 - Q'_{cb} c'_{cb}$$

where Q_6 and Q'_{cb} are the rates of advection in the surface layer from the lower Patuxent River into Chesapeake Bay and in the bottom layer from Chesapeake Bay into the river. The values c_6 and c'_{cb} are the concentrations of N and P associated with advecting water.

The box model and resulting N and P fluxes were computed by month for the composite average years within the pre-BNR (1985-1990) and post-BNR (1993-1999) periods. Seasonal and annual average transport was computed from the monthly means.

Internal Storages of N and P

There were four categories of internal N and P storages evaluated in this budget and these included water column (dissolved and particulate), surficial sediments (particulate in the surface 1 cm of sediments), macrobenthic infauna and zooplankton. In each case estimates were made for the upper and lower estuary. Seasonal estimates were also made for all catogories except surficial sediments where there were not enough measurements to justify such an estimate. In addition, seasonal estimates were further categorized into pre and post-BNR periods for water column nutrient and zooplankton stocks; limited data precluded making such estimates for sediment and macroinfaunal N and P storages.

> <u>Water column nutrients:</u> Data were obtained from the **Chesapeake Bay Water Quality Monitoring Program (2001**) and consisted of vertical profiles of dissolved and particulate N and P compounds (NO_3, NO_2, NH_4, DON, PN, PO_4, DOP, PP) collected 16-20 times per year from 1985 –2000 at 13 locations along the main axis of the estuary. Average volume-weighted concentrations for the

upper and lower estuary were obtained using an interpolation algorithm developed by **Hagy (1996**). All subsequent seasonal and pre and post-BNR averaging was completed using the volume-weighted values.

Sediments: Storage of particulate N and particulate P in the surface 1 cm of sediments was based on samples collected using a box corer (**Boynton and Rohland 2001**) and from sources listed in **Boynton et al (1995**). Values of %N and %P from the upper and lower estuary were converted to mass per area using measured sediment dry weight per volume values.

Mesozooplankton: The N and P storage associated with mesozooplankton biomass was estimated using data collected by the **Chesapeake Bay Zooplankton Monitoring Program (2001).** Samples were collected via stepped oblique tows using 202 um mesh paired bongo nets. Samples were mainly collected monthly between 1985 and 1999 at a site in the tidal fresh portion of the upper estuary and at a site in the middle of the mesohaline estuary. Numerical abundances were converted to biomass using conversion factors provided in **Chesapeake Bay Zooplankton Monitoring Program (2001) and Jorgensen et al (1991**). Conversion of dry weight biomass to N and P were based on conversion factors given in **Walve and Larsson (1999**).

Macrofauna: The N and P storage associated with macrobenthic biomass was estimated using data collected by the **Chesapeake Bay Benthic Monitoring Program (2001)**. Samples were collected at sites spaced throughout the estuary. Several sampling devises were used depending on water depth and bottom substrate but all samples were sieved through 0.5 mm screening and preserved in buffered formalin. Mean biomass (ash-free dry weight; AFDW) was computed by month and seasonal averages computed from the monthly means. Because there was a great deal less benthic sampling during the post-BNR period we did not compute pre and post-BNR means. Thus, seasonal and annual means include the period 1985-1999. We assumed that ash-free dry weight was 50% carbon. Percent N and P of AFDW were estimated to be 15% and 0.62%, respectively.

Water Column Uptake, Zooplankton Excretion and Sediment Recycling of N and P

There were three categories of N and P uptake and recycling evaluated in this budget and these included water column uptake of N and P by phytoplankton, net sediment releases of N and P and mesozooplankton excretion of N and P. In each case seasonal and annual (pre and post-BNR) estimates were made for the upper and lower estuary.

Mesozooplankton: Abundances were obtained from the **Chesapeake Bay Zooplankton Monitoring Program (2001)** for 1984-1999 from sampling stations located in tidal fresh and mesohaline portions of the estuary.

The sampling strategy changed during the course of the monitoring program from stratified tows to a single oblique tow. It was determined that there were no clear differences in the abundance patterns based on sampling procedures. Zooplankton abundances were enumerated to species and were separated by life stage for some of the taxa. When life stages were present, average adundances were computed by life stage to account for differences in the sizes of the different life stages.

Nitrogen (NH_3) excretion rates were computed using the following equation (**Mauchline 1998**):

$$\log E = \left(-0.00941T + 0.8338\right)\log W + \left(0.02836T - 1.3665\right) \quad (1)$$

where E=excretion rate (µg NH_3-N copepod^{-1} hr^{-1}), W=mg dry weight copepod^{-1}, and T=water temperature (°C). Dry weights were obtained from literature sources (**Heinle 1966; Jorgensen et al 1991; Chesapeake Bay Zooplankton Monitoring Program 2001**). Monthly average water temperature for each station was computed from the Chesapeake Bay Water Quality Monitoring Program (2001).

Monthly mean abundances and NH_3 excretion rates were computed for the pre-BNR (1984-1990) and post-BNR years (1993-1999). In the post-BNR years, zooplankton abndance was not estimated for January and Feburary. Therefore, for the purposes of computing seasonal and annual means, the January and Feburary data for the pre-BNR years were used in the post-BNR years. Excretion rates per unit volume per hour were converted to areal rates using a mean depth of 2 m for the upper estuary and 5 m for the lower estuary and 24 hr day^{-1}.

<u>Sediment Recycling</u>: Data used to estimate N and P releases from sub-tidal estuarine sediments were obtained from **Boynton and Rohland (2001**) and from earlier work reported by **Boynton et al (1982a**). Most measurements of sediment nutrient fluxes were obtained from shipboard incubation of intact sediment cores; some values from the upper estuary were based on in-situ chamber measurements (**Boynton et al 1982a**). Sediment flux data were averaged by month and then used to estimate annual average fluxes for the upper and lower estuary. Data from December – March were limited for the upper estuary and not available for the lower estuary. Lower estuary sediment fluxes for N and P for those months were estimated to be zero. Because only summer data (June – September) had been routinely collected (1985-2000), only summer season pre and post-BNR values were computed for the upper and lower estuary.

<u>Phytoplankton uptake:</u> Nutrient uptake by phytoplankton was based on measured rates of primary production and Redfield stoichiometry. Primary production data were obtained from the **Chesapeake Bay Phytoplankton Monitoring Program (2001).** Rates were estimated using the C-14 technique with incubation (4 hr) in shipboard constant light incubators. Volumetric rates were converted to areal rates by assuming that the single measured volumetric rate was P_{max} and that production decreased in a linear fashion to the depth of 1% light. The euphotic depth was based on secchi disk measurements.

Extrapolation of hourly rates to daily rates was accomplished by multiplying hourly rates by 80% of the daylight hours at the time of measurement. Finally, N and P uptake were estimated by assuming Redfield proportions of 106:16:1 for C:N:P. Measurements at these sites were routinely made 10-16 times per year from 1986 – 1999. Upper and lower estuary N and P uptake rates were computed for seasonal and annual periods during both the pre and post-BNR periods.

Internal Losses of N and P

The data sources for internal losses of N and P consisted of a combination of new data collected in the Patuxent and other literature sources. Specifically, we depended on measurements of marsh nutrient burial from the work of Merrill (1999), Merrill and Cornwell (2000) and Greene (2005a). Marsh denitrification measurements were from Merrill (1999) and Greene (2005a). Subtidal N and P burial rates were estimated from new measurements of ^{210}Pb-based sedimentation rates from cores collected in 2000, and estuarine denitrification rates were from measurements also made in 2000.

Denitrification in Estuarine and Marsh Sediments: Subtidal denitrification was determined from flux cores using time courses of N_2 changes based on N_2:Ar ratio changes (Kana et al. 1994; Owens et al. submitted). At 6 sites in May and December of 2000, we examined fluxes in duplicate cores fitted with magnetic stirrers. Flux cores (7 cm inside diameter) were incubated at *in situ* temperatures for ~6 hours; samples were collected for dissolved gases using 7 mL ground glass tubes with Hg used as a preservative. Samples were analyzed using a membrane inlet mass spectrometer, with O_2 and N_2 ratios to Ar measured (i.e. Kana and Weiss 2004). The slope of the N_2 concentration versus time, minus that of control cores without sediments, was used to estimate denitrification rates. In the case of tidal freshwater marsh sediments, similar cores (10 cm inside diameter) were collected, flooded with ambient river water, and denitrification measured as with subtidal cores (Merrill 1999; Merrill and Cornwell 2000; Greene 2005a).

Burial in Estuarine and Marsh Sediments: Subtidal cores were collected using a Benthos gravity corer, extruded into 2 cm segments to 10 cm depth, 5 cm segments from 10-30 cm depth, and 10 cm segments to the bottom of the core (75-110 cm). The analysis of ^{210}Pb, total P and total N followed that of Cornwell et al. (1996). Sedimentation rates were calculated via regression of cumulative mass versus excess ^{210}Pb. Marsh cores were collected using a MacAuley or Russian peat corer to minimize compaction and nutrient burial calculations were similar to those of the subtidal cores (Merrill 1999). A total of 29 marsh cores were collected throughout the marsh ecosystem, including several transects from the marsh bank to the upland area. We grouped the nutrient burial rates on the basis of the vegetation community (Merrill and Cornwell 2000; Greene 2005a).

Results and Discussion

Nutrient Inputs

Inter-Annual Variability

We begin by examining TN, TP and DIN and DIP loads from all sources to this estuarine system on an annual time scale for a 13 year period (1985-1997). TN and DIN loading rates ranged from 4300 to 8600 kg N d^{-1} and 3200 to 5500 kg N d^{-1}, respectively, and averaged 6200 and 4300 kg N d^{-1} (**Fig. 3**). Annually averaged DIN loads were correlated with TN loads (r^2=0.71; p<0.01) and represented an average of 69 % of TN loads during the study period. TP and DIP loading rates ranged from 207 to 690 kg P d^{-1} and 113 to 414 kg P d^{-1}, respectively, and averaged 453 and 242 kg P d^{-1} during the same period (**Fig. 3**). DIP loads also closely tracked TP loads (r^2=0.92; p<0.01) and represented an average of 53 % of TP loads. Inter-annual range in loads, both total and inorganic, was about a factor of two for N and 3.5 for P. Similar levels of variability have been observed in other large basins of the Chesapeake Bay (**USGS 2004**). Such levels of inter-annual variability exceed the annual load reductions (~40%) that local, state and federal agencies are trying to achieve in this estuary.

Relationships to Regional Climate Conditions

A portion of the variability in nutrient loading rates was associated with variability in local weather conditions (**Fig 4**). Annual average river flow at the head of tide (HoT) ranged from 5.5 to 17.5 m^3 s^{-1} and averaged 10.3 m^3 s^{-1} during the 25 year period flow has been gauged at this site (1978-2003). On a seasonally averaged basis, river flows were generally highest during the winter and/or spring and considerably lower during summer and/or fall. However, during two drought years (1992 and 1995) river flow was low all year while during 1996 flow remained relatively high all year. During 1989 flow was lowest during the winter and highest during spring and summer, almost a complete reversal of the most common pattern.

Typically, N concentrations at HoT were highest during winter and spring (100-200 uM) coinciding with periods of highest flow and generally lower in summer and fall (25-75 uM). Thus, loads tend to be higher in wet years, especially when river flows are highest in winter or spring. **Hagy et al (1998**) reconstructed upper Patuxent River TN and TP loading rates at HoT for the period 1960-1997 and found a strong relationship between river flow and loads with the slope of the TN and TP relationships to flow being 180 kg N d^{-1}/m^3 s^{-1} and 65 kg P d^{-1}/m^3 s^{-1}, respectively. TN and TP loads for the entire basin exhibited the same general relationship although there was more scatter. Higher and lower loads were clearly associated with wetter and drier years, respectively.

Later in this analysis the impact of instituting biological nitrogen removal (BNR) during warm portions of the year at all major sewage treatment plants in the basin is examined. Upgrading plants to BNR was initiated in the early 1990's and was completed by 1993. In subsequent analyses the years 1985-1990 and 1993-1997 were considered to be from the pre and post-BNR periods, respectively. Four of the six pre-BNR years were relatively dry (average river flow = 8.8 m^3 s^{-1}) while during the post-BNR period wetter conditions prevailed for four of the five years (average river flow = 13.0 m^3 s^{-1}; **Fig. 4**).

To place the effect of inter-annual climate variability in perspective, loading rates of TN, TP, DIN, and DIP from all external sources were summed for each year and the years with the highest and lowest loading rates identified (**Table 2**). Results indicate both the importance of local climate variability and the impact of management actions on nutrient loading rates. Specifically, the lowest loads for all nutrient groups occurred during 1991, a dry year. Highest loads for all nutrient groups, except DIP, occurred during wet years (1989, 1993, and 1996). Highest DIP loads occurred during 1985, a relatively dry year, but this was the last year in this record before P was effectively removed from major sewage discharges throughout the basin. Thus, for this compound, management actions at sewage treatment plants were evident at the scale of whole estuary DIP inputs. However, the highest and lowest loading years for TN occurred after and before implementation of BNR, respectively, clearly indicating the importance of sources other than point sources in the TN budget at the scale of the whole estuary. Additionally, lowest TN and DIN loads were observed during 1991, prior to implementation of BNR. However, there was a clear reduction in both P and N loads from the upper basin (above HoT), where 9 of the 10 major sewerage treatment plants are located, after implementation of P and then N removal from discharges. Thus, at a sub-basin scale, load reductions in both nutrient groups were evident.

Loading Rates Relative to Other Estuarine Systems

In an earlier nutrient budget analysis **Boynton et al (1995)** assembled nutrient input data (TN and TP) for 18 estuarine sites. That effort was expanded and input data for 34 sites are shown in **Figure 5**. Annual loading rates ranged from 1.1 to 188 g N m^{-2} yr^{-1} and from 0.1 to 32 g P m^{-2} yr^{-1} or by factors of 170 and 320 for TN and TP, respectively. Of the 34 sites, 6 had TN loading rates in excess of 50 g N m^{-2} yr^{-1}, 15 had loads less than 10 g N m^{-2} $yr^{-1}$and 13 locations had loads between these extremes. Loads of both TN and TP to the Patuxent River estuary were moderate compared to other sites. Inspection of the multi-year data for the Patuxent River estuary provides a clear indication that many of the points shown on the diagram might be better represented as clouds of points, if such data were available. Multi-year TN and TP input data for whole estuaries are not very common so there remains uncertainty about the magnitude of inter-annual scales variability, but variability may be large. For example, wet and dry year input data were available for the Guadaloupe estuary and TN and TP loads varied by factors of 3.7 and 2.5, respectively. Similar values for the Patuxent River estuary were 2.0 and 2.6 for TN and TP, respectively. TN and TP loads to Kaneohe Bay were adjusted downward by factors of 2.0 and 4.5, respectively, due to management actions related to sewage diversions.

The bold line in **Figure 5** represents the Redfield ratio expressed on a weight basis (N: P = 7.2:1). In this selection of sites, N: P ratios of inputs ranged from 2 to 38. About a quarter of these locations (9 of 34) had load ratios that were considerably lower (<5.0) than the Redfield ratio while 50% (18 of 34) had ratios equal to or higher than 9.0. **Boynton et al (1995)** suggested that point source dominated systems would favor lower load ratios because of the abundance of P relative to N in sewage and the opposite in diffuse sources. However, it is clear that this is not always the case. For example, Himmerfjargen had a very high load ratio (38) even though point sources were the dominant nutrient sources because P (and not N) was removed from treatment plant effluent. A similar situation was also present in the Back and Potomac River estuaries where N: P ratios were elevated but point sources (with P removal) were a component of nutrient inputs.

It would be useful to be able to compare nutrient loading rates from different estuarine ecosystems and come to some conclusions regarding water quality and habitat conditions. In such a simple conceptual model, those systems with low inputs would have oligotrophic characteristics (e.g., seagrasses important, limited phytoplankton accumulations, absent or rare HABs, well-developed microphytobenthic and macroinfaunal communities) while those with the highest loads would have eutrophic characteristics (e.g., large phytoplankton biomass accumulations, HABs, hypoxia/anoxia, degraded benthic communities). To a limited extent this may be true. For example, those systems with very high nutrient loads (e.g., Tokyo Bay, Back River, W. Scheldt) have severe water quality problems while those with low loads (e.g., Maryland coastal bays, Buzzards Bay) have few symptoms of eutrophication. However, there are numerous exceptions and these indicate there are other important processes influencing trophic condition besides loading rate (**Vollenweider 1976; Wulff et al. 1990**). Loading rates to the Baltic Sea are relatively low (**Larsson et al. 1985**) but persistent stratification and very long water residence times produce large volumes of hypoxic/anoxic water. Conversely, TN loading rates to Mobile Bay and the Potomac River estuary are similar but only the Potomac has severe indications of eutrophication, possibly because of much greater depth, longer water residence time and seasonal stratification. However, the selection of estuaries presented here was based on availability of nutrient load data and is very diverse, including coastal waters, estuaries, fjords and lagoons. It might be argued that nutrient loads from more similar or localized groups of systems might be more prescriptive. **Nedwell et al (2002**) organized inorganic N and P loads to 93 estuaries of the United Kingdom and found several significant relationships between loads and biological responses in adjacent coastal waters. However, even in this relatively localized analysis there was substantial unresolved variability, again indicating influence of other factors.

Components of Nitrogen and Phosphorus Loads

Atmospheric Deposition

An annual time-series of total atmospheric nitrogen deposition was constructed for the years 1985-1999 (**NADP 2001**). In this time series TN was composed of wet deposition of NH_3 and NO_3, dry deposition of HNO_3 and NO_3, and net dry exchange of NH_3/NH_4 (**Fig. 6**). Atmospheric deposition ranged from about 575 to 1125 mg N m^{-2} yr^{-1} and was generally higher in wet years (e.g., 1989, 1994) than in dry years (e.g., 1985, 1987, 1992) but there were exceptions where dry or wet year deposition remained higher (e.g., 1987) or lower (e.g., 1998) than expected. Overall, TN inputs from atmospheric deposition varied by about a factor of two, in the same range as for TN loading from all sources. Monthly TN deposition rates ranged from about 30 to 120 mg N m^{-2} $month^{-1}$ and were higher during late spring and summer than during fall and winter (**Fig. 7**). This pattern is significant because the generally much larger diffuse source inputs are at a minimum during summer and fall. In addition, much of the atmospheric N deposition going directly to the surface waters of the estuary is in a chemical form directly available to phytoplankton (**Paerl 1997**). The dominant form of N deposition was $NH_x + NO_3$ in wet fall, comprising about 67% of the total followed by organic N (17%) and all measured forms of dry fall N (15%; **Table 3**).

Little information was available concerning atmospheric P deposition in this region, but indicated that loading rates were a small portion of total P inputs to the estuary on both seasonal and annual time scales.

As expected, direct N deposition to the surface waters of the estuary was largest in the lower estuary where estuarine surface area was also large and minor in the upper estuary. In the lower estuary annual loads of atmospheric deposition averaged about 360 kg N day^{-1} and were larger in spring and summer than in fall and winter. As we will show later, direct atmospheric deposition during summer was a significant source of N to the lower estuary.

The full contribution of atmospheric deposition of N to the estuary is greatly underestimated when only direct deposition to the surface waters is considered. However, this approach has the advantage of being readily and more directly estimated from a variety of concentration measurements and rainfall. However, regional assessments of nitrogen additions and losses from landscapes have become more common and some have focused on estimating the portion of N losses from landscapes coming from atmospheric deposition of N (**Howarth et al. 1996; Jaworski et al. 1997**). In the case of the Chesapeake Bay basin **Fisher and Oppenheimer (1991**) and more recently **Castro et al (2003**) estimated about 25% and 22%, respectively, of atmospheric N deposition to the landscape makes it to estuarine waters. No estimate is available for the Patuxent basin. However, if the most recent estimate of 22% is applied to the Patuxent basin, about 990 kg N m^{-2} day^{-1} would reach estuarine waters as a component of diffuse source loading. This turns out to be a substantial portion of the total diffuse source load.

Point Sources

Point sources of N and P were substantially reduced due to sewage treatment plant modifications, with first P removal (1986) and then seasonal N removal (1993). Point source loads of TP declined from about 250 kg P day $^{-1}$ before upgrades to about 50 kg day $^{-1}$ following upgrades (**Fig. 8**). TN sewage loads prior to seasonal N removal varied between 1200 – 1900 kg day $^{-1}$ and were reduced to annual averages of about 700 kg day $^{-1}$. During the post-BNR period TN loads were higher during winter (~900 – 1000 kg N day $^{-1}$) than during summer periods (500 – 600 kg N day $^{-1}$; **Fig 8**).

During the pre-BNR period N and P loads did not vary appreciably during the year as might be expected for sewage treatment plant operations having relatively constant daily inputs and discharges (**Table 4**). However, during the post-BNR period TN and DIN loads exhibited considerable seasonal change with summer and fall loads about 30% lower than winter and spring loads due to the higher N-removal efficiencies at higher temperatures. There were very small variations in P loads among seasons of the year.

One strong distinguishing feature of point source N and P loads concerns the distribution between dissolved inorganic and total N and P. For sewage N, 92% and 82% of the load was DIN during the pre and post-BNR periods, respectively. The remaining N was mainly dissolved organic nitrogen. Sewage P was 78% and 80% DIP during the pre and post-BNR periods, respectively. While point source N and P were not the single largest sources of N or P to the estuary, the fact that most was in chemical forms directly available to plant communities enhances the importance of this source.

Diffuse Sources

The substantial interannual variability in loading rates is largely the result of interannual changes in diffuse source inputs of N and P **(Fig. 3)**. For example, annual TN loads from the middle basin ranged from 760 to 3469 kg N day $^{-1}$ and averaged 1716 and 2659 kg N day $^{-1}$ for the pre and post-BNR periods, respectively. For the same region, P loads ranged from 37 to 415 kg P day $^{-1}$ and averaged 114 and 284 kg P day $^{-1}$ during the pre and post-BNR periods, respectively (**Fig. 9**). In general, higher and lower loads were associated with wet and dry years, respectively, although there was substantial variability not accounted for by climate conditions alone. Presumably, the time of year when flows were high or low, intensity of rain events, large storm events and changing land uses and practices all played a role in determining annual loads. In any case, diffuse source loads of N were the largest single source both before and after BNR implementation; diffuse sources of P were slightly smaller than point sources before P removal at point sources was implemented after 1985.

The proportion of diffuse source loads as DIN varied from 44 to 85% of TN and averaged 67%, well less than for point sources. The same ratio for P from diffuse sources was about 60%, again much less than point source P.

There was a consistent seasonal pattern of diffuse source inputs, as might be expected based on river flows which were generally highest during winter-spring and lowest during summer-fall. For example, TN loads at HoT averaged about 2300 kg N day $^{-1}$ during winter-spring and about 1450 kg N day^{-1} during summer-fall in the pre-BNR years. During the generally wetter post-BNR years these averages were 2700 kg N day^{-1} and 1200 kg N day $^{-1}$, for winter-spring and summer-fall, respectively. Thus, there is a substantial difference in the seasonality of nutrient inputs from this important source compared to direct atmospheric deposition and point sources.

Septic Sources

At the basin level, N and P estimated to come from septic systems was small (< 5% of total N inputs to the middle basin and < 2% of total N loads to the lower basin) and has not changed much during the pre and post-BNR periods (**Table 5**). However, in a few heavily developed residential areas adjacent to tidal creeks, septic system N appeared to be an important local source (**Barnes et al. 2004).** Septic system P was assumed to be effectively bound to sub-surface soils and not contribute to diffuse source P loads.

Input Summary

Annual average inputs of TN and TP from all external sources were compiled for the pre and post-BNR periods (**Fig. 10**) and several important findings emerged. First, improved treatment of point source discharges had a substantial effect on both N and P loads entering the estuary from the upper and middle basin. For example, TN and TP loads from point sources located in the upper basin decreased from 1577 to 744 kg N day $^{-1}$ and from 124 to 57 kg P day $^{-1}$, respectively. Smaller reductions were also observed in the middle basin where point sources of TN and TP decreased from 744 to 454 kg N day $^{-1}$ and from 60 to 50 kg P day $^{-1}$, respectively. Overall, point sources represented 37 % of TN and 46 % of TP inputs during the pre-BNR period and were reduced to 18 % of TN and 19 % of TP during the post-BNR period. Thus, due to the changes in sewage treatment plant operations, there were substantial changes in the relative importance of sources. Secondly, direct atmospheric deposition of N and P to the surface waters of the estuary were relatively small during the pre and post-BNR periods (TN~ 7%; TP~ 7-10%) as was TN derived from septic system drainage (~5%). The largest inputs of TN and TP were from diffuse sources during both the pre and post-BNR periods. TN and TP from diffuse sources represented 51% and 48% of total inputs during the pre-BNR period and 70% and 77% during the post-BNR period. The post-BNR period was wetter than the pre-BNR period and this is reflected in substantial increases in diffuse source loading during the latter period. In fact, total loading of TN and TP to the estuary was about 6% and 43% larger during the period following sewage treatment plant improvements, again emphasizing the importance of diffuse sources in this system.

Major Storages of N and P

Four N and P storages in the estuary were evaluated, including water column dissolved and particulate nutrient stocks, macrobenthic invertebrate and macrozooplankton biomass and surficial sediment stocks (**Table 6**). Detailed seasonal and spatial distributions of N and P concentrations in the water column have been described for this estuary elsewhere (**Mihursky and Boynton 1978; Kemp and Boynton 1984**). In brief, TN concentrations were higher in both the upper and lower estuary during winter-spring than summer-fall and were 20-30% higher in the upper than lower estuary during all seasons (**Table 7**). On an annual basis, about 50% of the TN in the water column was DIN, mostly nitrate, in the upper estuary while about 26% of TN was DIN, again mostly nitrate, in the lower estuary. There was a decrease in TN concentration in the upper estuary of about 30% between the pre and post-BNR periods and a much smaller decrease in TN concentration in the lower estuary (~7%). At the scale of the full estuary the average annual total mass of TN in the water column was about 580 and 520 x 10^3 kg N during the pre and post-BNR periods, respectively. There were also clear spatial and seasonal differences in P concentrations in the estuary. TP concentrations tended to be higher during summer-fall than during winter-spring and only about 20% higher in the upper estuary compared to the lower estuary. In addition, dissolved inorganic P (DIP) was a smaller fraction of TP than was the case for the ratio TN:DIN, comprising about 20% and 30% of TP in the upper and lower estuary, respectively. At the scale of the full estuary the total mass of TP in the water column was about 48 and 36 x 10^3 kg P during the pre and post-BNR periods, respectively, a decrease of about 25% following implementation of BNR technology (**Table 6**).

Monthly estimates of benthic invertebrate biomass ranged from 4 to 19 gAFDW m^{-2} in the upper estuary and from about 1 to 10 gAFDW m^{-2} in the lower estuary and averaged 12.5 and 4.2 gAFDW m^{-2}, respectively (**Table 8**). In both the upper and lower estuary biomass was highest during spring and lowest during fall and winter seasons. When these annual average biomass estimates were converted to N and P equivalents, there were 119 x 10^3 kg N and 5 x 10^3 kg P in the system associated with benthic animal biomass. This represented only about 4.4% and 0.7% of the N and P in the system (**Table 6**).

While clearly an important part of pelagic estuarine food webs, macrozooplankton contained a very small fraction of the N and P in the system. Average annual N and P in macrozooplankton stocks amounted to 4.9 x 10^3 kg N and 0.83 x 10^3 kg P or about 0.2 and 0.1% of the total N and P, respectively (**Table 6**).

Most of the N and even more of the P in this system were contained in the sediments (**Table 9**). We have somewhat arbitrarily used only the upper 2 cm of the sediment column in this analysis but we did this to include only the relatively recently deposited N and P. If a deeper sediment column were used, an even higher percentage of N and P would be associated with sediments. Average surface sediment N content averaged 0.35 and 0.31% of sediment dry weight in the upper and lower estuary, respectively, and sediment P content averaged 0.125 to 0.093 % in the same areas. About 75% of TN and about 93% of TP in the system were in sediments (**Table 6**). We did not have a time series of sediment composition data sufficient to consider either seasonal or pre and post-BNR changes these features.

One simple way of relating nutrient stocks to nutrient dynamics of the whole system is to compute turnover times for N and P stocks. If all nutrient storages are combined (**Table 6**) and divided by average annual inputs (**Fig. 3**), turnover times of about 1.2 and 4.2 years result for TN and TP, respectively. Thus, if we have considered storages correctly, especially the very large sediment storage, it appears that there is not a huge reservoir of nutrients in the system compared to new inputs of N and P. If we delete sediment storage of TN and TP from turnover computations, seasonal-scale turnover times result (0.3 years for both TN and TP). This observation is consistent with other nutrient-related measurements such as primary production rates, algal biomass accumulation, volumes of hypoxic/anoxic water and sediment-water nutrient and oxygen exchanges, all of which respond on seasonal or even shorter time scales to changes in nutrient delivery rates (**Boynton and Kemp 2000; Hagy et al. 2004; Kemp et al. 2005; Fisher et al. 2005**). Thus, it also seems reasonable to expect rapid responses of such processes as those indicated above to either increases or decreases in nutrient loading rates associated with continued development of the drainage basin and effective management actions, respectively.

One striking aspect of this evaluation of nutrient stocks is that most of the N and P in this moderately eutrophic estuary is contained in sediments and is detrital organic matter in the case of N and particulate inorganic material in the case of P. A very small fraction is in living biota. It seems likely that the fraction contained in living biota was once much higher for several reasons. First, it appears that benthic infaunal biomass has been substantially reduced from earlier levels. **D'Elia et al. (2003)** make reference to the substantial commercial fishery, especially for oysters and crabs, which once flourished in this estuary and is now largely absent. Compared to benthic biomass estimates assembled by **Herman et al. (1999),** Patuxent values were 2 to 3 times lower than those observed at similar levels of primary production in other estuarine systems. Second, **Stankelis et al. (2003**) assembled available data concerning seagrass communities in the Patuxent at present and as far back in time as the late 1930's. It is clear that seagrasses were a large feature of the Patuxent and represented a substantial storage of nutrients in living tissue. Old records from the **Academy of Natural Sciences of Philadelphia (1965-1975**) also indicated that epiphytic and benthic diatoms were a significant feature of the Patuxent but these autotrophs have largely been lost in recent decades. The status of fish stocks, both commercial and forage, are far less clear although long-term residents uniformly insist that fish were far more abundant prior to the 1970's. These observations suggest that the partitioning of N favored living as opposed to detrital storages prior to the estuary becoming eutrophic. If any of this is true, it would seem like these longer-lived N storages would represent a nutrient buffer, restricting nutrient recycling to rates below those associated with very rapid bacterial remineralization of labile substrates commonly observed under present conditions.

Nutrient Transport

Box models (**Hagy et al. 2000**) were constructed to compute monthly average physical transport of nitrate plus nitrite, ammonium, TN, DIP and TP for the pre and post-BNR periods. Nutrient transport was evaluated at two locations in the estuary. The first was at a location between the narrow, shallow, turbid and vertically well-mixed upper estuary where it joins the wider, deeper, clearer and seasonally stratified mesohaline portion of the system (**Fig.11**). About 90% of the tidal marshes of the Patuxent are located upstream of this location. The second site was at the junction of the Patuxent estuary with Chesapeake Bay. These locations were chosen, in the first case, to obtain closure of the budget at a location between very different portions of the estuary and, in the second case, to have an export/import estimate for the whole estuarine system.

Transport from Upper to Lower Estuary

During both the pre and post-BNR periods there were very strong seasonal patterns in DIN and TN transport between the upper and lower estuary (**Fig. 11a**). Transport was highest during winter and early spring, intermediate during fall and early winter and lowest during summer, generally following seasonal patterns in river flow and ambient nutrient concentrations. It is interesting, and discouraging from a management viewpoint, to note that both TN and DIN transport estimates were higher during the post-BNR winter seasons than during pre-BNR winters. This likely reflected the fact that the post-BNR period included several years characterized by particularly high river flow (1993, 94, 96, 98) and only two low flow years (1995 and 1999). In contrast, flow was below average during much of the pre-BNR period. Moreover, BNR does not routinely reduce N loading from sewage treatment plants during cold seasons. During summer, when BNR was active and river flow differences were less dramatic, reductions in N loading to the lower estuary were substantial. Seasonal average DIN loading for summer and fall decreased by 46% and 50%, respectively. Decreases in TN loading were smaller, but still substantial at 33% during summer and 21% during fall. However, annual mean DIN and TN loading to the lower estuary decreased by only 6% and 7%, respectively, following adoption of seasonal BNR technology.

There were also clear seasonal patterns evident for P transport between the upper and lower estuary. Again, rates were highest during winter and spring and lowest during summer and fall. For the most part, pre-BNR rates were lower than post-BNR rates, again probably because of higher river flows and more diffuse source inputs from the landscape during the wetter post-BNR period. There were almost no differences in annual average DIP and TP inputs to the lower estuary between the pre and post-BNR periods.

Exchange at the Seaward Margin

Nutrient exchange at the seaward margin of the estuary was more variable than transport between the upper and lower estuary (**Fig.11b**). This reflects the fact that the net direction of this transport depends only on the difference in N concentration in the seaward (outward) flowing surface water and the landward (inward) flowing bottom water. The net N or P transport results from a relatively small vertical concentration gradient, which can easily change.

On an annual average basis, DIN was imported from the Bay to the Patuxent during both pre- and post-BNR periods, while TN was always exported to the Bay. Inflow of DIN was greater in the post-BNR period by 582 kg d^{-1}, increasing from an annual average of 136 to 718 kg d^{-1}. This increase was about half the size of the decrease in DIN input (1074 kg d^{-1}) from landside point sources due to BNR implementation, leading to a smaller than expected reduction in overall DIN input to the lower Patuxent estuary. TN export from the estuary during the pre-BNR and post-BNR period averaged 1250 and 869 kg d^{-1}, respectively, and contrasted sharply with DIN exchanges. TN was consistently exported during the pre-BNR period and exports were largest during spring and fall. During the post-BNR period TN was exported as well but at a lower rate (870 kg N d^{-1}) and there were periods during spring and fall when TN was imported into the estuary. Both TP and DIP were exported from the estuary during almost all months of the year. Annual DIP export averaged 105 and 40 kg P d^{-1} during the pre-BNR and post-BNR periods, respectively. During both periods, exports were highest during late summer and fall. TP exports averaged about 125 kg P d^{-1} during both pre-BNR and post-BNR periods. However, seasonal patterns were quite different. Exchanges were variable during the pre-BNR period and monotonic, with a summer maximum, during the post-BNR period.

There are currently three estimates available of nutrient exchanges at the mouth of the Patuxent River estuary (**Table 10**). The first was generated by subtraction of internal losses of TN and TP from all terrestrial plus direct atmospheric inputs of N and P, the second was computed from a coupled hydrodynamic/water quality model and the third was based on the box model computations described above. Estimates of TN export were remarkably similar, ranged from 0.21 to 0.45 kg N x 10^6 y^{-1}, and all were directed from the estuary to the Bay. The range in estimates of TP exchange was larger (- 0.06 to 0.05 kg P x 10^6 y^{-1}) and one estimate indicated a small import of TP from the Bay to the estuary. On the one hand it is comforting to largely see convergence of these estimates indicating export from the estuary to the Bay but it remains difficult to judge the accuracy of these estimates. Several of these estimates were made using data from the same years but the two estimates based on box model computations were made using data averaged for multiple years. **Nixon et al (1986a**) indicated that making estimates of net nutrient exchange at the mouths of estuaries is extremely difficult largely because of large bi-directional water flows and small and variable nutrient concentration gradients associated with these water flows.

Ecosystem Level Export Comparisons

The current estimates of nutrient export from the estuary can be compared to total nutrient inputs from all external sources and from this some understanding of nutrient retention versus export characteristics of the estuary can be developed. Using export estimates based on box model computations, about 20% and 13% of TN was exported to the Bay during pre and post-BNR periods, respectively. In the case of TP about 34% and 23% of total inputs were exported to the Bay. For both nutrients, export was not a major pathway of loss, especially not for N. To provide some perspective we can compare these levels of export to those summarized by **Nixon et al (1996**) for a selection of estuaries and lakes. They reported a strong inverse relationship between percent of nutrient inputs exported and the log mean of estuarine water residence time. This strong relationship suggests that if estuarine communities have time to process nutrients, they will, in effect reducing the nutrients exported as a function of the time available for nutrient uptake, sinking to sediments, burial or denitrification. Thus it appears estuaries can act as either “pipes” where transport rather than transformation/loss is the dominant process or as “sinks”, largely as a function of how long water remains in the system. However, the Patuxent appears to remove substantially more nutrients than expected, based on water residence times. Some of this difference may simply be the result of accumulated errors in developing these budgets. However, it is interesting to note that the Patuxent is a “sediment-rich” and eutrophic system; there are both abundant particulate nutrients and sediments to facilitate burial. Of the estuaries examined by **Nixon et al (1996**) only the Chesapeake systems had substantial burial losses, probably because of these features and moderately long water residence times. In addition, the Patuxent also has substantial areas of tidal marshes in the upper estuary and these marshes have been found to sequester both N and P (**Merrill 1999; Greene 2005a**). Thus, it’s possible that some estuarine features, such as tidal marshes or extensive seagrass communities, may further modify nutrient export characteristics (**Valiela et al 2001**).

Magnitude of Nutrient Recycling and Nutrient Demand

Recycling rates for N and P were organized for several time periods, seasons and location within the estuary to allow for comparisons between the magnitudes of new versus recycled nutrient inputs to this estuary and phytoplanktonic nutrient demand (**Dugdale and Goering 1967**). Recycling rates of N and P associated with sediments and macrozooplankton are summarized in **Tables 11 and 12**, respectively, and estimates of phytoplanktonic nutrient demand are provided in Table **13**. Unfortunately, no direct estimates water column nutrient recycling associated with microzooplankton and bacterial communities were available.

Annual average rates of N and P releases from sediments were substantial, being about twice as large as modal rates summarized for 48 other estuarine systems by **Bailey (2005**). This result was not surprising given the eutrophic condition of this estuary (**Fig. 5**). Sediment releases of N and P were best documented for warm periods of the year. However, it still appears that there was strong seasonality in flux magnitude with highest values observed during summer and lowest values during winter. Fluxes of both N and P were higher (23-45%) in the upper than lower estuary and this may be related to the supply rate of labile organic matter from the water column to sediments which is probably higher in the upper estuary, especially during summer (**Cowan and Boynton 1996; Hagy 1996**). Ammonium and phosphate fluxes were also consistently higher during the post-BNR period, although differences were not large (< 30%).

Excretion rates of N by macrozooplankton were based on size/temperature relationships developed by **Mauchline (1998**). Dominant zooplankton included the copepods Acartia spp., Eurytemora spp., and Bosmina spp.; Bosmina was only found in the upper estuary and was extremely abundant during the post-BNR period. As a result of enhanced Bosmina abundances N excretion rates in the upper estuary were 2 to 12 times higher during the post-BNR period than during earlier years or during any time period in the lower estuary (**Table 12**). In most cases N recycling by zooplankton was highest during either spring or summer and much lower during fall and winter. We were not able to find a suitable size/temperature relationship to estimate P excretion by zooplankton.

Phytoplankton primary production rates ranged from 191 to 582 g C m^{-2} yr^{-1} during the pre-BNR period and from 172 to 458 g C m^{-2} yr^{-1} during the post-BNR period (**Table 13**). Rates estimated for the mesohaline region were high relative to measurements available for many other estuarine systems (**Boynton and Kemp 2005**). Rates were highest in the mesohaline region, intermediate in the tidal freshwater region and lowest in the oligohaline areas. It is probable that the extreme turbidity (secchi disk depth ~0.3-0.5 m) associated with the oligohaline region acts to limit primary production rates (**Hagy 1996**). During both pre and post-BNR periods and in all salinity zones, rates were highest during summer, lowest during winter and intermediate during spring and fall.

The purpose of developing estimates of nutrient recycle and phytoplankton productivity was to extrapolate these values to the scale of the whole estuary and compare the relative importance of new nutrient inputs to recycled nutrients and to phytoplankton nutrient demand (**Table 14**). Inputs of new DIN were highest during winter associated with higher river flows and lowest during summer; these seasonal differences were much larger for the lower than upper estuary. In addition, new inputs of DIN and DIP were not substantially different during the pre and post-BNR periods.

Recycle of DIN in the upper estuary was smaller than new inputs, especially during winter, when new inputs were about 6 times larger than recycle rates. In contrast, DIP recycle rates were larger than new inputs, especially during summer, and were about twice new inputs on an annual basis. Except for the winter period, both DIN and DIP recycling rates were higher during the post-BNR period. While we do not have experimental evidence to explain these differences they are likely due to wetter conditions that prevailed during the post-BNR period (**Fig.4**). Wetter conditions lead to higher inputs of nutrients, larger phytoplankton crops, and, ultimately, more organic matter available for recycling from sediments (**Cowan and Boynton 1996**). Finally, estimated phytoplankton nutrient demand was similar to nutrient recycle rates and always much smaller than the combined rates of new inputs plus nutrients supplied via recycling. This result is not surprising since this zone of the estuary almost never shows any nutrient limitation but is often severely light limited (**Fisher et al 1999**).

In contrast, recycle of DIN in the lower, mesohaline estuary was larger than new inputs, except during winter. Summer recycling rates, largely from sediments, were about 7 times larger than new inputs of DIN. DIP recycle rates were also much larger than new inputs, even during winter. Both DIN and DIP recycling rates were higher during the post-BNR period and the reason is probably the same as suggested above. Finally, estimated phytoplankton nutrient demand in the mesohaline estuary was always greater, or much greater, than nutrient recycle rates evaluated here and always exceeded the combined rates of new inputs plus nutrients supplied via the two recycling pathways evaluated. During the pre and post-BNR periods recycle plus new inputs of DIN and DIP supplied an average of 32% and 41% of phytoplankton demand, respectively.

There was a large discrepancy between phytoplankton nutrient demand in the mesohaline region and the supplies of nutrients from both external sources and the two recycle pathways evaluated. The most obvious missing source is nutrients recycled in the water column by bacteria and other microheterotrophs, a pathway we could not directly evaluate because such measurements have not been made in the Patuxent. However, we can make some crude estimates based on water column respiration measurements coupled with Redfield ratios of respired material. **Boynton et al (1982a) and Mikita (2002)** made a series of plankton community respiration measurements in the mesohaline estuary. Respiration rates in the lower estuary ranged from about 0.8g C m^{-2} day $^{-1}$ during winter to 2.0 g C m^{-2} day $^{-1}$ during summer. Similar rates were reported by **Smith (2000**) for the mesohaline portion of Chesapeake Bay. If typical summer respiration rates are converted to nitrogen and phosphorus equivalents (assuming C:N:P ratio of 106:16:1) and extrapolated to the area of the estuary, this represents N and P recycle rates of about 42,000 kg N day^{-1} and 5,700 kg P day^{-1} in the lower estuary. These rates are large enough to satisfy estimated phytoplanktonic nutrient demand when coupled with smaller, but still significant, sediment nutrient releases.

Several interesting point emerge from these whole-estuary computations. First, new inputs of N and P during any season do not approach phytoplanktonic nutrient demand in the lower estuary. Even during winter, when inputs of new N and P are highest and demand lowest, about 25% of demand is supplied by new nutrients. During summer, and on an annual average basis, sediments supply more recycled N and P than is derived from new inputs of these compounds but the sediment source is still much smaller than estimated plankton demand. **Kemp et al (1992**) were able to put sediment and water column respiration (a proxy here for nutrient regeneration) in perspective by examining the percentage of community respiration (water column plus sediments) attributable to sediments as a function of water column depth using data from about a dozen estuaries. They found a sharp decline in the relative importance of sediment processes with increasing depth. Using their relationship, and 6m average depth of the Patuxent, sediments would constitute about 30% of total community respiration, similar to the percentage of N and P recycled by sediments found in this evaluation (**Table 14**). It appears that even in relatively shallow estuaries, such as the Patuxent, water column nutrient recycling dominates N and P recycling.

Internal Nutrient Losses

Internal nutrient losses included denitrification and burial of particulate N and P in sub-tidal and tidal marsh habitats. Nutrient losses due to commercial and recreational fisheries extraction were not considered here because they were found to be small in an earlier analysis (Boynton et al. 1995) and no new information was available to substantially revise these estimates.

Denitrification rates for sub-tidal areas were based on measurements reported by **Jenkins and Kemp (1984), Twilley and Kemp (1987)** and measurements made during this study (**Greene 2005a; Cornwell, unpublished data**). Lower estuary rates ranged from about 6 to 50 uMoles N m^{-2} hr^{-1} during spring and from 0.0 to 102 uMoles N m^{-2} hr^{-1} during late fall. Summer rates in the lower estuary were non-detectable, probably because of low oxygen conditions and resultant lack of sediment nitrification activity **(Kemp et al. 1990; Rysgaard et al 1994**). A similar seasonal pattern of denitrification was evident in the upper estuary. Annual average rates for the upper and lower estuary were about 38 and 32 uMoles N m^{-2} hr^{-1}, respectively (**Table 15**).

Rates of denitrification for tidal marsh areas were based on a limited number of measurements made by **Merrill (1999**) and a considerably larger number of more recent measurements made in low, mid and high marsh locations by **Greene (2005a**). Rates ranged from non-detectable during late winter to over 500 uMoles N m^{-2} hr^{-1} in the high marsh during spring. There was a clear decrease in dinitrification rates from the high to the low marsh and a general decrease in rates from early spring through fall. Annual average rates were computed using both temporal and spatial weightings related to season and marsh type (e.g., extent of high, mid or low marsh areas) and found to be about 111 uMoles N m^{-2} hr^{-1} (**Table 15).** Most of the tidal marshes of the Patuxent are located in the upper estuary (~80 %) where all tidal marsh denitrification measurements were collected. However, small tidal marshes are associated with most of the tributary creeks flowing into the lower estuary and we used a slightly smaller denitrification rates for these marshes as suggested by the lower rates associated with mid and low marshes characterizing these smaller marshes. When these rates were extrapolated to include all sub-tidal and marsh areas, denitrification removed about 0.91 x 10^6 kg N yr-1 from the system; sub-tidal sediments removed about 60 % and tidal marshes the remaining 40%.

Estimates for sediment deposition rates in sub-tidal areas were based on Pb^{210} measurements made by **Cornwell (unpublished data**) and similar measurements from **Merrill (1999**) and **Greene (2005a**) for tidal marshes. Largest deposition rates were found for the sub-tidal upper estuary (2722 g dry sediment m^{-2} yr^{-1}) and smallest rates for the lower estuary (1143 g dry sediment m^{-2} yr^{-1}; **Table 16**). Rates were variable in the tidal marshes but yielded estimates of about 2140 g dry sediment m^{-2} yr^{-1} when deposition rates for low, mid and high marsh were spatially weighted. We assumed these rates were also characteristic of the small marshes in the lower estuary. Sediment PN and PP concentrations in sub-tidal areas (at sediment depths of 10-15 cm) were higher in the upper than lower estuary, especially for PP. Marsh values for PP were similar to those observed in sub-tidal areas of the upper estuary. In contrast, sediment PN values in tidal marsh sediments were about twice those in the sub-tidal areas (**Table 16**). Areal estimates of PN burial ranged from 2.9 to 12.6 g N m^{-2} yr^{-1}; burial rates were greater in the upper than lower estuary. Burial rates of PP ranged from 0.6 to 3.4 g P m^{-2} yr^{-1} and were much higher in the upper than lower estuary.

When these rates of PN and PP burial were extrapolated to include all sub-tidal and marsh areas, long-term burial removed about 0.89 x 10^6 kg N yr^{-1} and 0.21 x 10^6 kg P yr^{-1} from the system; about 41 % and 59 % of PN was buried in marshes and sub-tidal sediment, respectively. About 30% of PP burial occurred in tidal marshes and the rest in sub-tidal sediments.

While we benefited from having many more observations of these processes than were available for earlier nutrient budget analyses there are certainly errors associated with these estimates of whole system denitrification and burial. Until far more measurements of both processes are made, not a likely event in the near future, rigorous estimates of error are not possible. However, we can compare our estimates to those made in other estuarine and tidal marsh ecosystems and thereby obtain a qualitative sense as to whether our estimates are within the range of others made in similar environments. In a recent summary, **Greene (2005b**) assembled a large number of denitrification rate measurements from a variety of coastal habitats and found about 66% of measured rates were less than 100 uMoles N m^{-2} hr^{-1} and median rates for coastal wetlands and estuaries were 71 and 31 uMoles N m^{-2} hr^{-1}, respectively. Rates used for marshes in our analysis were slightly higher than this median value and values for sub-tidal sediments were very close to the median value. Thus, our whole system values reflect rates that have been commonly observed; in fact, we would not have reached substantially different conclusions if we had based our analysis on median literature values.

A similar situation exists regarding burial rates. The data set has improved but there is ample room for further measurement and more formal error analysis. In lieu of this we have examined burial rates observed in other coastal systems (**Table 17**) and found rates for PN and PP burial to range from 6 to 25 g N m^{-2} yr^{-1} and from 0.1 to 2.6 g P m^{-2} yr^{-1}, respectively. Again, burial rates used in this analysis were very comparable to those observed elsewhere. An additional step we took to help judge the adequacy of our measurements was to organize data concerning sediment sources. Essentially we asked, is there enough sediment entering the system to support the measured accretion rates. In the lower Patuxent estuary, like other mesohaline regions of Chesapeake Bay, a primary source of fine sediments is from shoreline erosion (**Yarbro et al. 1983; Hobbs et al. 1992**). In the case of the lower Patuxent, **Halka (personal communication**) estimated shoreline erosion yielded sufficient fine-grained sediments to support an average annual deposition rate of about 750 g (dry sediment) m^{-2} yr^{-1}, close to the value estimated using ^{210}Pb technique in the mesohaline region of the estuary. In the upper estuary we combined multi-year (1984-1997) average inputs of sediments at the head of tide with the same multi-year estimates of sediment load from the land-use model and found that these sources provided enough sediment to support deposition rates of about 2900 g (dry sediment) m^{-2} yr^{-1} in the upper estuary. Again, this spatially averaged rate is very similar to those used in the upper estuary (**Table 16**). These considerations suggest that our estimates of deposition are not wrong by a large margin.

Unfortunately, we have no time-series of burial or denitrification rates to evaluate interannual variability and this is unfortunate because we had such information for nutrient inputs. It would be very instructive to see how responsive these important losses are relative to changes in inputs. It does seem intuitively clear that burial rates would be higher during wet than dry years and that this would lead to enhanced burial of particulate nutrients. For example, **Schubel and Zabawa (1977**) found very large deposition rates in the upper portion of Chesapeake Bay following tropical storm Agnes in 1972. **Khan and Brush (1994**) reported substantial variation in deposition rates in the upper Patuxent in response to decadal-scale changes in land uses and **Roberts and Pierce (1974**) found very large increases in sediment inputs in response to urbanization, particularly during wet years. Thus, it seems reasonable that climate variability (i.e., wet or dry years), large storms, and land use changes would lead to inter-annual variability in particulate nutrient burial, but quantification of this remains a challenge.

Similarly, we suspect inter-annual variability in denitrification rates to be substantial. It is well known that denitrification rates respond to changes in nitrate concentrations at seasonal (e.g., **Rysgaard et al 1995**) and shorter time scales (**Greene 2005a**). In the Patuxent estuary, there were large differences in nitrate loads between wet and dry years (**Table 2**) and this would presumably enhance denitrification rates in wet years. Additionally, wet years produce larger phytoplankton communities and possibly more organic matter deposition to the bottom, as has been observed in Chesapeake Bay (**Boynton and Kemp 2000**). Thus, it seems likely that denitrification rates would be larger during wet than dry years. However, larger supplies of labile organic matter from phytoplankton production also contribute to hypoxic conditions in deep waters, particularly in wet years (**Fisher et al. 2005**), and this seriously impedes coupled nitrification-denitrification during summer periods (**Jenkins and Kemp 1984; Rysgaard et al (1994). Hagy and Kemp (2002)** developed a preliminary LOICZ-type budget (**Gordon et al 1996**) for the lower Patuxent estuary for a 12 year period. This approach yielded estimates of annual net denitrification and these rates ranged from 24 to 78 umoles m^{-2} hr^{-1}, spanning the range of rates used in the current budget analysis. During the period of time analyzed with the LOICZ approach there several wet and dry years; higher denitrification rates were associated with wet years and lowest rates with drought years. Thus, while we do not have direct measurements of inter-annual variability, indirect evidence indicates that internal loss rates (burial and denitrification) are in proportional to external loading rates.

Patuxent Estuary Responses to Nutrient Loading Rates

The long-term record of water quality data collected for Patuxent estuary shows that water quality, specifically algal biomass and hypoxia, varies predictably on an interannual basis in response to external forcing of the system by nutrient loading and freshwater inflow. The observed patterns of water quality can also be understood reasonably well in terms of known and often quantified ecosystem processes. Earlier research on Patuxent estuary water quality (**Hagy 1996**) also showed that different regions of the estuary had different seasonal patterns of water quality and responded differently to external forcing. A qualitative understanding of the ecological processes controlling water quality patterns was used to inform the development and interpretation of simple quantitative models of ecosystem response **(Fig. 12**). These models reflect the same general responses observed by **Hagy (1996**), but now with greater certainty due to the addition of 10 years' additional data.

Summer algal biomass (chlorophyll-a concentration) in tidal fresh surface water varied within a broad range of 30-60 µg l^{-1} during periods of normal summertime freshwater inflow. During above average summer (June-August) freshwater inflow, however, algal biomass tended to be much lower, approximately 10 µg l^{-1} **(Fig. 12)**. This pattern likely reflects the large increase in flushing of this region as flow increases (**Hagy et. al. 2000**). Low winter biomass may reflect the combination of slow algal growth and rapid flushing rate which occurs in most winters. Whereas winter average biomass was nearly always low, biomass increased several-fold in 2002, to 10 µg l^{-1}, when record low flow occurred in winter-spring. Tidal fresh algal biomass did not respond discernibly to the decrease in nitrogen loading at HoT which occurred in the early 1990s. This pattern likely reflects the apparent dominance of physical controls on phytoplankton biomass over nutrient limitation. In contrast, submersed aquatic vegetation increased robustly after nutrient loadings decreased, perhaps in response to nutrient input reductions (**Fisher et al. 2005**).

Phytoplankton biomass and production in the mesohaline portion of the estuary proceeds through several distinct phases during the year. During late winter, nutrient concentrations are high, while biomass remains low, suggesting light limitation associated with short photoperiod and a well-mixed water column (**Hagy 1996, Hagy et al. 2000**). In late winter to early spring, a phytoplankton bloom develops throughout the well-mixed water column, responding to compensating light levels. This bloom usually concludes in late spring. High algal biomass during summer, apparently controlled by nutrients and grazing, occurs only in surface waters. Algal biomass declines into fall until the lowest levels are reached in late fall. Annual mean values for chlorophyll-a in surface waters of the mesohaline Patuxent estuary were significantly correlated with both annual mean total nitrogen (TN) loading (r^2=0.46) and annual mean freshwater inflow as measured at HoT (r^2=0.59). Average chlorophyll-a values for the mesohaline estuary were better correlated with freshwater flow (**Fig. 12**) than with TN loading; it is probable that freshwater inflow correlates with factors affecting delivery of nutrients to the mesohaline portion of the estuary. For example, freshwater flow correlates with both diffuse nutrient loading from the middle portion of the watershed and downstream transport of nutrients from HoT to the mesohaline estuary. In addition, TN loading measured at HoT was affected by large decreases in point source discharges within the upper watershed. Within the lower watershed, the Western Branch treatment plant implemented biological N removal, but also increased the quantity of discharge (**Fisher et al. 2005**). Thus, it is very likely that freshwater flow tracks N availability to phytoplankton in the lower watershed better than TN loading at HoT.

Hypoxia and anoxia occur annually in mesohaline bottom waters of the Patuxent estuaryr, affecting at times nearly all of the below-pycnocline volume, but usually a smaller volume. **Hagy (1996)** observed that hypoxia usually occurs within an approximately 20 km stretch of the middle estuary, at the up-stream limit of landward circulation. At times, apparent intrusions of hypoxic bottom water from Chesapeake Bay affect the lower reaches of the estuary as well, dramatically increasing the volume of water affected (**Fisher et al. 2005**). The annual extent of hypoxia during 1986-2004 was significantly ($p<0.01$) correlated with freshwater inflow at HoT, averaged in any of several reasonably ways (e.g., October-August, January-August). March-August average inflow was the best predictor of hypoxic volume (**Fig. 12**), whereas a much weaker correlation was obtained when the average did not include the high-flow period in late spring. As with algal biomass, average TN loading at HoT did not predict the extent of hypoxia as well as freshwater inflow.

Hypoxia in 1987 and 1993 was more extensive than expected from inflow due to large hypoxic volumes associated with intrusions of hypoxic water from Chesapeake Bay. Hypoxia was substantially less extensive than expected in some other years (e.g., 1996, 1998), for unknown reasons. Whereas Hagy (1996) excluded the 1987 observation before fitting a regression, to better characterize typical system behavior during 1985-1992, the addition of 12 years' data renders this unnecessary. The general pattern of hypoxia in relation to freshwater flow is now more clearly rendered, as is the frequency of years in which hypoxia is unusually extensive or limited.

Budget Synthesis and Comparisons with Earlier Budgets

In the previous sections we described various individual N and P processes, transport and storages. In this section we put the pieces together in the quantitative framework of a budget and examine the results of our measurements and current level of understanding.

The annual scale TN budget appeared to be well balanced with inputs closely approximating internal losses plus export (**Fig. 13a and 13b**). To our knowledge this is the first estuarine nutrient budget where all terms were independently evaluated; all previous budgets had at least one term that was estimated by difference (**Nixon et al. 1996**). The rather close agreement between inputs and the sum of internal losses and export suggests we have captured most of the significant processes.

In addition to finding closely balanced budget, there are other important aspects that emerge from this budget evaluation. In the case of the Patuxent, most of the TN input is to the upper estuary (5389 kg N day-1; ~80% of total; **Fig. 12a**). However, in this portion of the system about 47% of these inputs were lost via long-term burial and denitrification. Loss processes occurring in the adjacent tidal marshes accounted for 64% of all losses in this region of the estuary. In the upper estuary long-term burial and denitrification were of about equal importance as loss terms. While this region represents only 12% of estuarine surface area (25% if adjacent tidal marshes are included) about 45% of all internal losses occur in this zone of the estuary. In the lower estuary losses associated with tidal marshes were small because of limited marsh area in this zone of the estuary. Denitrification and long-term burial in sub-tidal estuarine sediments were again of equal importance. Of the total annual TN load to the lower estuary, 75% is lost to burial and denitrification and the rest, mainly as DON and PON, exported to the Chesapeake Bay. Overall, only about 13% of the TN load to the entire estuarine system reaches Chesapeake Bay. The clear message here is that this estuary does not act as a passive pipe conveying nitrogen from the drainage basin to Chesapeake Bay.

The annual scale TP budget also appeared to be reasonably balanced but not to the same degree as the TN budget (**Fig. 12b**). Burial of TP in both tidal marshes and sub-tidal sediments was particularly important in the upper estuary. While the upper estuary constitutes only 25% of the area of the entire marsh-estuary system, about 61% of all TP inputs are buried in this region. Burial also sequestered a large fraction of inputs to the lower estuary (~ 95%). Box model-based estimates of TP transport to the lower estuary are more than twice that estimated by subtracting internal losses from external inputs (310 vs 120 kg P day^{-1}) indicating possible over-estimates of burial rates, an over-estimate of transport or an under-estimate of new TP inputs. The same result occurred in the lower estuary wherein TP transport to the Bay exceeded the residual obtained by subtracting internal losses from inputs. However, in both cases, these differences are not huge and neither changed the direction of transport. It is difficult to identify the most probable source of error leading to the discrepancies in the TP budget. Evaluations by **Williams et al (2005**) and **Jordan et al (2003**) both argue that accurately measuring TP inputs to the estuary is extremely difficult because such a large fraction of P travels attached to sediment particles. TSS transport is responsive to rain and storm events and very transitory; it is quite possible to miss quantitatively important but very short-lived runoff events. While the number of accretion rate estimates for marshes and sub-tidal area has improved substantially since we last produced a budget, additional sediment accretion rate measurements would be useful to further refine loss rate estimates.

One of the objectives of this work was to compare the earlier budget for the Patuxent (**Boynton et al. 1995**) with this more intensive effort; in a sense, see if we got it right the first time (**Table 18**). At the outset, it seemed like this exercise would be straightforward, but it turned out to be more complicated than expected. Both management actions (i.e., improved treatment of point source discharges) and climate variability (wetter in recent years) complicated the comparison. Inputs of TN were larger (~40%) in the current budget because wetter conditions resulted in larger diffuse source TN inputs that more than off-set TN reductions at sewage treatment plants. TP inputs, in contrast, were smaller (~12%) because decreases in point source TP inputs were larger than the increased TP inputs from diffuse sources. When these inputs were expressed on an areal basis, differences were small and certainly not large enough to suggest either an increased or decreased trophic condition. Internal losses of both TN and TP were computed to be larger (TN by 28 %; TP by 6 %) in the current budget and this is consistent with larger inputs in more recent times. In addition, the earlier budget did not include tidal marshes while in this effort they appeared to be important sinks for both N and P. Had marshes not been included there would have been a good deal of N and P not accounted for by the sum of internal losses and export, particularly in the upper estuary. **Williams et al (2005**) reported that the degree of overprediction of water column NO_3 concentration by a water quality model for the upper estuary was proportional to the area of adjacent tidal marshes. The addition of marshes to this evaluation clearly influenced the results and supports the ideas expressed by **Valiela et al (2001**) concerning the importance of exchanges of materials among adjacent coastal community types. Finally, TN exports to Chesapeake Bay constituted about 13 % of total inputs in both budgets. While export was arrived at differently in these budgets the answer in both is the same; not much nitrogen escapes from this estuary. However, there were substantial differences in TP export. The earlier budget indicated a net import (negative export) of TP amounting to about 30 % of total landside inputs of TP. The current TP budget indicates a net export, also close to 30 % of landside inputs. Thus, there is a difference in both the direction and magnitude of TP exchange with Chesapeake Bay.

Management Issues and Ecosystem-Scale Experiment

There has been considerable effort expended to reduce nutrient inputs, mainly from point sources, and thereby restore the Patuxent estuary to a less eutrophic condition (**Malone et al. 1993; D’Elia et al. 2003**). However, there has not been a quantitative evaluation of all nutrient inputs, storages, internal losses, and exchanges with Chesapeake Bay before and after these management actions occurred. Nutrient budgets are a useful framework for such an evaluation and we summarize here the main management-related point derived from this budgeting effort.

There is clear evidence of nutrient load reduction at the head of the estuary. This pattern, for both TN and TP, is substantial (25 % for TN and 23 % for TP) and caused by decreased nutrient concentrations in point source discharges (**Table 4**). Load reductions occurred earlier for P and were caused by the P-ban in detergents and improved P-removal at sewage plants. Reductions in N occurred later, were not as large and were caused by use of biological N removal technologies (denitrification) at sewage treatment plants. These load reductions have been broadly touted as evidence of progress towards meeting Chesapeake Bay restoration goals. However, there is no evidence that annual time-scale nutrient loads to the much larger lower estuary have declined in response to these management actions. Pre and post-BNR TN and TP fluxes from the upper to the lower estuary were almost identical (**Fig. 11**). In fact, if TN and TP loads to this estuarine system were ranked from largest to smallest, the largest occurred during a wet year in the post-BNR period (1996) and the smallest during a dry year in the pre-BNR period (1991). Thus, diffuse sources, particularly those from the middle portion of the drainage basin, dominate the nutrient input signature for this estuary. Water quality improvements will not likely occur until there are substantial reductions in diffuse source inputs. Further reductions in N concentrations (to ~ 3 mg N l^{-1}) in point source discharges are planned; these reductions, if implemented, could reduce N loads by about 20-25 % to the upper estuary and about 9 % when all N sources to the estuary are considered.

There has been a prolonged debate concerning the relative importance of Patuxent basin versus Chesapeake Bay nutrient sources contributing to the eutrophication of the Patuxent estuary (e.g., **Domotor et al. 1989**). Some agencies claim that Patuxent basin nutrient reductions would be ineffective because large amounts of N and P are imported from the nutrient enriched Chesapeake Bay to the Patuxent estuary. Several estimates of nutrient exchange at the mouth of the Patuxent indicate that this is not the case; TN and TP are exported from the Patuxent to the Chesapeake Bay rather than the reverse (**Fig. 11**). In addition, regression models relating nutrient loading rates to algal biomass accumulation and to hypoxic volumes account for much of the variability, suggesting that nutrients derived from the Patuxent basin are centrally involved (**Hagy 1996**). Finally, spring algal blooms and development of hypoxic waters first occur within the Patuxent rather than in the adjacent Chesapeake Bay; there is little evidence for importation of these features from the Bay to the Patuxent. Thus, nutrient load reductions in the Patuxent should, if of sufficient size, contribute to a lessening of eutrophic characteristics.

Nixon et al (1996) compiled N and P budgets for about a dozen estuaries. The magnitude and characteristics of inputs, losses and exports varied widely, as might be expected from a selection of estuaries that ranged from shallow lagoons to deeper, stratified coastal plain estuaries. However, they found a striking relationship between the percent of N and P exported and the log mean residence time of estuarine water. Thus, in rapidly flushed estuaries a large percent of inputs were exported while in more slowly flushed systems a smaller percent of inputs were exported. The Patuxent exported (as a percent of inputs) even less than predicted by the **Nixon et al (1996**) analysis. The practical issue here is that the Patuxent does not rapidly export nutrients. In fact, only about 13 % and 23% of TN and TP inputs, respectively, are exported. Most of the TN and TP exported are as dissolved or particulate organic compounds, indicating that they have been transformed from dissolved inorganic forms during transit through the estuary. Because of these large internal losses, the Patuxent contributes little to the eutrophication of Chesapeake Bay and probably even less than suggested by export estimates because a large fraction of the TN and TP exported is in forms not immediately utilizable by phytoplankton communities.

One of the unexpected outcomes of this budget analysis was the importance of the tidal marshes as sinks for both N and P. Investigations elsewhere (**e.g., Bricker and Stevenson 1996; Stevenson et al. 2002**) have reached similar conclusions. Marshes removed about 30 and 31 % of all TN and TP inputs, respectively, despite the fact they are a small part of the land/seascape (1.3 %) of the Patuxent basin and 18% of the estuarine/marsh system. Thus, accreting marshes, such as those in the Patuxent, seem to act as an efficient "ecosystem-scale kidney" and should continue to be protected for the many values they provide. However, should the tidal marshes of the Patuxent fail to keep pace with rising sea level, as has occurred in about 50% of other Chesapeake Bay tidal marshes (**Kearney et al. 2002**), the nutrient buffering effect of marshes would be lost; further still, eroding marshes could serve as a source of organic matter and nutrients, reversing the current role marshes appear to play (**Stevenson et al. 2002**).

There is substantial recycling of N and P from both the water column and sediments, especially during the warm periods of the year. Water column recycling, while large, can not support further increases in algal biomass but only maintain existing biomass. Nutrient releases from sediments, however, represent a "new" source of nutrients to the euphotic zone and can support increased algal standing stocks. There is field evidence from the Patuxent and other portions of Chesapeake Bay that deep water hypoxic/anoxic conditions facilitate efficient recycling of N and P from estuarine sediments (**Boynton and Kemp 1985; Cowan and Boynton 1996; Kemp et al. 2005)**. We would expect sediment nutrient releases to diminish under conditions in which sediments remain oxidized through the summer months. Under such conditions P releases would be reduced due to reactions with oxidized iron at the sediment-water interface and N releases would also be reduced because coupled nitrification-denitrification would remain active. Thus, nutrient input reductions sufficient to relieve seasonal hypoxic/anoxic conditions might lead to larger improvements in water quality than expected because sediment nutrient recycling processes become less efficient. The quantitative impact of a drop in sediment nutrient recycling efficiency is not available at this time. However, we might expect there to be something other than a linear response to load reductions, possibly similar to the more complex hysterisis in ecosystem response observed in the Potomac River estuary (**Jones 2000**).

Our analyses indicate that major features of the estuary can be related to nutrient load changes. For example, the volume of hypoxic water and the size of algal standing crop were proportional to nutrient loading rates. In addition, time-series measurements of community metabolism and sediment releases of N also appear to be related to nutrient loading rates (**Boynton and Rohland 1998; Sweeney 1995**) in the Patuxent and mainstem Chesapeake Bay (**Boynton and Kemp 2000**). The practical aspect of these findings is that these processes, central to water quality, are very responsive to changes in nutrient inputs. There does not seem to be a large nutrient memory embedded in the sediments or water column of the Patuxent or other portions of Chesapeake Bay (**Boynton and Kemp 2000**). Should substantial nutrient reductions occur, we would predict measurable improvements in water quality conditions within a year or slightly longer period.

A central issue concerning eutrophication of the Patuxent concerns how much nutrient load reduction is needed. The Patuxent is currently among the aquatic systems in Maryland cited as not being in compliance with water quality guidelines; a Total Daily

Maximum Load (TMDL) computation is currently being developed for this estuary. Much of the TMDL result will be based on values computed from coupled land-use and water quality models and will thus be a function of how well those models capture features of the land and estuary. There are also several approaches to estimating needed load reductions based on field measurements; in the long run, use of both approaches would be useful. **Fisher et al (2005**) examined deep water dissolved oxygen concentrations in the Patuxent for an 18 year period (1986-2004). During summer average oxygen concentrations were below 1 mg l^{-1} for 6 of those years and below 2 mg l^{-1} for 10 additional years. During two drought years (1986 and 1992) summer dissolved oxygen concentration were at or slightly above 2 mg l^{-1}. Whole system TN and TP loads during those years averaged 5100 and 313 kg N and P day^{-1}, about 80 % and 70%, respectively, of average loads and 60 % and 45 %, respectively, of loads during high flow years. TN input reductions on the order of 1500 to 2500 kg N day^{-1} and TP reductions on the order of 100 kg P day^{-1} would be needed to be consistent with load conditions associated with deep water dissolved oxygen concentrations at or above 2 mg l^{-1}. We recognize that factors other than nutrient inputs (e.g., freshwater input and resultant strength of water column stratification, storm frequency and resultant vertical mixing) play a role in determining water quality conditions so these values are most useful as a first approximation rather than as firm targets. An alternative approach is to examine nutrient loading rates when the estuary exhibited few symptoms of eutrophication (**Mihursky and Boynton 1978; Heinle et al 1980**). The earliest load estimates were developed by **Hagy et al (1998**) and extend back to 1960, a period before sewage treatment plants were a significant feature of the basin (**Domotor et al 1989**) and before intensive urban/suburban development was initiated in the watershed (**D'Elia et al 2003**). TN and TP inputs at HoT averaged about 1200 kg N day-1 and 224 kg P day-1 during the decade of the 1960's. TP loads at the head of tide are now lower than during the 1960's by almost a factor of two. However, TN loads at the same location are still a factor of 1.6 greater than the earlier loads, despite BNR technology at the sewage treatment plants located above the head of tide. This comparison suggests the need for modest reductions in TN. However, about 70% of the contemporary TN load to the estuary comes from the basin located downstream of HoT. If we apply a modest diffuse TN yield for the basin area below HoT (areal rate = 5 kg N ha yr-1) to represent inputs appropriate for the 1960's, a total TN load to the estuary of 3100 kg N day^{-1} results. This is about half of average contemporary TN loads and about 30% higher than TN loads estimated for recent dry years. While also crude, this analysis reaches a conclusion not dissimilar from the previous one; TN loads need to be decreased on the order of 2500 - 3000 kg N day^{-1} to be comparable to loads associated with far less eutrophic conditions of the 1960's. The second estimate is somewhat larger than the first and this might reflect the fact that the first only required that deep water dissolved oxygen conditions be above 2 mg $^{-1}$ in summer while the latter estimate was associated with an ecosystem having a vibrant seagrass community, well developed benthos and oyster reefs as well as better deep water oxygen conditions.

Whatever nutrient input reductions are eventually agreed to during the TMDL process, several things seem clear. First, TN reduction will need to be substantial to reduce hypoxic conditions during normal and wet years and larger still to restore other community components (SAV, benthos) to this ecosystem in addition to improving oxygen conditions in deep waters. Second, further reductions in point source discharges are technically possible and, if instituted, will measurably reduce loads. However, most of the needed reductions will involve diffuse sources and to date there appears to have been little progress in dealing with this source of nutrients.

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Figure 1. A map showing regional location (a) and spatial details (b) of the Patuxent basin and Patuxent River estuary.

Figure 2.Conceptual model of the nutrient budgets evaluated for the Patuxent River estuary. Geographic boundaries are shown in Figure 1. The model is described in the text. Abbreviations on the diagram are as follow: I = inputs, L = internal losses due to long-term burial or denitrification, T = transport between estuarine regions or Chesapeake Bay. Sunscripts u, m and l indicate upper, middle or lower basin; subscripts a = direct atmospheric deposition of N or P to surface waters of the estuary, p = point source, d = diffuse source and s = septic source; dn and b refer to denitrification and long-term burial, respectively; m and l indicate processes occurring in tidal marshes and sub-tidal estuarine sediments, respectively.

Figure 3. Annual average TN, DIN, TP and PO4 loading rates (kg N or P day-1) for the full Patuxent River estuarine system. Loads include combined sources from above the head of tide (HoT) and all diffuse, point, septic and direct atmospheric deposition to tidal waters of the upper and lower estuary. Dashed and dotted lines indicate average values of total and inorganic loads for the years 1985-1997.

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(Nixon et al 1986b), 32 Back River MD (Boynton et al 1998), 33 Boston Harbor, pre-sewage diversion (Nixon et al 1996), 34 Western Scheldt Netherlands (Nixon et al 1996). Loads to the Patuxent River estuary for the years 1985 – 1997 are shown as solid squares. The solid diagonal line represents the Redfield ratio of TN:TP inputs (weight basis).

Figure 6. Annual time series of TN wet deposition. Data were collected at the NADP site at Wye, MD (NADP 2001). See text for definition of TN

Figure 7. Box and whisker plot of monthly atmospheric TN deposition rate. Data were collected at the NADP site at Wye, MD (NADP 2001) and were averaged from 1985 – 1999. See text for description of TN components.

Figure 8. Time series plot of average monthly sewage treatment plant discharge, TP and TN loads from above HoT in the Patuxent River basin. The distinct oscillation in TN load is due to seasonal removal of N via denitrification at these facilities. Data were from Chesapeake Bay Program (2001) and Wiedeman and Cosgrove (1998).

Figure 9. Time-series plots of diffuse source TN, DIN, TP and DIP loads from the middle basin of the Patuxent River estuary. Horizontal lines represent average inputs of TN and TP (solid lines) and DIN and DIP (dashed lines) for the pre (1985-1990) and post-BNR periods (1993-1997). Data were from Shenk and Linker (2001).

Figure 10. A summary of annual TN and TP loads by source to the upper and lower Patuxent River estuary during the pre and post-BNR periods. Data sources were listed in Tables 1 – 5.

Figure 11. Estimated N and P transport between the upper and lower portions of the Patuxent River estuary (a) and transport between the Patuxent River estuary and Chesapeake Bay (b). Transport was estimated using the box model developed by Hagy et al (2000) and nutrient concentration data from Chesapeake Bay Water Quality Monitoring Program (2001).

Figure 12. Responses of Patuxent River estuary water quality to interannual variations in freshwater inflow at Bowie, MD. (A) The relationship between summer (June-August) average surface water chlorophyll-a at a tidal freshwater station (TF1.4) and summer average freshwater inflow. (B) The relationship between annual average surface water chlorophyll-a and annual mean chlorophyll-a at a mesohaline station (LE1.1). (C) The relationship between March-August average freshwater inflow and the temporal and spatial extent of hypoxia ($DO<2.0$ mg l^{-1}). Regression lines are least squares regressions with 95% confidence bands for the mean. All regression slopes are statistically significant ($p<0.01$).

Figure 13. A synthesis of annual TN (a) and TP (b) inputs, transport between estuarine regions, internal losses and stocks for the Patuxent River estuary. Inputs are multi-year averages of combined point, diffuse, direct atmospheric deposition to tidal waters, and septic. Spatial locations of inputs (from top to bottom of the diagram) are at the head of

tide (HoT), from the basin region between HoT and Benedict, MD and from the basin between Benedict and Chesapeake Bay (Fig. 1). Abbreviations WC, Biota, and Seds refer to multi-year, average annual TN and TP concentrations in the water column, animal biota and sediments, respectively. Abbreviations M and ST refer to tidal marsh and sub-tidal areas of the estuary. All flows have units of kg N or P day^{-1} and all stocks have units of kg N or P x 10^3.

Figure 1.

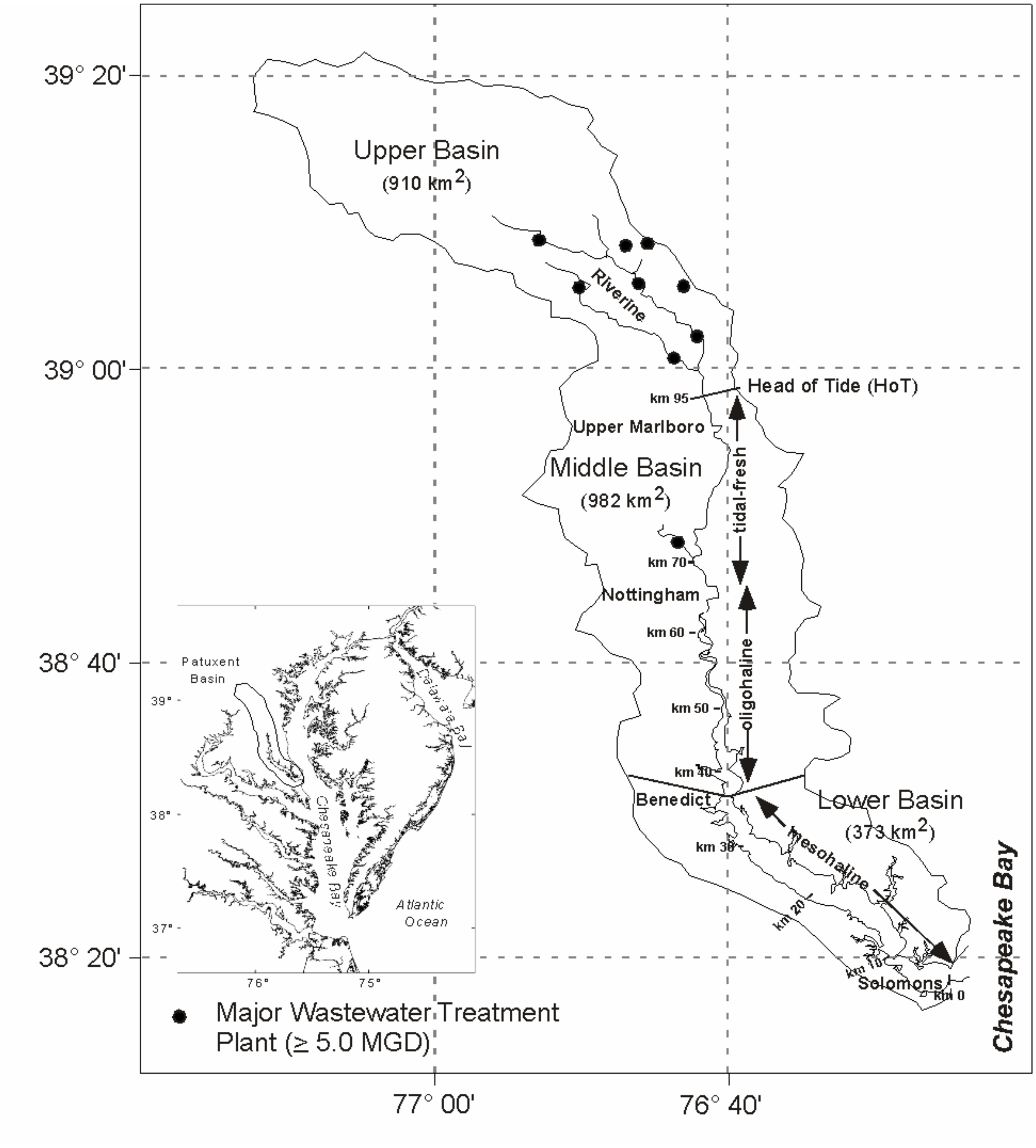

39° 20'
39° 00'
38° 40'
38° 20'
77° 00'
76° 40'
Upper Basin
(910 km²)
Riverine
Head of Tide (HoT)
km 95
Upper Marlboro
Middle Basin
(982 km²)
tidal-fresh
km 70
Nottingham
km 60
oligohaline
km 50
km 40
Benedict
Lower Basin
(373 km²)
km 30
mesohaline
km 20
km 10
Solomons
km 0
Chesapeake Bay
Patuxent Basin
39°
38°
37°
76°
75°
Chesapeake Bay
Delaware Bay
Atlantic Ocean
● Major Wastewater Treatment Plant (≥ 5.0 MGD)

Figure 2.

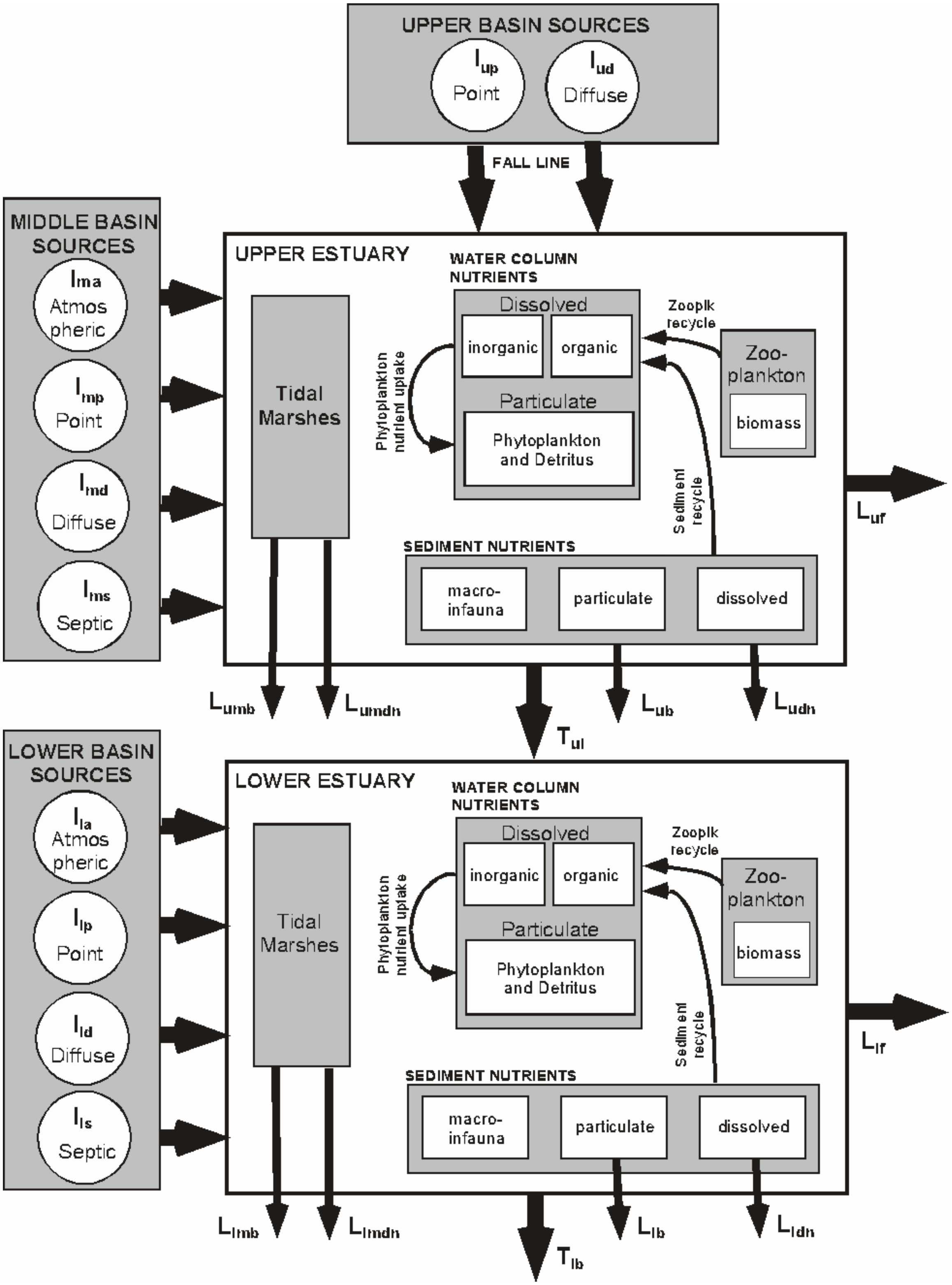

UPPER BASIN SOURCES
I_{up} Point
I_{ud} Diffuse
FALL LINE
MIDDLE BASIN SOURCES
I_{ma} Atmospheric
I_{mp} Point
I_{md} Diffuse
I_{ms} Septic
UPPER ESTUARY
Tidal Marshes
WATER COLUMN NUTRIENTS
Dissolved
inorganic
organic
Particulate
Phytoplankton and Detritus
Phytoplankton nutrient uptake
Zooplk recycle
Zoo-plankton
biomass
Sediment recycle
SEDIMENT NUTRIENTS
macro-infauna
particulate
dissolved
L_{uf}
L_{umb}
L_{umdn}
T_{ul}
L_{ub}
L_{udn}
LOWER BASIN SOURCES
I_{la} Atmospheric
I_{lp} Point
I_{ld} Diffuse
I_{ls} Septic
LOWER ESTUARY
Tidal Marshes
WATER COLUMN NUTRIENTS
Dissolved
inorganic
organic
Particulate
Phytoplankton and Detritus
Phytoplankton nutrient uptake
Zooplk recycle
Zoo-plankton
biomass
Sediment recycle
SEDIMENT NUTRIENTS
macro-infauna
particulate
dissolved
L_{lf}
L_{lmb}
L_{lmdn}
T_{lb}
L_{lb}
L_{ldn}

Figure 3.

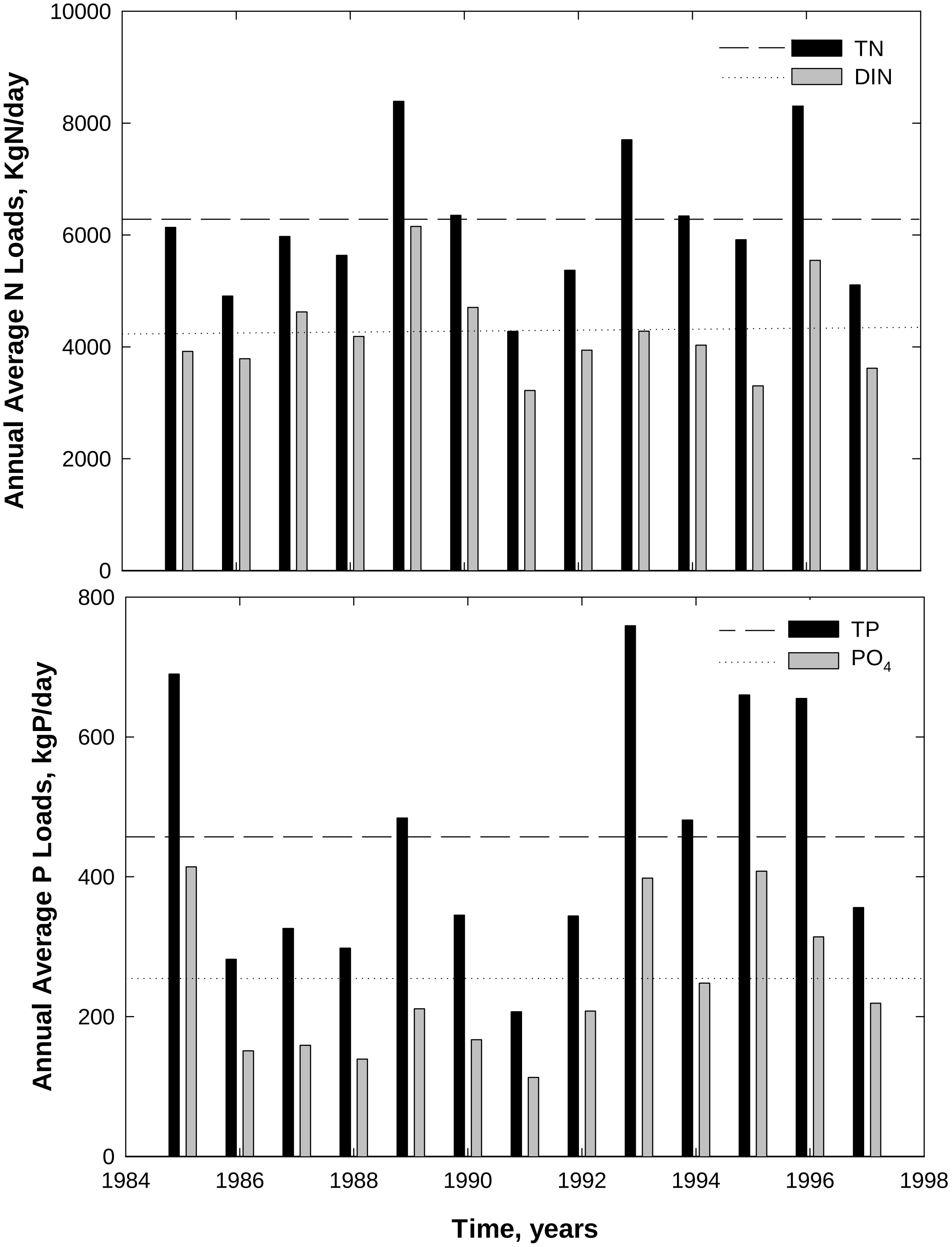

10000
8000
6000
4000
2000
0
TN
DIN
Annual Average N Loads, KgN/day
800
600
400
200
0
TP
PO$_4$
Annual Average P Loads, kgP/day
1984
1986
1988
1990
1992
1994
1996
1998
Time, years

Figure 4.

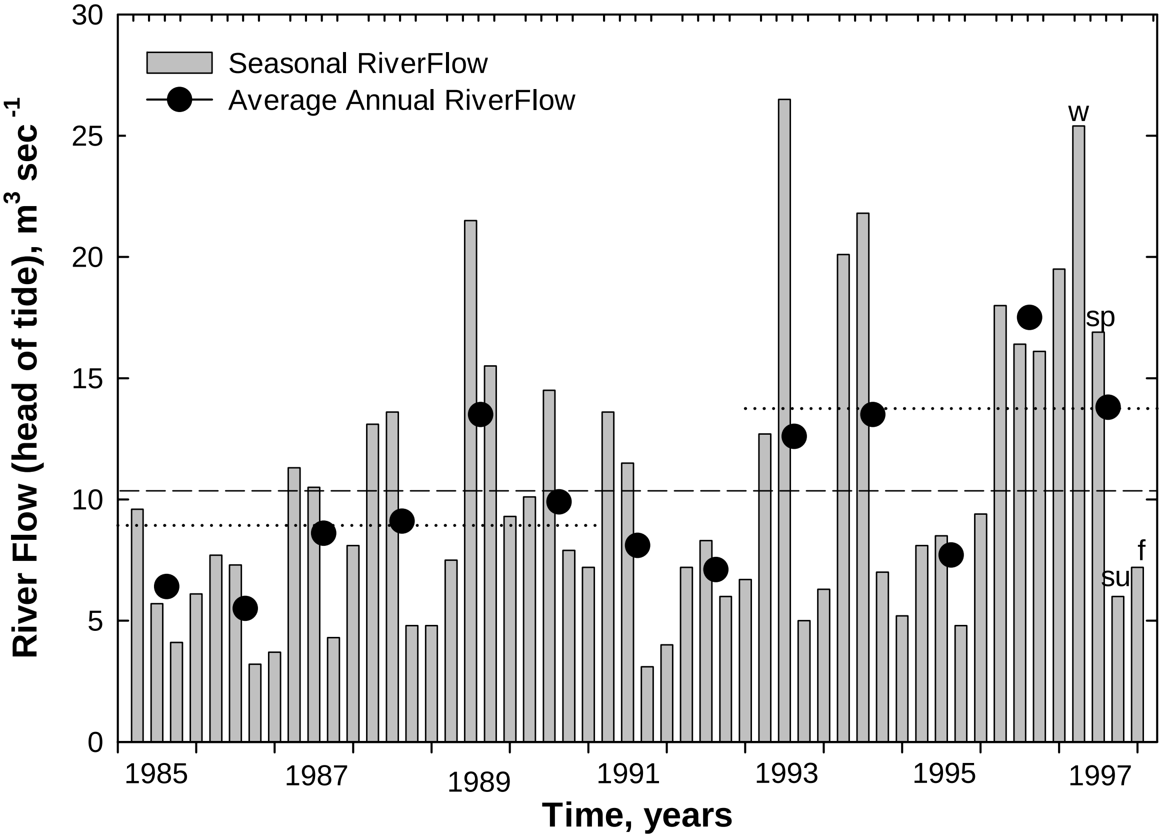

Seasonal RiverFlow
Average Annual RiverFlow
River Flow (head of tide), m3 sec-1
Time, years
0
5
10
15
20
25
30
1985
1987
1989
1991
1993
1995
1997
w
sp
su
f

Figure 5

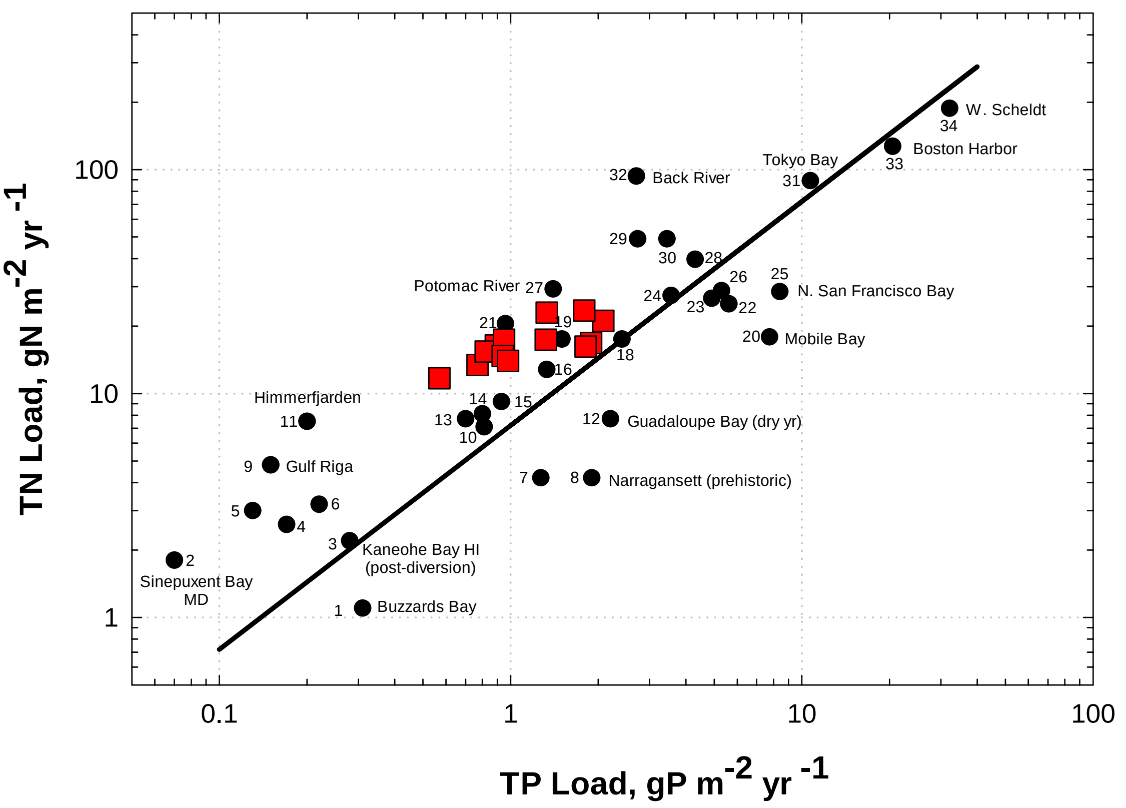

TN Load, gN m^{-2} yr^{-1}
TP Load, gP m^{-2} yr^{-1}
0.1
1
10
100
1
10
100
W. Scheldt
34
Boston Harbor
33
Tokyo Bay
31
32 Back River
29
30
28
26
25
N. San Francisco Bay
24
23
22
Potomac River 27
21
19
18
16
20 Mobile Bay
Himmerfjarden
11
14
15
13
10
12 Guadaloupe Bay (dry yr)
9 Gulf Riga
7
8 Narragansett (prehistoric)
5
6
4
3 Kaneohe Bay HI (post-diversion)
2
Sinepuxent Bay MD
1 Buzzards Bay

Figure 6

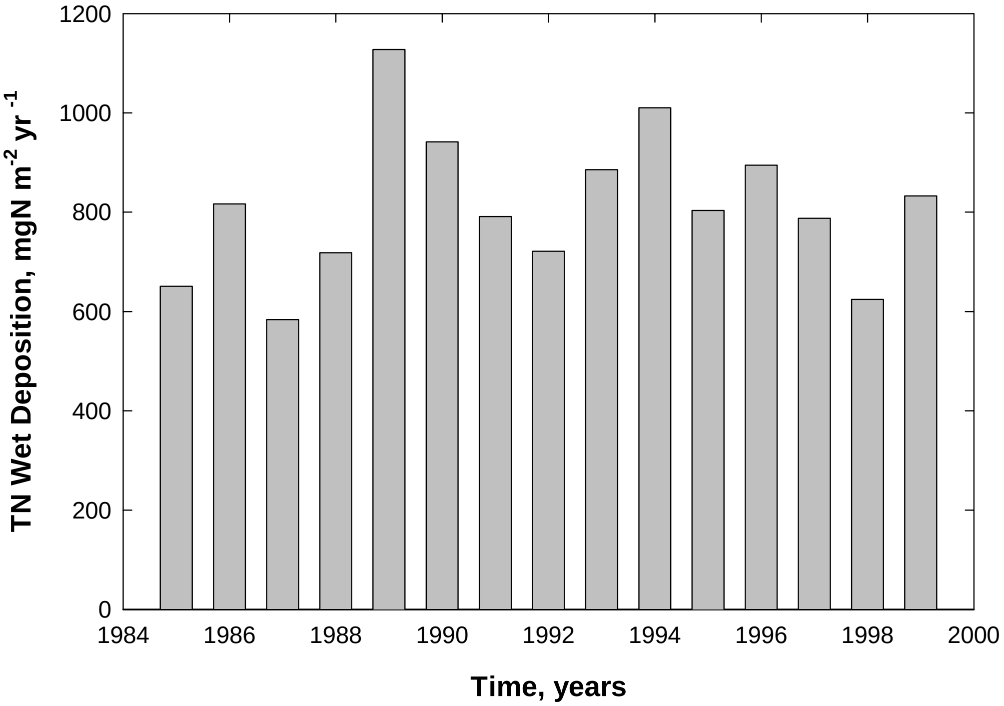

TN Wet Deposition, mgN m^{-2} yr^{-1}
0
200
400
600
800
1000
1200
1984
1986
1988
1990
1992
1994
1996
1998
2000
Time, years

Figure 7

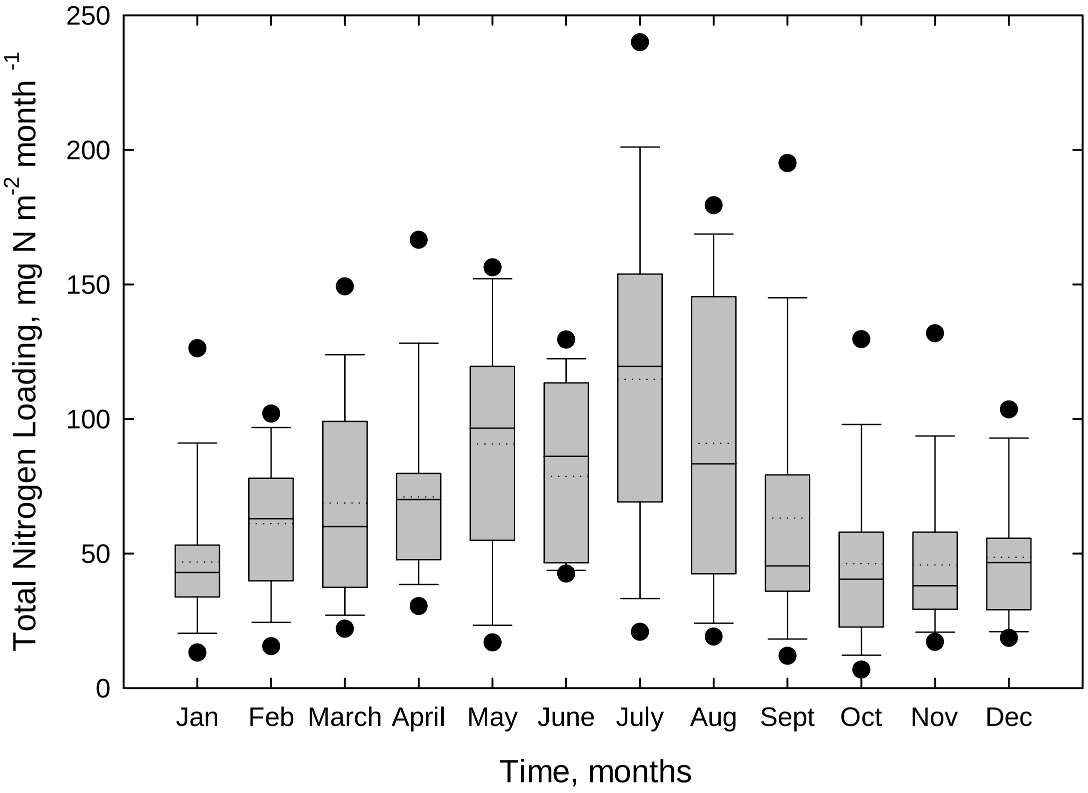
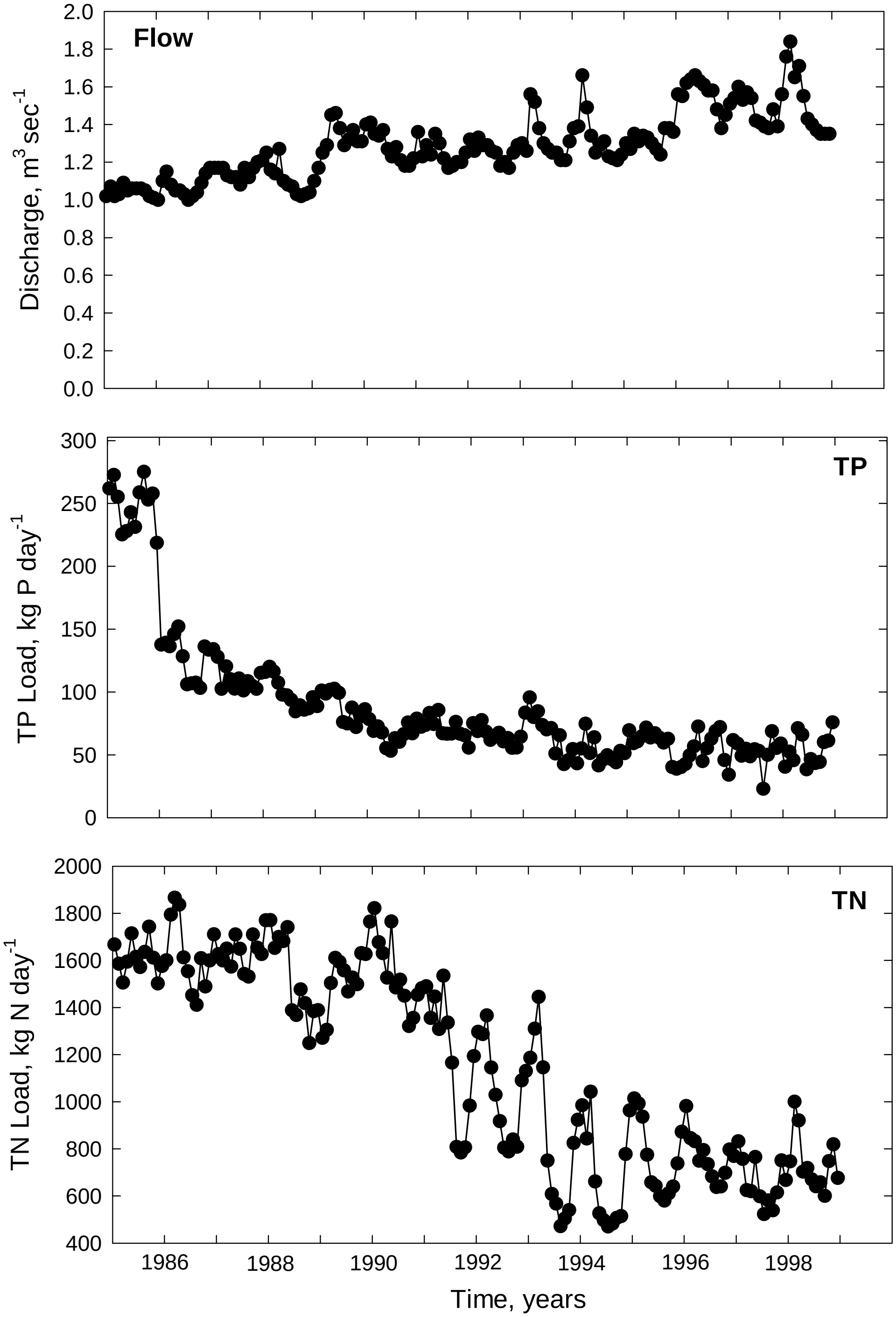

Total Nitrogen Loading, mg N m-2 month -1
0
50
100
150
200
250
Jan
Feb
March
April
May
June
July
Aug
Sept
Oct
Nov
Dec
Time, months

Figure 8



Flow
Discharge, $m^3 sec^{-1}$
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
TP
TP Load, kg P day^{-1}
300
250
200
150
100
50
0
TN
TN Load, kg N day^{-1}
2000
1800
1600
1400
1200
1000
800
600
400
1986
1988
1990
1992
1994
1996
1998
Time, years

Fig. 9

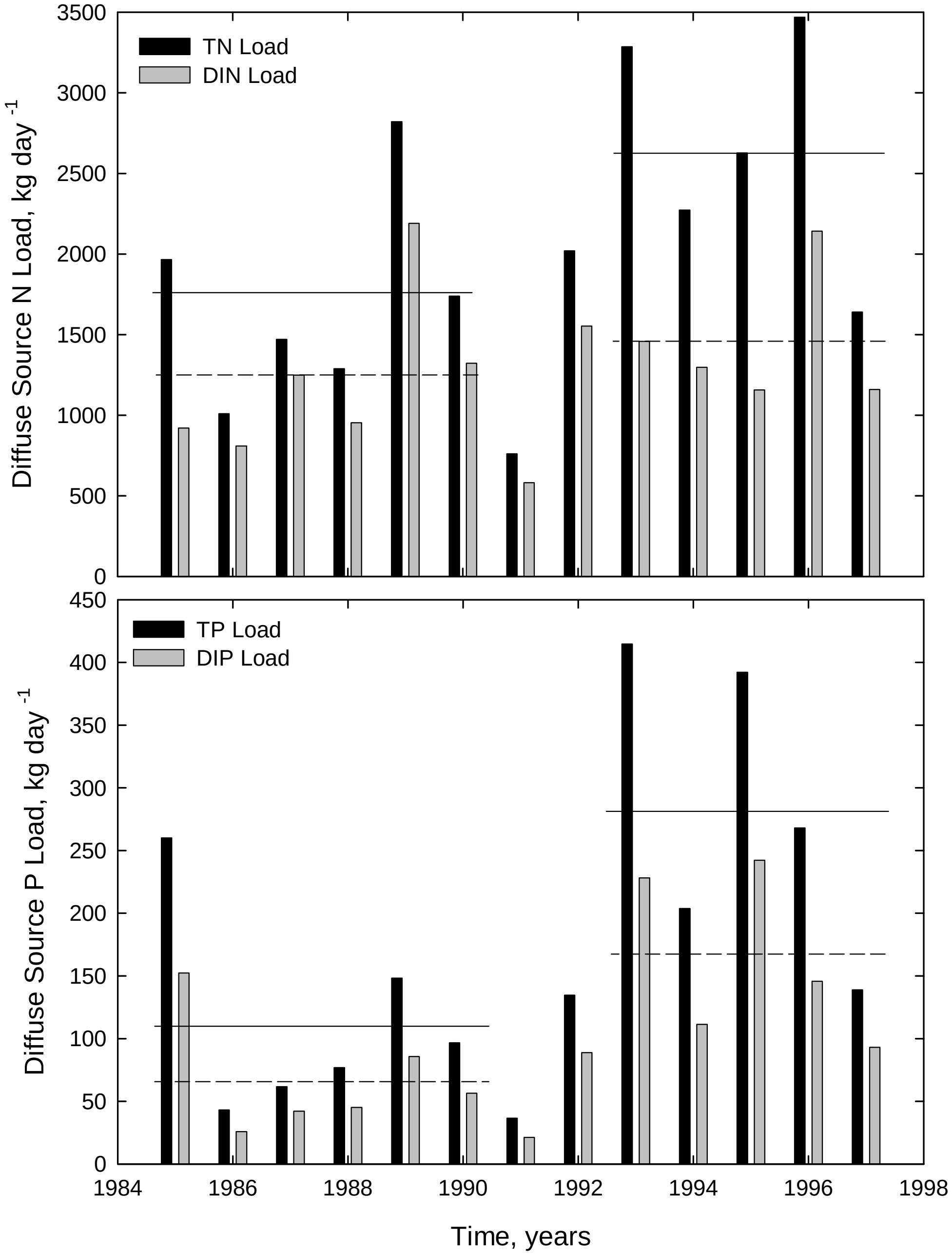
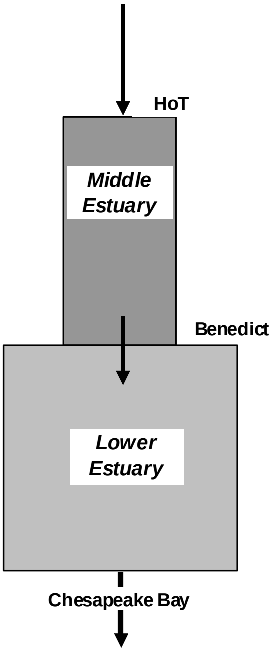

TN Load
DIN Load
Diffuse Source N Load, kg day $^{-1}$
3500
3000
2500
2000
1500
1000
500
0
TP Load
DIP Load
Diffuse Source P Load, kg day $^{-1}$
450
400
350
300
250
200
150
100
50
0
1984
1986
1988
1990
1992
1994
1996
1998
Time, years

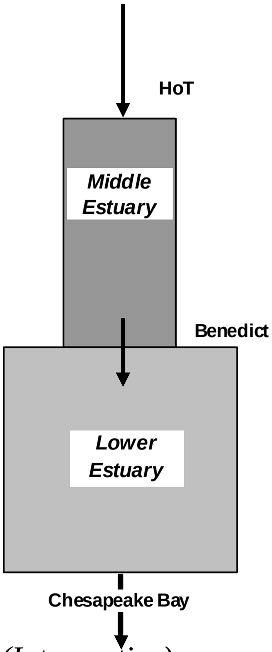
Figure 10

TN Loading: Annual (kg N d^{-1})



		Pre-BNR (1986-1990)	*Post-BNR (1993-1999)*	
UPPER BASIN	*Diffuse*	984	1189	*Diffuse*
	Point	1577	744	*Point*
	Total	2561	1933	*Total*
MIDDLE BASIN	*Atmosph*	85	85	*Atmosph*
	Diffuse	1716	2659	*Diffuse*
	Point	744	454	*Point*
	Septic	222	258	*Septic*
	Total	2767	3456	*Total*
TRANSPORT (mid to lower estuary)	*Total*	3137	2929	*Total*
LOWER BASIN	*Atmosph*	361	361	*Atmosph*
	Diffuse	504	794	*Diffuse*
	Point	0	0	*Point*
	Septic	72	84	*Septic*
	Total	937	1239	*Total*
CHES BAY EXCHANGE	*Total*	1234	868	*Total*

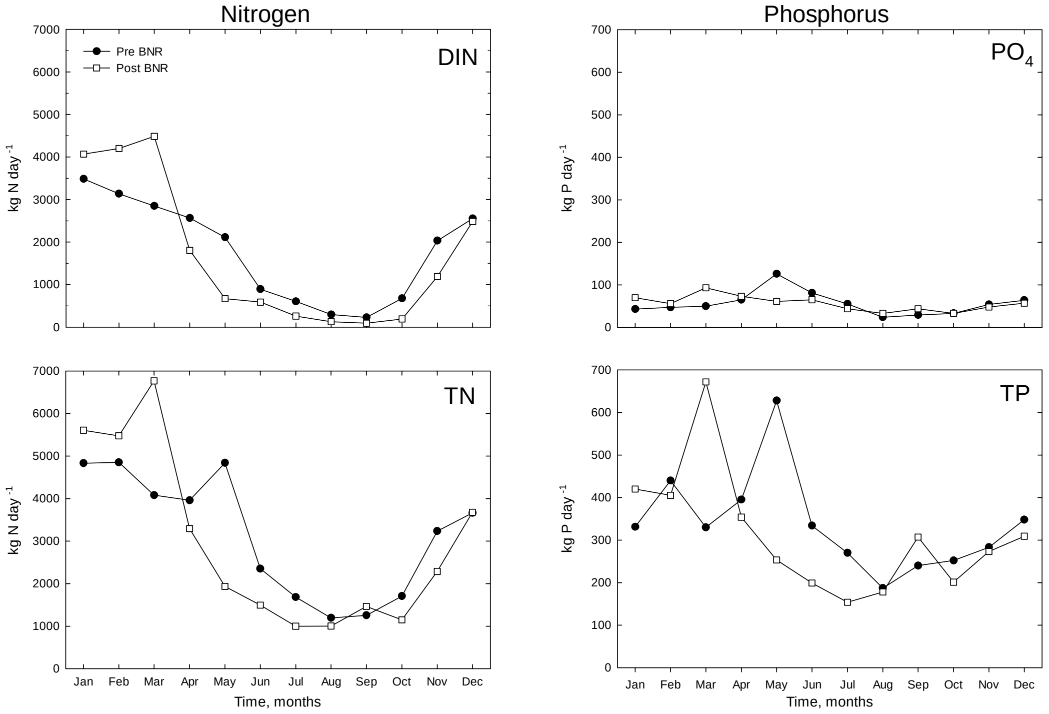
TP Loading: Annual (kg P d^{-1})



		Pre-BNR (1986-1990)	*Post-BNR (1993-1999)*	
UPPER BASIN	*Diffuse*	43	72	*Diffuse*
	Point	124	57	*Point*
	Total	167	129	*Total*
MIDDLE BASIN	*Atmosph*	5	5	*Atmosph*
	Diffuse	114	284	*Diffuse*
	Point	60	50	*Point*
	Septic	0	0	*Septic*
	Total	179	339	*Total*
TRANSPORT (mid to lower estuary)	*Total*	337	310	*Total*
LOWER BASIN	*Atmosph*	19	19	*Atmosph*
	Diffuse	34	84	*Diffuse*
	Point	0	0	*Point*
	Septic	0	0	*Septic*
	Total	53	103	*Total*
CHES BAY EXCHANGE	*Total*	138	132	*Total*

Figure 11

(a) Transport between Upper and Lower Portions of Patuxent River Estuary



(b) Transport between Patuxent River Estuary and Chesapeake Bay

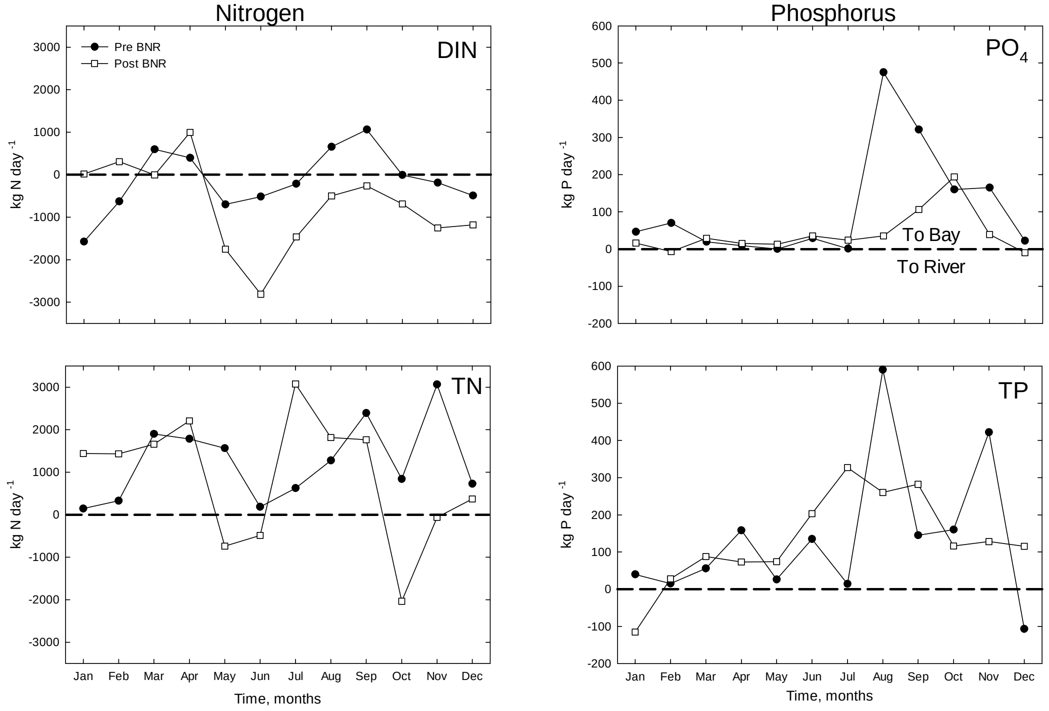


Figure 12

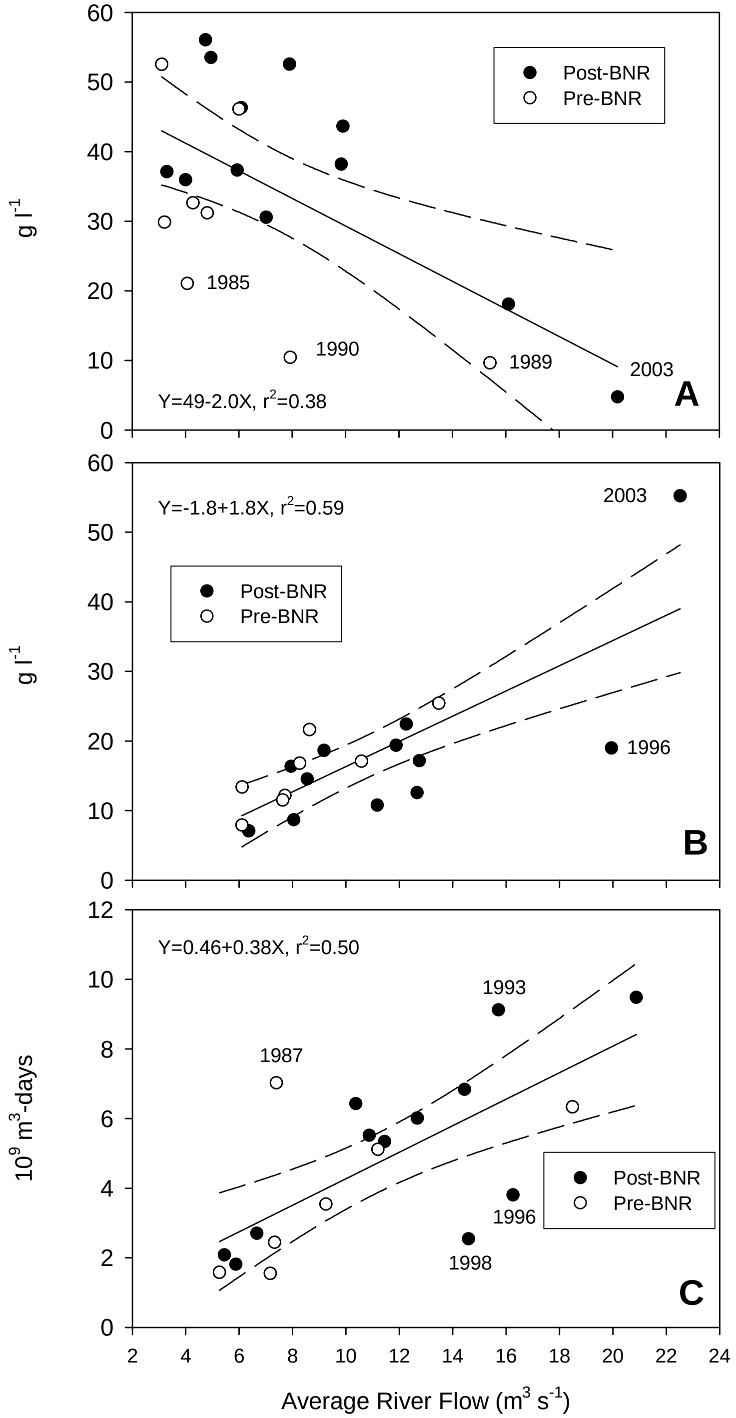

60
50
40
30
20
10
0
g l^{-1}
● Post-BNR
○ Pre-BNR
1985
1990
1989
2003
Y=49-2.0X, r^2=0.38
A
Y=-1.8+1.8X, r^2=0.59
2003
1996
B
12
10
8
6
4
2
10^9 m^3-days
Y=0.46+0.38X, r^2=0.50
1993
1987
1996
1998
C
2 4 6 8 10 12 14 16 18 20 22 24
Average River Flow (m^3 s^{-1})

Figure 13a

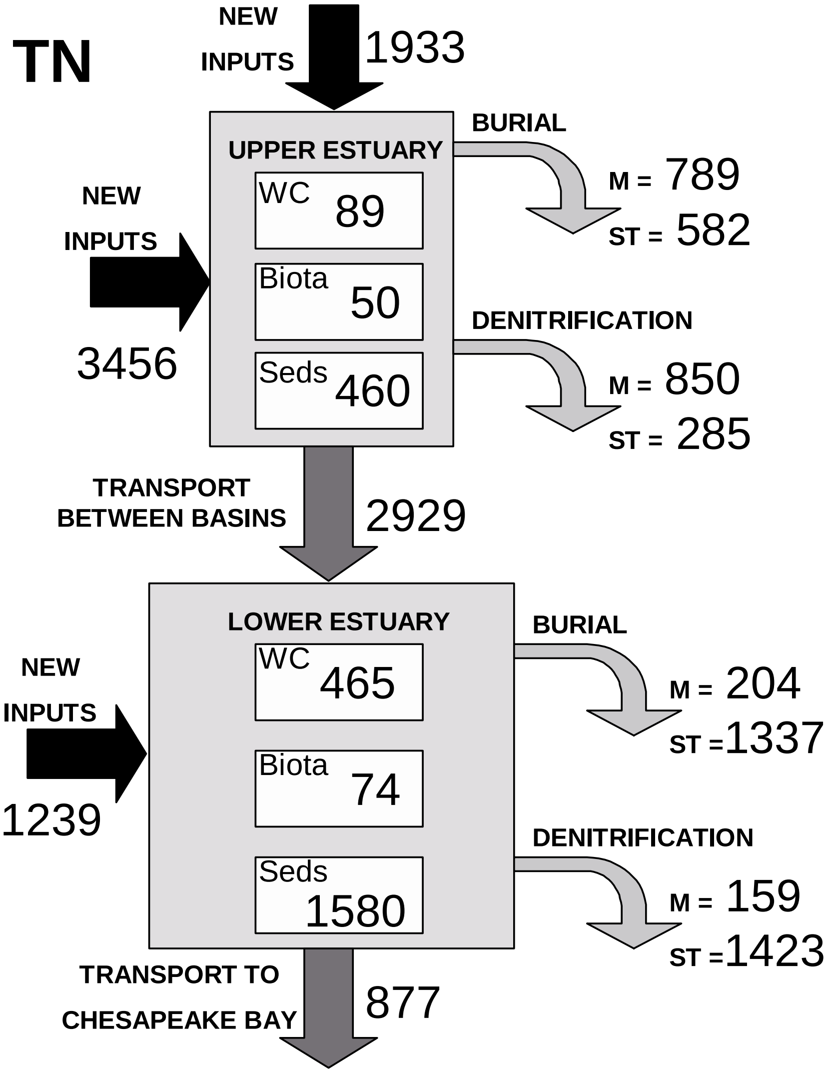
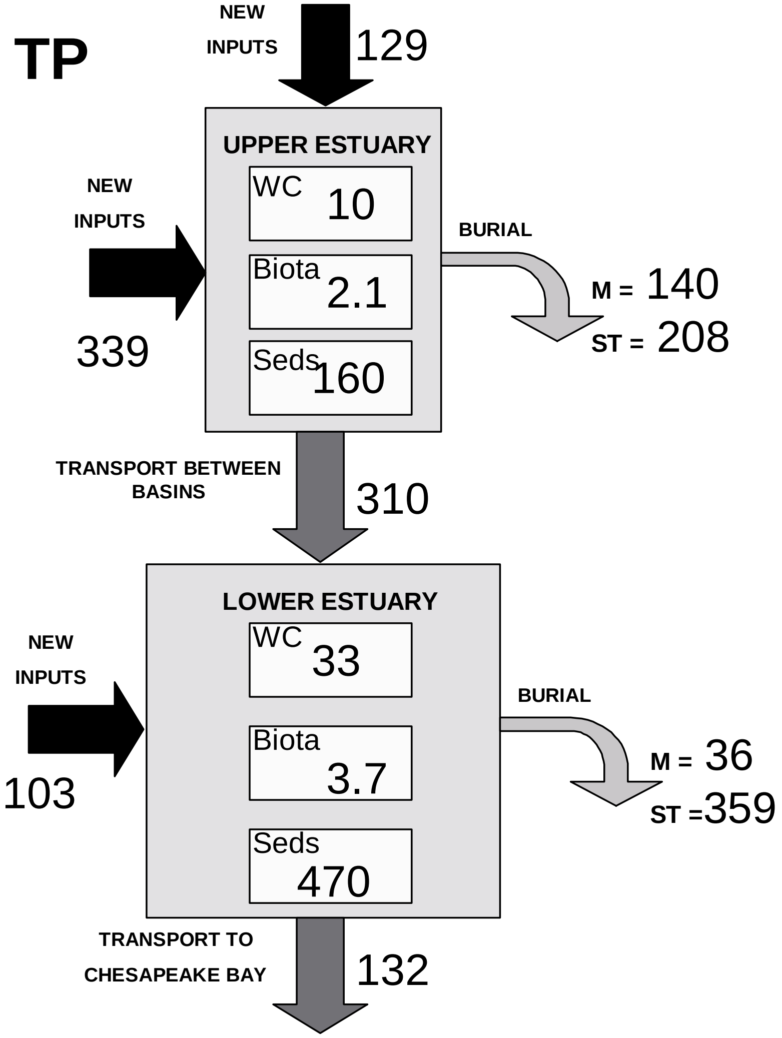

TN
NEW
INPUTS
1933
UPPER ESTUARY
WC 89
Biota 50
Seds 460
NEW
INPUTS
3456
BURIAL
M = 789
ST = 582
DENITRIFICATION
M = 850
ST = 285
TRANSPORT
BETWEEN BASINS
2929
LOWER ESTUARY
WC 465
Biota 74
Seds 1580
NEW
INPUTS
1239
BURIAL
M = 204
ST =1337
DENITRIFICATION
M = 159
ST =1423
TRANSPORT TO
CHESAPEAKE BAY
877

Figure 13b


TP
NEW
INPUTS
129
UPPER ESTUARY
WC 10
Biota 2.1
Seds 160
NEW
INPUTS
339
BURIAL
M = 140
ST = 208
TRANSPORT BETWEEN
BASINS
310
LOWER ESTUARY
WC 33
Biota 3.7
Seds 470
NEW
INPUTS
103
BURIAL
M = 36
ST =359
TRANSPORT TO
CHESAPEAKE BAY
132

List of Tables

BNR periods. Data were from the Chesapeake Bay Water Quality Monitoring Program (2001).

Table 8. Summary of macrobenthic infaunal biomass and N and P stock in the upper and lower portions of the Patuxent River estuary. Data were averaged by month for the period 1985-1999 and then averaged by seasons (Winter = Dec-Feb; Spring = Mar-May; Summer = Jun-Aug; Fall = Sep-Nov). Percent nitrogen and phosphorus of ash-free dry weight material was taken to be 15% and 0.62%, respectively. Biomass data were from the Chesapeake Bay Benthic Monitoring Program (2001).

Table 9. Estimates of annual average particulate nitrogen (PN) and phosphorus (PP) in the surface 2 cm of sediments in the Patuxent River estuary. Data are from Boynton et al. (1980), Boynton et al. (1995) and Boynton and Rohland (1998). There were not sufficient data available to make pre and post-BNR estimates. Seasonal variations in surficial sediment PN and PP were small and erratic.

Table 10. Summary of estimates of annual TN and TP exports from the Patuxent River estuary to Chesapeake Bay. Negative value indicates net annual import of TP from Chesapeake Bay to the Patuxent River estuary.

Table 11. Summary of sediment ammonium and phosphate releases in the oligohaline and mesohaline regions of the Patuxent River estuary. Data were from Boynton et al (1982a) and Boynton and Rohland (1998). Data were not available for the tidal-fresh portion of the estuary. Most data were collected during summer periods, fewer during spring and fall and only scattered observations during winter. Composite seasonal patterns of ammonium and phosphate flux indicated that highest values always occurred during summer. Spring and fall fluxes were about 40% of summer values and winter fluxes were about 10% of summer values. These proportions are reflected in the table.

Table 12. Summary of macrozooplankton abundance and excretion rates in the Patuxent River estuary. Zooplankton abundance data were from Chesapeake Bay Zooplankton Monitoring Program (2001). Macrozooplankton excretion rates were computed using the relationship developed by Mauchline (1998). Data were not available for the oligohaline portion of the estuary.

Table 13. A summary of seasonal and annual primary production estimates from three locations in the Patuxent River estuary during pre and post-BNR periods. Data were collected by the Chesapeake Bay Phytoplankton Monitoring Program (2001). Measurements were based on C^{14} incubations in constant light incubators. Volumetric rates were converted to areal rates by assuming measured rate represented P_{max} at the surface and production was a linear function of light to the depth of 1% light penetration. Euphotic depth was determined from secchi measurements.

Table 14. Whole system scale estimates of nitrogen (NH_4 and DIN) and phosphorus (PO_4) inputs, recycle rates from estuarine sediments (Table 11) and macrozooplankton (Table 12) and phytoplankton uptake rates of NH_4 and PO_4. Phytoplankton demand for

N and P was estimated using a Redfield C:N:P ratio of 106:16:1 and primary production rates provided in Table 13. Surface areas for upper and lower estuary were 26 x 10^6 and 117 x 10^6 m^2, respectively.

Table 15. A summary of nitrogen losses due to denitrification in tidal marshes and sub-tidal estuarine sediments of the Patuxent River estuary.

Table 16. Summary of sub-system areas, sediment deposition rates, sediment composition, and areal and whole-system annual PN and PP burial rates for major subsystems of the upper and lower Patuxent River estuary.

Table 17. Estimates of vertical accretion rates and long-term PN and PP burial rates measured in a variety of wetlands using radiotracer techniques. This table was adapted from Greene (2005a).

Table 18. A comparison of earlier (Boynton et al. 1995) and current TN and TP nutrient budgets for the Patuxent River estuary. In the earlier budget marshes were considered to be neutral regarding TN and TP inputs and losses, export to Chesapeake Bay was computed by subtracting internal losses from all external inputs and septic inputs were included in the diffuse term. Areal loads have units of g N or P m^{-2} yr^{-1}.

Table 1. Summary of pre (1985) and post (1995) BNR human population and 1990 land uses for three sub-basins and the full Patuxent River basin. Sub-basin divisions are shown in Figure 1. Tilled land includes both conventional and conservation tillage, Urban includes both pervious and impervious residential and urban areas, Open Space is non-agricultural and non-forest lands (e.g., golf courses). Data are from Chesapeake Bay Watershed Model Land Use and Linkages to the Airshed and Estuarine Models (2000).

Locations	**Pop Density, indiv km-2**			**Forest**	**Tilled Land**	**Pasture and Hay**	**Urban**	**Open Space**	**Non-Tidal Waters**	**Totals**
	Pre-BNR	**Post-BNR**								
Upper Basin	261	356	***km2***	364	129	94	209	106	7	910
			%	40.0	14.2	10.3	23.0	11.7	0.8	
Middle Basin	135	154	***km2***	419	137	78	239	109	9	991
			%	42.0	14.0	8.0	24.0	11.0	1.0	
Lower Basin	104	157	***km2***	211	35	20	74	32	5	377
			%	56.0	9.0	5.0	20.0	8.0	1.0	
Basin Totals	181	235	***km2***	995	302	191	522	247	21	2278
			%	44.0	13.0	8.0	23.0	11.0	1.0	

Table 2. Highest and lowest average daily nutrient loading rates, and years when these were observed, during the 13 year time-series. All point, diffuse, direct atmospheric and septic inputs were included. Data sources listed in Tables 3-5 and Figure 9.

Loading Category	Average Loads, kg N or P day^{-1}			
	TN	DIN	TP	DIP
Highest	8574	6153	759	414
(year)	1996	1989	1993	1985
Lowest	4276	3218	207	113
(year)	1991	1991	1991	1991

Table 3. Estimates of atmospheric N and P loads directly to the surface waters of the Patuxent estuary. The upper portion of the table indicates areal N delivery rates based on data collected at Wye, MD (NADP 2001). P delievery rates are the same as those used in Boynton et al. (1995). The lower table provides N and P delivery rates to the upper (HoT to Benedict) and lower estuary (Benedict to estuary mouth). Direct atmospheric deposition to surface waters was not estimated for the region above HoT because of the very small surface area of the river. Pre and post BNR periods are not differentiated. Nitrogen wet fall data were averaged from 1984-1999, NH_x dry deposition from 1997-1999 and HNO_3/NO_3 dry deposition from 1992-1997. Seasonal average total N deposition rates do not include estimates of organic N. Units in the upper and lower table are mg N or P m^{-2} $month^{-1}$ and kg N or P day^{-1}, respectively.

LOCATION	SEASON	N Wet Fall (NH_x+NO_3)	NHx Dry Deposition	HNO3/NO3 Dry Deposition	Organic N Deposition	Total N Deposition	P Wet Fall (PO4)	Total P Wet Fall
NADP Site at Wye, MD	Winter	50.0	11.5	10.5	na	72.0	na	na
	Spring	74.7	3.8	14.2	na	92.7	na	na
	Summer	91.6	-6.3	12.9	na	98.2	na	na
	Fall	49.4	6.0	8.5	na	63.9	na	na
	Ann Avg	66.4	3.8	11.5	17.4	99.0	1.3	5.3

Patuxent Estuary	SEASON	N Wet Fall (NH_x+NO_3)	NHx Dry Deposition	HNO3/NO3 Dry Deposition	Organic N Deposition	Total N Deposition	P Wet Fall (PO4)	Total P Wet Fall
Benedict	Spring	63.8	3.2	12.1	na	79.2		
	Summer	78.3	-5.4	11.0	na	83.9		
	Fall	42.2	5.1	7.2	na	54.6		
	Ann Avg	56.8	3.2	9.8	14.8	84.7	1.1	4.5
Benedict to Mouth	Winter	182.4	42.0	38.3	na	262.7		
	Spring	272.6	13.9	51.8	na	338.3		
	Summer	334.2	-23.0	47.1	na	358.3		
	Fall	180.3	21.9	30.9	na	233.1		
	Ann Avg	242.4	13.7	42.0	63.3	361.4	4.7	19.3

Table 4. A summary of point source N and P loads to the Patuxent River above and below the HoT. All entries have units of kg N or P day^{-1}. The pre and post BNR periods are 1986-1990 and 1993-2000, respectively. The location of HoT and major sewage treatment plants are shown in Figure 1. DIN = ammonium, nitrite, and nitrate; TN = DIN plus dissolved and particulate organic N; DIP = dissolved inorganic phosphorus; TP = DIP plus dissolved organic and particulate phosphorus. Seasons were defined as: winter (Dec-Feb), Spring (Mar-May), Summer (Jun-Aug), and Fall (Sep-Nov). Data in this table were from Chesapeake Bay Program (2001) and Wiedeman and Cosgrove (1998).

		DIN		**TN**		**DIP**		**TP**	
LOCATION	**SEASON**	**Pre-BNR**	**Post-BNR**	**Pre-BNR**	**Post-BNR**	**Pre-BNR**	**Post-BNR**	**Pre-BNR**	**Post-BNR**
Above HoT	Winter	1387	741	1614	909	85.1	33.6	131.9	56.4
	Spring	1443	638	1656	815	85.3	42.7	127.5	63.3
	Summer	1339	457	1511	591	82.4	35.5	116.1	52.5
	Fall	1349	528	1527	659	84.0	44.0	120.0	54.8
	Ann Avg	1379	591	1577	744	84.2	38.9	123.9	56.7
Below HoT	Winter	699	908	752	966	45.7	43.6	53.2	48.9
	Spring	694	249	763	298	53.8	41.2	61.3	45.7
	Summer	674	91	724	132	57.2	50.4	64.2	53.3
	Fall	696	372	739	421	54.5	47.3	61.3	50.9
	Ann Avg	691	405	744	454	52.8	45.6	60.0	49.7

Table 5. Estimates of septic system N discharges to the middle and lower Patuxent River estuary. Data were from Chesapeake Bay Watershed Model Land Use and Linkages to the Airshed and Estuarine Models(2000).

Time Period	Middle Basin (kg day^{-1})	Lower Basin (kg day^{-1})
Pre-BNR (1985-1990)	222	72
Post-BNR (1993-1997)	258	84

Table 6. A summary of annual average N and P stocks in the upper (tidal fresh and oligohaline) and lower (mesohaline) regions of the Patuxent River estuary. Pre and post-BNR data have been averaged in this summary. All values as kg N or P x 10^3. Data sources and details were provided in Tables 7 - 10.

Nutrient Stock	Nutrient Type	Upper Estuary	Lower Estuary	Total
Water Column	TN	89	465	554
	TP	10	33	43
	DIN	46	123	169
	DIP	2	9	11
Sediments	TN	460	1580	2040
	TP	160	470	630
Benthic Invertebrates	TN	49	70	119
	TP	2	3	5
Macro-Zooplankton	TN	1.05	3.80	4.85
	TP	0.13	0.70	0.83
Totals	TN			2718
	TP			679

Table 7. Mean seasonal and annual N and P concentrations in the water column for the upper and lower Patuxent River estuary during pre (1986-1990) and post (1993-2000) BNR periods. Data are from the Chesapeake Bay Water Quality Monitoring Program (2001).

Nitrogen Concentrations, mg N l^{-1}

Pre-BNR

	Upper Estuary			Lower Estuary		
Month	TN	NO_{23}	NH_4	TN	NO_{23}	NH_4
Winter	2.39	1.35	0.22	0.82	0.18	0.04
Spring	2.00	1.07	0.13	0.92	0.27	0.06
Summer	1.40	0.36	0.10	0.77	0.07	0.12
Fall	1.63	0.62	0.11	0.72	0.09	0.08
AVG	1.86	0.85	0.14	0.81	0.15	0.08

Post-BNR

	Upper Estuary			Lower Estuary		
Month	TN	NO_{23}	NH_4	TN	NO_{23}	NH_4
Winter	1.98	1.18	0.19	0.75	0.20	0.02
Spring	1.44	0.69	0.08	0.95	0.30	0.04
Summer	0.99	0.18	0.06	0.73	0.05	0.07
Fall	1.08	0.24	0.06	0.58	0.03	0.02
AVG	1.37	0.57	0.10	0.75	0.15	0.04

Phosphorus Concentrations, mg P l^{-1}

Pre-BNR

	Upper Estuary		Lower Estuary	
Month	TP	PO_4	TP	PO_4
Winter	0.193	0.029	0.050	0.009
Spring	0.198	0.035	0.051	0.010
Summer	0.211	0.054	0.074	0.026
Fall	0.209	0.047	0.077	0.026
AVG	0.203	0.041	0.063	0.018

Post-BNR

	Upper Estuary		Lower Estuary	
Month	TP	PO_4	TP	PO_4
Winter	0.148	0.025	0.033	0.004
Spring	0.153	0.029	0.045	0.007
Summer	0.148	0.045	0.058	0.016
Fall	0.172	0.037	0.052	0.018
AVG	0.155	0.034	0.047	0.011

Summary of macrobenthic infaunal biomass and N and P stock in the upper and lower
of the Patuxent River estuary. Data were averaged by month for the period 1985-1999
averaged by seasons (Winter = Dec-Feb; Spring = Mar-May; Summer = Jun-Aug; Fall =
). Percent nitrogen and phosphorus of ash-free dry weight material was taken to be 15%
%, respectively. Biomass data were from the Chesapeake Bay Benthic Monitoring
(2001).

Infaunal Biomass		***Infaunal N and P Stock***			
Upper Estuary	***Lower Estuary***	***Upper Estuary***		***Lower Estuary***	
g (AFDW) m^{-2}	***g (AFDW) m^{-2}***	***g N m^{-2}***	***g P m^{-2}***	***g N m^{-2}***	***g P m^{-2}***
8.1	1.9	1.22	0.050	0.29	0.012
15.1	7.8	2.27	0.094	1.17	0.048
13.4	5.5	2.01	0.083	0.82	0.034
13.3	1.7	2.00	0.082	0.26	0.011
12.5	4.2	1.87	0.077	0.63	0.026

Table 9. Estimates of annual average particulate nitrogen (PN) and phosphorus (PP) in the surface 2 cm of sediments in the Patuxent River estuary. Data are from Boynton et al. (1980), Boynton et al. (1995) and Boynton and Rohland (1998). There were not sufficient data available to make pre and post-BNR estimates. Seasonal variations in surficial sediment PN and PP were small and erratic.

Estuary Region	Sediment PN, % wgt	Sediment PP, % wgt	Sediment Volume g cm^{-3}	PN Stock g N m^{-2}	PP Stock g Pm^{-2}
Lower Estuary	0.31	0.093	0.23	14.3	4.3
Upper Estuary	0.35	0.125	0.25	17.5	6.3

Table 10. Summary of estimates of annual TN and TP exports from the Patuxent River estuary to Chesapeake Bay. Negative value indicates net annual import of TP from Chesapeake Bay to the Patuxent River estuary.

Study / Computation	**Observation Years**	**TN** kg N x 10^6 y^{-1}	**TP** kg P x 10^6 y^{-1}	**Source**
Patuxent Nutrient Budget (Inputs - Internal Losses)	1985-1986	0.21	-0.060	Boynton et al. 1995
Hydrodynamic/Water Quality Model	1985-1986	0.33	0.020	Cerco and Cole (1992) in Boynton et al (1995)
Patuxent Box Model				This study
Pre-BNR	1986-1990	0.45	0.050	
Post-BNR	1993-2000	0.32	0.048	

Table 11. Summary of sediment ammonium and phosphate releases in the oligohaline and mesohaline regions of the Patuxent River estuary. Data were from Boynton et al (1982a) and Boynton and Rohland (1998). Data were not available for the tidalfresh portion of the estuary. Most data were collected during summer periods, fewer during spring and fall and only scattered observations during winter. Composite seasonal patterns of ammonium and phosphate flux indicated that highest values always occurred during summer. Spring and fall fluxes were about 40% of summer values and winter fluxes were about 10% of summer values. These proportions are reflected in the values in the table.

	Oligohaline		**Mesohaline**	
Pre-BNR (1986-1990) Seasons	Ammonium uMoles N m^{-2} h^{-1}	Phosphate uMoles P m^{-2} h^{-1}	Ammonium uMoles N m^{-2} h^{-1}	Phosphate uMoles P m^{-2} h^{-1}
Winter	31	4.1	23	2.2
Spring	126	16.3	93	8.9
Summer	314	40.7	232	22.2
Fall	126	16.3	93	8.9
Annual	149	19.4	110	10.6
Post-BNR (1993-1999) Seasons	Ammonium uMoles N m^{-2} h^{-1}	Phosphate uMoles P m^{-2} h^{-1}	Ammonium uMoles N m^{-2} h^{-1}	Phosphate uMoles P m^{-2} h^{-1}
Winter	43	4.2	30	3.2
Spring	171	16.8	119	13.0
Summer	428	42.2	298	32.4
Fall	171	16.8	119	13.0
Annual	203	20.0	142	15.4

Table 12. Summary of macrozooplankton abundance and excretion rates in the Patuxent River estuary. Zooplankton abundance data were from Chesapeake Bay Zooplankton Monitoring Program (2001). Macrozooplankton excretion rates were computed using the relationship developed by Mauchline (1998). Data were not available for the oligohaline portion of the estuary.

	Tidalfresh		**Mesohaline**	
Pre-BNR (1986-1990) **Seasons**	Zooplankton Abundance Number m^{-3}	Zooplankton NH_3 Recycle mg N m^{-2} d^{-1}	Zooplankton Abundance Number m^{-3}	Zooplankton NH_3 Recycle mg N m^{-2} d^{-1}
Winter	10395	1.8	8856	0.9
Spring	27966	11.9	36283	22.5
Summer	14715	11.3	8446	11.5
Fall	6514	2.0	7349	5.8
Annual	14898	6.7	15233	10.2
Post-BNR (1993-1999) **Seasons**	Zooplankton Abundance Number m^{-3}	Zooplankton NH_3 Recycle mg N m^{-2} d^{-1}	Zooplankton Abundance Number m^{-3}	Zooplankton NH_3 Recycle mg N m^{-2} d^{-1}
Winter	123712	15.6	7239	1.2
Spring	173055	87.3	49967	31.7
Summer	110915	99.0	11643	12.3
Fall	29212	12.3	8437	4.7
Annual	109223	53.5	19322	12.5

Table 13. A summary of seasonal and annual primary production estimates from three locations in the Patuxent River estuary during pre and post-BNR periods. Data were collected by the Chesapeake Bay Phytoplankton Monitoring Program (2001). Measurements were based on C^{14} incubations in constant light incubators. Volumetric rates were converted to areal rates by assuming measured rate represented P_{max} at the surface and production was a linear function of light to the depth of 1% light penetration. Euphotic depth was determined from secchi measurements.

Pre-BNR (1986-1990) **Seasons**	***Tidalfresh*** ***(mg C m^{-2} d^{-1})***	***Oligohaline*** ***(mg C m^{-2} d^{-1})***	***Mesohaline*** ***(mg C m^{-2} d^{-1})***
Winter	30	491	1003
Spring	599	232	1632
Summer	1655	1017	2486
Fall	1147	358	1256
Annual Average	858	524	1594
Annual Total (g C m^{-2} y^{1})	313	191	582

Post-BNR (1993-1999) **Seasons**	***Tidalfresh*** ***(mg C m^{-2} d^{-1})***	***Oligohaline*** ***(mg C m^{-2} d^{-1})***	***Mesohaline*** ***(mg C m^{-2} d^{-1})***
Winter	40	65	654
Spring	677	393	1585
Summer	1332	943	1750
Fall	858	489	1026
Annual Average	727	472	1254
Annual Total (g C m^{-2} y^{1})	265	172	458

Table 14. Whole system scale estimates of nitrogen (NH_4 and DIN) and phosphorus (PO_4) inputs, recycle rates from estuarine sediments (Table 11) and macrozooplankton (Table 12) and phytoplankton uptake rates of NH_4 and PO_4. Phytoplankton demand for N and P was estimated using a Redfield C:N:P ratio of 106:16:1 and primary production rates provided in Table 13. Surface areas for upper and lower estuary were 26×10^6 and 117×10^6 m^2, respectively.

Input/Recycle/Uptake Component	**Upper Estuary, kg day^{-1}**						***Lower Estuary, kg day^{-1}***					
	Annual		**Summer**		**Winter**		**Annual**		**Summer**		**Winter**	
	NH_4/DIN	***PO_4***	***NH_4/DIN***	***PO_4***	***NH_4/DIN***	***PO_4***	***NH_4/DIN***	***PO_4***	***NH_4/DIN***	***PO_4***	***NH_4/DIN***	***PO_4***
Pre-BNR (1986-1990)												
New Inputs	4122	129	3558	129	4191	125	2510	80	1320	68	3702	68
Recycle												
Sediments	2524	212	2743	787	655	39	4560	966	9120	1924	912	192
Macrozooplankton	175	24	294	41	47	nd	265	37	300	41	105	nd
Total	2699	236	3037	828	702	39	4825	1003	9420	1965	1017	192
Uptake												
Phytoplankton	-3349	-463	-6484	-876	-1264	-175	-34726	-4806	-54382	-7526	-21840	-3023
Post-BNR (1993-1999)												
New Inputs	3576	243	2541	159	4177	189	2478	110	1136	75	4226	98
Recycle												
Sediments	1856	309	3739	816	374	81	5857	1410	11715	2820	1172	282
Macrozooplankton	1392	193	2574	356	406	nd	324	45	320	44	140	nd
Total	3248	502	6313	1172	780	81	6181	1455	12035	2864	1312	282
Uptake												
Phytoplankton	-2905	-402	-5508	-766	-252	-35	-27300	-3778	-38220	-5289	-14196	-1977

Table 15. A summary of nitrogen losses due to denitrification in tidal marshes and sub-tidal estuarine sediments of the Patuxent River estuary.

Estuarine Zone	Area of Zone ($m^2 * 10^6$)	Annual Average Denitrification Rate (umol N m^{-2} hr^{-1})[a]		Total Denitrification (Kg N yr^{-1})[b]
Sub-Tidal Estuarine Sediments				
Upper estuary	22.3	38		103925
Lower estuary	111.0	32		435617
			Total	**539542**
Tidal Marshes				
Upper estuary	22.8	111		310377
Lower estuary	5.9	80		57886
			Total	**368263**
		System Total		**907806**

[a] Estimates of sub-tidal denitrification rates for the upper estuary were from Twilley and Kemp (1987) as reported in Boynton et al. (1995). Lower estuary rates were based on data from Jenkins and Kemp (1984) and Cornwell (unpublished data). Tidal marsh rates of denitrification were from Greene (2005) and were spatially weighted (high, mid and low marshes) for upper estuary marshes but not weighted for the much smaller lower estuary marshes.

[b] Total denitrification was estimated as the product of marsh area and annual average denitrification rate.

Table 16. Summary of sub-system areas, sediment deposition rates, sediment composition, and areal and whole-system annual PN and PP burial rates for major subsystems of the upper and lower Patuxent River estuary.

Location	Sub-System Area (km^2)	Sediment Deposition Rate[a] (g dry sed m^{-2} yr^{-1})	Sediment Composition[b] PN (mgN g dry sediment^{-1})	Sediment Composition[b] PP (mgP g dry sediment^{-1})	Annual Burial Rate[c] PN (g N m^{-2} yr^{-1})	Annual Burial Rate[c] PP (g P m^{-2} yr^{-1})		Total Burial Rate[d] PN (kg N yr^{-1})	Total Burial Rate[d] PP (kg P yr^{-1})
Upper Estuary									
tidal marsh	22.8	2140	5.9	1.05	12.6	2.2		287873	51232
sub-tidal estuary	22.3	2722	3.5	1.25	9.5	3.4		212452	75876
							total	**500325**	**127107**
Lower Estuary									
tidal marsh	5.9	2140	5.9	1.05	12.6	2.2		74493	13257
sub-tidal estuary	111	1143	2.5	0.55	2.9	0.6		317183	69780
							total	**391676**	**83037**
						System Total		**892001**	**210145**

[a] Deposition rate estiamtes for the tidal marshes were from Pb^{210}-based measurements made by Merrill (1999) and Greene (2005); lower estuary sub-tidal deposition rates were from Pb^{210}-based measurements by Cornwell (unpublished data); upper estuary sub-tidal deposition rates were based on riverine plus diffuse source sediment inputs corrected for sediment deposition in adjacent tidal marshes and assuming no sediment transport into the lower estuary.

[b] Sediment composition data were from Merrill (1999) and Greene (2005) for tidal marsh habitats; upper estuary sub-tidal sediment PN and PP concentrations were from Boynton et al (1995) and lower estuary data were from Cornwell (unpublished data) and Boynton et al (1995).

[c] Annual areal burial rates were estimated as the product of deposition rate times PN or PP concentration at sediment depth where nutrient concentration change with further depth in the sediment column approached zero. In the tidal marshes this depth was about 20-30 cm and in the sub-tidal estuary about 5-10 cm.

[d] Total burial rates were estimated as the product of areal annual rates times the area of tidal marsh and sub-tidal estuary.

Table 17. Estimates of vertical accretion rates and long-term PN and PP burial rates measured in a variety of wetlands using radiotracer techniques. This table was adapted from Greene (2005a).

Wetland Type	Tracer Technique	Vertical Accretion (mm yr-1)	N Burial	P Burial	References
Brackish					
Barataria Bay, LA	^{137}Cs				Hatton et al. 1982
levee		14.0	25.0	2.4	
backmarsh		5.9	10.0	0.5	
Barataria Basin, LA	^{137}Cs				DeLaune et al. 1981
7 m inland		13.5	21.0	--	
45 m inland		7.5	13.4	--	
Choptank Estuary, MD	^{210}Pb	9.2	23.0	2.0	Merrill 1999
Monie Bay, MD	^{210}Pb	5.5	11.1	0.3	Merrill 1999
Tidal Freshwater					
Patuxent Estuary, MD	^{210}Pb	8.5	12.6	2.2	Greene 2005a
Otter Creek, MD	^{210}Pb	5.0	8.8	1.2	Merrill 1999
Freshwater					
Riparian Forest, WI	^{137}Cs	5 to 13	12.8	2.6	Johnston et al. 1984
Barataria Bay, LA	^{137}Cs				Hatton et al. 1982
levee		10.6	16.0	1.0	
backmarsh		6.5	9.0	0.5	
Everglades, FL	^{137}Cs	0.3 - 6.6	6.3 - 14.1	0.11 - 0.7	Craft and Richardson 1993

Table 18. A comparison of earlier (Boynton et al. 1995) and current TN and TP nutrient budgets for the Patuxent River estuary. In the earlier budget marshes were considered to be neutral regarding TN and TP inputs and losses, export to Chesapeake Bay was computed by subtracting internal losses from all external inputs and septic inputs were included in the diffuse term. Areal loads have units of g N or P m^{-2} yr^{-1}.

	(kg N or P x 10^6 yr^{-1})			
	Old Budget		New Budget	
	TN	TP	TN	TP
Nutrient Source				
Atmospheric	0.22	0.009	0.16	0.009
Point	0.83	0.116	0.44	0.039
Diffuse	0.68	0.070	1.69	0.124
Septic	0.00	0.000	0.13	0
Total	1.73	0.195	2.42	0.172
Areal Load	13.0	1.5	18.2	1.3
Internal Losses				
Burial				
Marshes	0.00	0.000	0.36	0.060
Sub-tidal	0.92	0.250	0.70	0.207
Denitrification				
Marshes	0.00		0.37	
Sub-tidal	0.54		0.62	
Total	1.46	0.250	2.05	0.267
Fisheries Yields	0.06	0.002	0.06	0.002

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