August 1994

Trends in Phosphorus, Nitrogen, Secchi Depth, and Dissolved Oxygen in Chesapeake Bay, 1984 to 1992

Chesapeake Bay Program

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Cooperative Agreement No. TCRD-93-08-01-000

CBP/TRS 115/94

August 1994

Printed by the U.S. Environmental Protection Agency for the Chesapeake Bay Program

ENDORSEMENT

The Chesapeake Bay Monitoring Subcommittee has reviewed the assumptions and methods of data analysis used in this report and finds them appropriate for the analysis conducted. The findings of this report are consistent with and supported by the analytical techniques employed.

ABSTRACT

The Chesapeake Bay Program (CBP) is a Federal-State partnership working to restore Chesapeake Bay. One of its primary goals is to improve water quality and habitat conditions for living resources. The CBP began monitoring water and habitat quality in 1984 and continues to sample the main stem and tributaries for their physical and chemical makeup.

Nutrient enrichment is a major water quality problem in Chesapeake Bay. Nutrients fuel phytoplankton growth, which has an adverse (reduction) effect on dissolved oxygen (DO) levels. Low DO levels threaten the existence of Chesapeake Bay's aquatic animals.

DO levels should increase if nutrient levels are reduced. A computer model predicted that a 40-percent reduction in nitrogen and phosphorus would reduce nutrient levels and cause an increase in DO levels in the main stem to Chesapeake Bay. Nitrogen and phosphorus control programs have been initiated. Trend analyses, involving various criteria, were performed over an 8-year period (from October 1984 through September 1992) to see how these programs affected water and habitat quality conditions in Chesapeake Bay.

Results of seasonal Kendall test analysis indicate that phosphorus levels decreased significantly baywide, especially in one upper Chesapeake Bay segment and two lower Chesapeake Bay segments. There were also marginally significant improvements in phosphorus levels in two upper Chesapeake Bay segments and in one lower Chesapeake Bay segment. Nitrogen levels were somewhat increased (marginally significant) in one segment of Chesapeake Bay. Secchi depths showed no significant trends baywide; however, there were marginally significant trends (improvements) in upper Chesapeake Bay. DO trends were not statistically significant baywide; however, segments at the mouth of Chesapeake Bay showed marginally significant degradation.

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ACKNOWLEDGMENTS

The Monitoring Subcommittee would especially like to express its gratitude to Peter Bergstrom and Marcia Olson for writing this report. The Monitoring Subcommittee would also like to express their gratitude to the field and lab crews that carefully and expertly collected and analyzed the water quality samples discussed in the report. A great many other people provided both information insights and support that contributed to the preparation of this report, and to all of them our heartfelt thanks.

ABBREVIATIONS

BDL	Below detection limit(s)
CBL	Chesapeake Biological Laboratory
CBP	Chesapeake Bay Program
CRL	(The U.S. Environmental Protection Agency's) Central Regional Laboratory (in Annapolis, Md.)
DIN	Dissolved inorganic nitrogen
DIP	Dissolved inorganic phosphorus
DO	Dissolved oxygen
KD	Light attenuation
MDE	Maryland Department of the Environment
MDL	Method detection limit(s)

ODU	Old Dominion University
P	Probability that an observed trend, correlation, or difference was due to chance
SAV	Submerged aquatic vegetation
TN	Total nitrogen
TP	Total phosphorus
VIMS	Virginia Institute of Marine Science
WY	Water year(s)

EXECUTIVE SUMMARY

The Chesapeake Bay Program (CBP) is a Federal-State partnership working to restore Chesapeake Bay. One of its main goals is to improve water quality conditions for living resources. The CBP started ambient water quality monitoring programs for Chesapeake Bay in 1984 to characterize current water quality, to assess trends in water quality over time, and to increase understanding of linkages between waster quality and living resources. Currently, over 150 stations in the tidal tributaries and main stem to Chesapeake Bay are sampled once or twice a month and analyzed for more than 20 physical and chemical parameters. The main stem to Chesapeake Bay is divided into 10 segments based on similar salinity circulation and geomorphology.

Nutrient enrichment is a major water quality problem in Chesapeake Bay. Spring and summer phytoplankton blooms, fueled by high nutrient levels, cause low dissolved oxygen (DO) levels in the summer when the plankton die and decompose. Low concentrations of DO can be lethal to Chesapeake Bay's aquatic animals. Thus, summer DO levels should improve if nutrient levels are reduced.

A computer model of Chesapeake Bay water quality predicted that 40 percent nitrogen and phosphorus load reductions would reduce ambient nutrient levels sufficiently to cause an increase in DO levels in the deeper areas of the main stem to Chesapeake Bay. The 1987 Chesapeake Bay Agreement and its 1992 amendments committed Pennsylvania, Maryland, Virginia, and the District of Columbia to achieve a 40-percent reduction of the 1985 nitrogen and phosphorus loads entering the main stem to Chesapeake Bay by the year 2000.

Both point source and nonpoint source reductions of nitrogen and phosphorus loads to Chesapeake Bay have been achieved since 1985. Trend analyses of ambient levels of nitrogen, phosphorus, DO, and related water quality parameters were performed to determine how these source reductions are affecting water quality conditions in Chesapeake Bay.

Trends in Chesapeake Bay main stem levels of total phosphorus (TP), dissolved inorganic phosphorus (DIP), total nitrogen (TN), dissolved inorganic nitrogen (DIN), Secchi depth, and DO were analyzed over 8 years (October 1984 through September 1992). Phosphorus trends were analyzed with the nonparametric seasonal Kendall test* and were classified as marginally sufficient improvements ($P<0.05$) or significant improvements ($P<0.01$). Data from 49 main stem monitoring stations were spatially averaged over 10 main stem segments using a three-dimensional interpolator. There were no adjustments for river flow, although correlations of Secchi depth with flow and trends in flow were examined. Monthly median values were analyzed because sampling frequency varied seasonally. Method detection limits declined over time for some parameters, but any trends that could have been caused by declining detection limits were eliminated.

Parameters important to submerged aquatic vegetation (SAV) growth were analyzed for trends over the whole year and also over the 7-month SAV growing season (April through October). DO trends were only analyzed for the four warm weather months (June through September) when most low DO conditions occur. Percent change estimates were

*The Kendall slope is a measurement of trend expressed as mg/L/yr.

based on the mean concentration for the first water year (October 1984 through September 1985) and a projection for the last water year based on the seasonal Kendall slope.

Interannual changes in Susquehanna River flow could produce the appearance of trends in water quality if there was a trend in flow, and water quality was correlated with flow; however, there were no significant trends in mean monthly Susquehanna River flow over any time period. In contrast, there were significant positive and negative correlations between the log mean monthly Susquehanna River flow and upper Chesapeake Bay water quality, but they did not follow a simple pattern.

TP concentrations showed a statistically significant downward trend ($P<0.01$) baywide, especially in one upper Chesapeake Bay segment and two lower Chesapeake Bay segments. There were also marginally significant improvements ($P<0.05$) in two upper Chesapeake Bay segments and in one lower Chesapeake Bay segment. The median baywide percent change (decline) in TP over 8 years (1984 to 1992) was 16 percent, plus or minus 8 percent (90 percent confidence interval). DIP showed significant downward trends over 12 months at the mouth of Chesapeake Bay and over 7 months (April through October) in central Chesapeake Bay, but the trend was not significant baywide.

TN concentrations showed a marginally significant increasing trend (degradation, $P=0.027$) in Mobjack Bay, including the mouth of the York River; however, there was no significant trend baywide or in any other segments. The possible increase in TN in Mobjack Bay was probably related to similar upward trends in TN in the York River. DIN showed no significant trends in any segments, although high detection limits made it impossible to assess trends in nitrogen concentrations in several lower Chesapeake Bay segments.

Secchi depths showed no significant trends baywide over a period of 7 or 12 months or for any segment over 12 months. There were marginally significant upward trends (improvements) in upper Chesapeake Bay over the 7-month SAV growing season (April through October). These trends may be related to statistically significant inverse correlations between the April-through-September Secchi depth and the mean monthly Susquehanna River flow, although there were no significant trends in flow. Secchi depth is not measured in the Susquehanna River, so it is not known whether there were trends in Secchi depth there.

DO concentration trends as well as trends in several metrics calculated from the concentration were examined. These trends included oxygen delta (the difference between DO at saturation and the actual DO concentration) and DO deficit (converting the delta concentration to the mass of DO that would have to be added to bring all the water in that segment to saturation). The volumes of water in each segment that were below four benchmark DO concentrations (5, 3, 1, and 0.2 mg/L) were also analyzed for trends.

DO concentration and the four metrics for volumes below specific concentrations had no statistically significant trends ($P>0.05$) in any segments in the June-to-September period. The mouth of Chesapeake Bay showed marginally significant degradation in both DO delta and DO deficit. However, DO concentrations are generally high in the mouth of Chesapeake Bay and DO delta is quite low, so these trends are unlikely to have any negative impact on aquatic animals living near the mouth of Chesapeake Bay.

Executive Summary Table. Summary of trend results (October 1984 through September 1992).

Parameter	No. of Months	Main Stem CBP Segments										
		All	CB1	CB2	CB3	CB4	CB5	CB6	CB7	CB8	WE4	EE3
TP	12	I	IM	I	IM	–	–	I	IM	I	–	–
DIP	12	–	–	–	–	–	–	–	–	I	–	–
DIP	7	–	–	–	–	I	–	–	–	–	–	–
TN	12	–	–	–	–	–	–	–	–	–	DM	–
DIN	12	–	–	–	–	–	–	+	+	–	+	+
DIN	7	–	–	–	–	–	–	+	+	–	+	+
Secchi Depth	12	–	–	–	–	–	–	–	–	–	–	–
Secchi Depth	7	–	IM	IM	–	–	–	–	–	–	–	–
DO Concentration	4	–	–	–	–	–	–	–	–	–	–	–
DO Delta	4	–	–	–	–	–	–	–	–	DM	–	–
DO Deficit	4	–	–	–	–	–	–	–	–	DM	–	–
DO<0.2	4	–	–	–	–	–	–	–	–	–	–	–
DO<1.0	4	–	–	–	–	–	–	–	–	–	–	–
DO<3.0	4	–	–	–	–	–	–	–	–	–	–	–
DO<5.0	4	–	–	–	–	–	–	–	–	–	–	–

Legend and note:
I—Significant improvement ($P<0.01$).
IM—Marginally significant improvement ($P<0.05$).
DM—Marginally significant degradation.
Dash—No significant trend ($P>0.05$).
+—DIN trends could not be assessed in these segments because detection limits did not stop declining until July 1990.
7 months—April through October only, same as SAV growing season in lower salinity zones; 4 months—June through September only, used as period of anoxia in three-dimensional model analyses.
DO data were not analyzed in EE3.
See text for explanation of DO delta, DO deficit, and DO volumes below the four concentrations.

INTRODUCTION

The Chesapeake Bay Program (CBP) is a Federal-State partnership working to restore Chesapeake Bay. One of the main goals of the CBP is to improve water quality conditions for Chesapeake Bay living resources. CBP's water quality monitoring programs were started in 1984 to characterize current water quality and to assess trends in water quality over time. Presently, over 150 stations are sampled once or twice a month and analyzed for more than 20 physical and chemical parameters.

A major water quality threat in Chesapeake Bay is low summertime concentrations of DO, a condition which is potentially lethal to Chesapeake Bay aquatic animals. Spring and summer phytoplankton blooms, fueled by high nutrient levels, cause low DO levels during the summer when the plankton die and decompose. Thus, summertime DO levels should improve if nutrient levels are reduced.

A computer model of Chesapeake Bay water quality predicted that 40 percent nitrogen and phosphorus load reductions would reduce ambient nutrient levels sufficiently to cause an increase in DO levels in the deeper areas of the main stem of Chesapeake Bay. The 1987 Chesapeake Bay Agreement and its 1992 amendments committed Pennsylvania, Maryland, Virginia, and the District of Columbia to achieve a 40-percent reduction of the 1985 nitrogen and phosphorus loads entering the main stem of Chesapeake Bay by the year 2000.

Both point and nonpoint source reductions of nitrogen and phosphorus loads to Chesapeake Bay have been achieved since 1985.[1] Trend analyses of ambient levels of nitrogen, phosphorus, DO, and related water quality parameters were performed to determine how these source reductions are affecting water quality conditions in Chesapeake Bay.

Trends in Chesapeake Bay main stem levels of total phosphorus (TP), total nitrogen (TN), and DO were analyzed over 6 years.[2–4] This report updates the previous trend analyses using 8 years of main stem monitoring data, spanning October 1984 through September 1992.

TP levels declined significantly between 1984 and 1990[3]; however, TN and DO levels showed little or no change over the same period.[2, 4] This update, with 2 additional years of data, was conducted to see if these trends continued. This update also added statistical analyses of trends in DO and trend analyses of three additional parameters: dissolved inorganic phosphorus (DIP), dissolved inorganic nitrogen (DIN), and Secchi depth (a measure of water clarity). These three parameters were added because their levels affect submerged aquatic vegetation (SAV) growth[5] and are also closely related to phytoplankton growth.

METHODS

PARAMETERS ANALYZED AND DATA PREPARATION

The CBP monitoring program and details of sample collection and analytical chemistry methods used are described in three previous reports.[2–4] The following water quality parameters were analyzed in this report:

- TP concentration

- DIP concentration
- TN concentration
- DIN concentration
- Secchi depth
- DO concentration.

The following calculated metrics derived from the water quality parameters were also analyzed in this report:

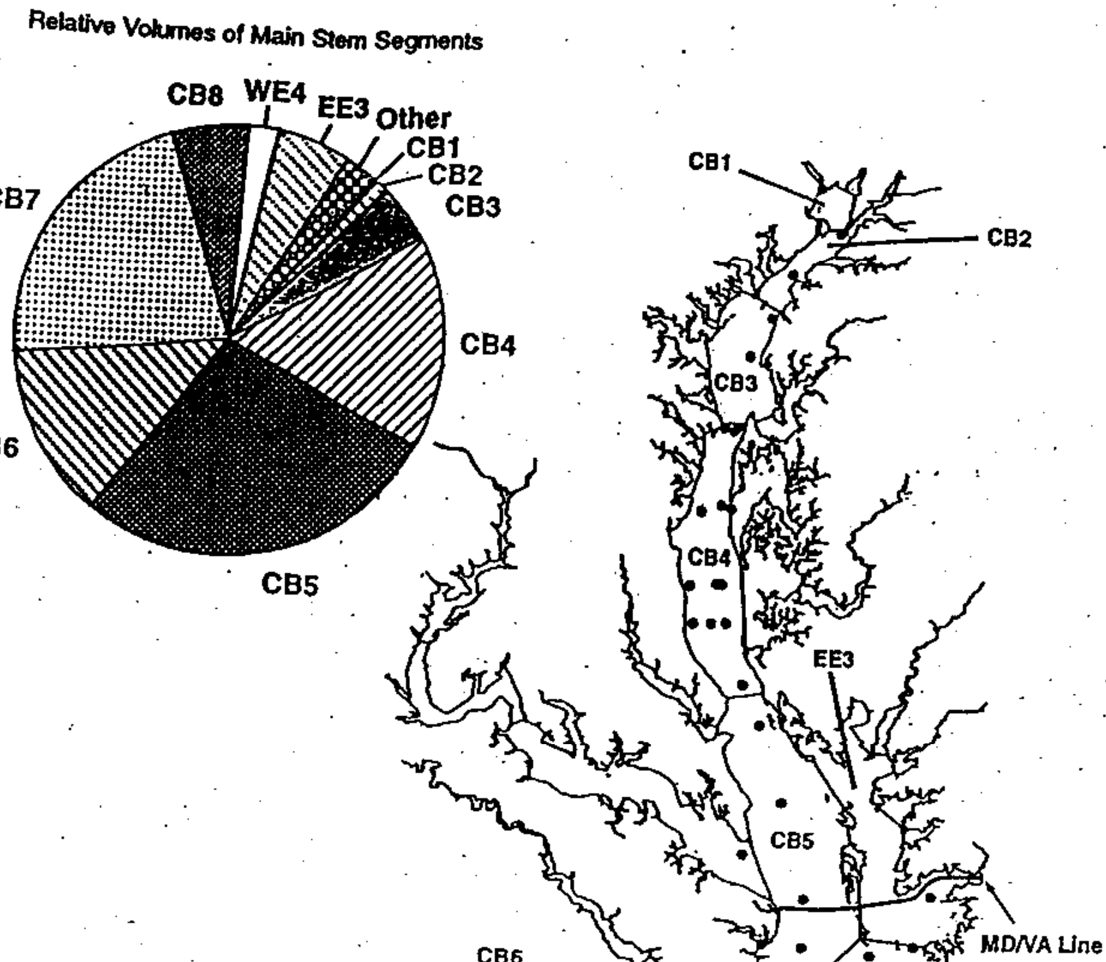
- DO delta: the difference between DO saturation concentration and observed DO concentration
- DO deficit: the difference between DO mass at saturation and the observed mass of DO
- Volume of water with DO concentrations below 5, 3, 1, and 0.2 mg/L.

A three-dimensional interpolator[6] was used to estimate baywide main stem mean concentrations and mean concentrations in each CBP main stem segment (CB1 to CB8, EE3, and WE4). (See Figure 1.) Data from all sampling depths were used, except for Secchi depth, which has only one measurement per station. The annual periods used were water years (WY), from October through September (which include a complete hydrological cycle). The monitoring data from October 1984 through September 1992 were used; the previous reports included data through September 1990. The possible outliers that were removed from nitrogen and phosphorus data in the two previous reports[3,4] were checked by the data submitters and were either verified or corrected. The Maryland monitoring data used in this report were resubmitted in 1992, incorporating numerous data corrections; there were also corrections made to Virginia monitoring data in 1992. Because the data had been verified or corrected, the analyses in this report used data as currently stored in the CBP data base without deleting any possible outliers.

Data were not adjusted for river flow. In the Chesapeake Bay monitoring program, flow is only measured at the fall line stations, and only the Susquehanna River fall line station at Conowingo, Md. is close enough to the main stem to have a direct impact on it.[7] Trend tests were performed on mean monthly Susquehanna River flow, and correlations between log mean monthly flow and all parameters were calculated to estimate the degree of association. However, a simple flow adjustment in the main stem of Chesapeake Bay is not possible because it would assume that flow has either an immediate effect on concentrations or an effect after a fixed time lag. The effects of Susquehanna River flow on main stem water quality must be highly variable because "Chesapeake Bay's response to a freshet is a function of Chesapeake Bay's recent history and cannot be linearized or easily predicted."[8]

TREND ANALYSIS METHODS

Trend analyses of nitrogen, phosphorus, and DO were performed on monthly mean concentrations, spatially interpolated in three dimensions. Trend analyses of Secchi depth were performed on monthly mean depths interpolated in two dimensions. Flow data used were monthly means of daily Susquehanna River flows measured at Conowingo, Md.



period. This update, with 2 additional years of data, was conducted to see if these trends continued. This update also added statistical analyses of trends in DO and trend analyses of three additional parameters: dissolved inorganic phosphorus (DIP), dissolved inorganic nitrogen (DIN), and Secchi depth (a measure of water clarity). These three parameters were added because their levels affect submerged aquatic vegetation (SAV) growth[5] and are also closely related to phytoplankton growth.

METHODS

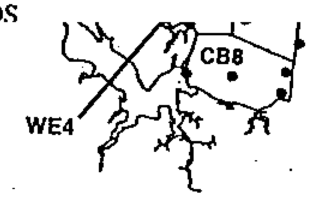


Figure 1. CBP main stem monitoring stations and segments.

Nutrient and Secchi monthly means for segment EE3 were estimated without using data from the Maryland tributary monitoring stations in this segment because the tributary data were not available for the whole time period. DO data were not estimated for segment EE3 because it has higher spatial variability than the other parameters. Some of the metrics used for DO were slightly different from those used before. Trend analyses were performed only on interpolator output, not on concentrations observed at individual stations (except for flow). Trend analyses were performed on DO, which was not done previously.[2] Trend analyses for some parameters were performed on data from either April through October or June through September to correspond with the period of maximum effects on living resources. A nonparametric trend test was substituted for the parametric test used in the previous analyses.[3, 4]

The trend test used was the seasonal Kendall nonparametric test, which tests for monotonic trends. Monotonic trends need not be linear, but they are assumed to have a slope that is consistently positive or negative.[9] Trends that change from positive to negative slope (or vice versa) may not be detected. The previous nitrogen and phosphorus reports used linear, quadratic, and cubic parametric regression to assess both monotonic and nonmonotonic trends.[3, 4] The seasonal Kendall test was performed with a custom SAS program[10] using the method described by Gilbert.[9]

The seasonal Kendall test assumes the successive monthly values are independent or have no serial correlation. This is not often true of Chesapeake Bay water quality data[3, 4]; serial correlation tends to inflate the significance of the test.[9] There are modifications to the seasonal Kendall test that account for serial correlation[9]; however, they assume that the correlation has a fixed structure, while the actual correlations are quite variable.[3, 4] Thus, the test was used without correcting for serial correlation. To account for the possible inflation of significance levels that results from serial correlation, *P* values falling between 0.05 and 0.01 were termed "marginally significant" because their actual *P* value might be more than 0.05. *P* values less than 0.01 were termed "significant" because their actual *P* value was probably less than 0.05. A similar approach to determining significant trends with the seasonal Kendall test was used and reported as part of the 1991 re-evaluation of the Chesapeake Bay nutrient reduction strategy,* except that marginally significant trends were not identified.

The tables of seasonal Kendall test results list the sample size in months, the median trend slope in mg/L per year, and the Z** score for significant trend. A large Z score indicates a statistically significant monotonic trend: Z between 1.96 and 2.58 was considered "marginally significant," with P between 0.05 and 0.01; $Z>2.58$ was considered "significant," with $P<0.01$. The χ^2 value for seasonality tests whether the trend is homogeneous over different months. A small χ^2 value and a large P value (>0.05) indicates there were no significant seasonal differences in the trend. (Trends were not upward in some seasons and downward in others.) Almost all parameters in which significant trends were found had homogeneous trends over different months. The results were corrected for ties or concentrations from the same month that are the same in 2 or more successive years. The results were also checked to see if ties affected more than 50 percent of the results for any

*"Water Quality Characterization Report for the 1991 Re-Evaluation of the Chesapeake Bay Nutrient Reduction Strategy," (draft). CBP, Annapolis, Md. (1991).

**Test statistic used to determine *P* value.

month. There were no cases when ties made up more than 50 percent of the observations for any month.

Percent change over 8 years (1984 to 1992) is shown for parameters and segments with statistically significant and marginally significant trends. This was calculated using the 1985 WY mean value (October 1984 through September 1985) and the median slope from the seasonal Kendall test:

$$\text{Percent Change} = \frac{\text{Slope (Per Year)} \times 8 \text{ Years}}{\text{1985 WY Mean}} \times 100 \ .$$

Multiplying the slope by the number of years gives the total estimated change over that period. The previous phosphorus and nitrogen trend reports[3, 4] used percent change values calculated using the means of the first and last years of data (1985 and 1990 WY). The advantage of using the seasonal Kendall slope to estimate the overall percent change is that it uses all the data. Percent change calculated with the median slope will not be affected as much if the last year of data had unusually high or low results. However, it will still be affected if the first year of data was unusually high or low. Using the seasonal Kendall slope also makes it possible to put confidence limits on the percent change estimate[9]; 90 percent confidence limits were used for the one parameter with a significant baywide change (for TP).

The trend line shown in the graphs of the data also came from the mean of the first year and the seasonal Kendall slope: The start point of the line was the 1985 WY mean, and the end point was calculated from the following equation:

$$\text{End Point} = \text{1985 WY Mean} + [\text{Slope (Per Year)} \times 8 \text{ Years}] \ .$$

Thus, the trend line represents the same data as the percent change estimate. The same percent change estimate could be calculated from the following equation:

$$\text{Percent Change} = \frac{\text{End Point} - \text{Start Point}}{\text{Start Point}} \times 100 \ .$$

Trend lines and percent change estimates are only shown for parameters and segments with statistically significant or marginally significant trends.

Statistically significant and marginally significant trends were called either "improvement" or "degradation." Declining levels are improvements for nutrients, DO delta, DO deficit, and DO volumes below specific concentrations. Increasing levels are improvements for Secchi depth and DO concentration.

What improvement and degradation mean in terms of the CBP efforts to preserve and restore Chesapeake Bay can be evaluated using the habitat requirements and CBP goals set for Chesapeake Bay's living resources. These have been established for SAV and for species sensitive to low DO levels. If there is an improving trend in an area that does not currently meet one of the SAV habitat requirements or DO goals, that trend will aid in living resource restoration efforts.

SAV habitat requirements have been established for three of the parameters analyzed: DIP, DIN, and Secchi depth.[5] The habitat requirements represent the maximum concentrations or the minimum Secchi depth that will permit SAV growth. They are based on growing season median values; the SAV growing season is April through October in most of Chesapeake Bay.[5] For this reason, trends in these three parameters were evaluated over the whole year (12 months) and also over the April through October period (7 months). There are also SAV habitat requirements for two parameters that were not analyzed in this report[5]: total suspended solids and chlorophyll *a*.

The benchmarks for improvements in DO are based on four target concentrations: 0.2, 1, 3, and 5 mg/L. The 0.2 mg/L benchmark is based on the anticipated effect of the 40 percent nutrient reduction strategy[1]: a reduction in the volume of anoxic waters (defined here as water with DO concentrations less than 0.2 mg/L). The last three benchmarks (1, 3, and 5 mg/L) were established by the Habitat Restoration Goal for DO.[11]

ADJUSTMENTS FOR CHANGING DETECTION LIMITS

CBP monitoring data have method detection limits (MDL), which represent the lowest detectable concentration of that parameter. Analytical results that are less than the MDL are censored by setting them to the MDL and are identified with a separate variable. Parameters with observations censored at the MDL pose two problems for trend analysis: They may bias the slope, since the detection limit values are greater than the true values, and they may produce a statistically significant trend when none existed if the MDL changed consistently over time. The first problem is avoided by the use of medians in the seasonal Kendall test. Censored data have no effect on the slope as long as the censored values make up less than half of the observations.[9] Resolving the second problem is more complex. Several of the parameters analyzed had reductions in MDL, and the seasonal Kendall test results were apparently affected by these reductions.

Reductions in MDL occurred in all four of the nitrogen and phosphorus parameters, but detection limits did not change for DO or Secchi depth. For nitrogen and phosphorus parameters, below detection limit (BDL) values were set to one-half the MDL before interpolation, as in the previous analyses. For one parameter (TN) the MDL reductions were small enough to be negligible.[4] The effects of moderate reductions in MDL, which occurred in TP data, were checked by raising any lower values to the highest MDL during the time period. When the detection limits went down substantially over time, as they did for DIN and DIP, the possible effects were checked with four separate analyses, using two MDL adjustments and two time periods. These included setting BDL values to zero and analyzing only data collected after October 1988, after the largest reductions in detection limits had occurred. The appendix provides a listing of the frequencies of BDL values for DIP and DIN.

SUSQUEHANNA RIVER FLOW

Correlations between upper Chesapeake Bay water quality and Susquehanna River flow were analyzed to examine the strength of any relationships. The flow data used were log-transformed monthly means of the daily flow at Conowingo, Md. Log transformations of flow data made their distribution closer to a normal distribution. Because flow data and water quality data tend to show serial correlation, the P values listed are approximate. The Pearson (parametric) correlation was performed with the correlation procedure in SAS.[10]

PHOSPHORUS

The two phosphorus parameters analyzed were TP and DIP, which is the same as orthophosphate (PO_4 filtered). TP was chosen because it shows total enrichment for phosphorus, while DIP is the form most readily utilized by phytoplankton. The three main stem laboratories changed methods for TP several times,[3] but their methods were consistent after October 1988. TP had moderate reductions in MDL levels. Although DIP had no method changes, it had large reductions in MDL, which can complicate trend analysis.[3] Since BDL values are censored at the MDL in the CBP data base, this could produce a significant down trend that was caused by the lower MDL. To eliminate trends that were due to MDL changes, different approaches were used for TP and DIP.

TP, with moderate MDL reductions, was interpolated two ways: with BDL values set to one-half the MDL and also with all values below the highest MDL raised to that value (0.01 mg/L). The results of the analyses were very similar, so the MDL changes did not appear to affect the TP trends.

DIP had larger MDL reductions, so four different analyses were performed: trends over all 8 years and over 4 years, starting in October 1988, when most detection limits had been lowered; and with BDL values set to either one-half the MDL or set to zero to assess the effects of BDL data on trends. Thus, the four BDL treatments for DIP consisted of the following:

1. Eight years of data (1984 to 1992), with BDL data set to one-half the MDL;
2. Four years of data (1988 to 1992), with BDL data set to one-half the MDL;
3. Eight years of data (1984 to 1992), with BDL data set to zero;
4. Four years of data (1988 to 1992), with BDL data set to zero.

Because DIP is one of the SAV habitat requirements, it was analyzed over 7 months (April through October) as well as over 12 months, so there were eight sets of analyses for DIP. The results of these four BDL treatments were compared to eliminate any significant trends that were caused by MDL changes. Statistically significant trends were eliminated if they met one or more of the following criteria:

- If there was a significant reduction with MDL set to one-half and no trend or a significant increase with MDL set to zero, the reduction was probably caused by declining MDL.
- If a trend was significant over 4 years but not over 8 years, there may be a nonmonotonic trend that is unrelated to MDL changes.
- If there was a significant increase with BDL set to zero over 8 years but not over 4 years, the increasing trend may be caused by lowering the early BDL values to zero.

This approach to identifying real trends was conservative because any trends that appeared to be caused by declining MDL were eliminated. However, it is still possible that some of the DIP trends identified were affected by MDL changes.

NITROGEN

The two nitrogen parameters analyzed were TN and DIN. TN was chosen because it shows total enrichment for nitrogen, while DIN includes the forms most readily taken by phytoplankton. TN is calculated from total Kjeldahl nitrogen whole plus nitrite/nitrate (NO_{23}) in early main stem data and from total dissolved nitrogen plus particulate nitrogen in later data. DIN is calculated from nitrite/nitrate plus ammonium (NH_4). As with phosphorus, the total parameter had method changes, although it had minimal MDL reductions, and the dissolved inorganic parameter had no method changes and large reductions in MDL.[12]

The changes in TN MDL were small enough to have no effect on trends.[12] The declining MDL for DIN were dealt with using the same four treatments used for DIP, except that trends could not be estimated for segments sampled by the Virginia Institute of Marine Science (VIMS). This affected the four segments with a majority of VIMS stations: Tangier Sound (EE3), Mobjack Bay (WE4), and lower Chesapeake Bay segments CB6 and CB7. VIMS detection limits for DIN had a series of large reductions that continued until July 1990, which left only 2 years of data after the reductions stopped. (See Table A.2 in the appendix.) This was not enough time to evaluate whether any trends were affected by declining MDL.

SECCHI DEPTH

Although Secchi depth has a lower MDL (0.1 meter), it did not change and it was almost never encountered. Thus, there were no MDL problems for Secchi depth. There were more ties in Secchi depth than in other parameters, but they still did not exceed 50 percent for any month.

DISSOLVED OXYGEN

Eight DO metrics were calculated and interpolated, and seven were analyzed statistically for trend over the whole main stem and for each of nine main stem segments. DO saturation trends were not analyzed, and data from EE3 were not analyzed for DO trends. All DO metrics were analyzed for trend over the 4 warm weather months (June through September) when low DO is most frequent. This time period is also used in the assessment of low DO levels in CBP time-variable model output. Other months were excluded because they would tend to obscure any trends that occurred during the warm weather months. DO has no detection limits, since values of zero can occur. The following eight metrics were calculated:

1. Monthly mean DO concentration: An upward trend shows improvement.
2. Monthly mean DO saturation concentration: This is calculated from water temperature and salinity[12] and expresses the potential DO concentration at that temperature and salinity if the water was saturated with DO. Trends are neither improvements nor degradation but represent changes in the amount of oxygen that can be held in solution due to changes in water temperature and/or salinity. For this reason, trends were not calculated for saturation; it was used as an intermediate step in calculating the next two parameters.
3. Monthly mean DO delta concentration: This is calculated from DO saturation minus DO concentration. To eliminate the effects of any supersaturated conditions, DO delta was set to zero if less than zero. A downward trend shows improvement. (The DO concentration is getting closer to saturation.)

4. Monthly mean DO deficit: This is calculated from DO delta, converting it from a concentration to the mass of DO that would need to be added to that segment to bring all areas up to DO saturation. DO deficit is the mass of oxygen at saturation minus mass of oxygen present, omitting any supersaturation. A downward trend shows improvement. (Less DO mass would need to be added to achieve saturation.)

5 to 8. Monthly mean volume of water below four DO concentrations: 5, 3, 1, and 0.2 mg/L. These were calculated using DO data from all depths, but since water in the surface layers rarely has low DO, almost all the volume with low DO was from below the pycnocline. A downward trend shows improvement. (A smaller volume of water was below the cutoff concentration.)

RESULTS AND DISCUSSION

SUSQUEHANNA RIVER FLOW

Susquehanna River flow data were analyzed because some water quality parameters may have positive or negative correlations with flow. If trends in flow were similar in magnitude and direction to the trends in one of the parameters analyzed and levels of that parameter were correlated with flow, that would indicate that interannual changes in flow might be responsible for the apparent trend in the water quality parameter.

Total annual Susquehanna River flow and the number of months with mean flow above the 1950 to 1992 median for that month are shown in Figure 2. In an average year there should be 6 months with flow above the median and 6 months with flow below the median. Annual Susquehanna River flow was relatively high in 1986, 1989, 1990, and 1991 and relatively low in 1985, 1988, and 1992 (see Figure 2). The WY with the highest total flow (1991) had relatively few months (5) with mean flows above the 1950 to 1992 median. This apparent discrepancy resulted from high flows in the first 5 months of that WY (October 1990 through February 1991), which produced the high total flow, followed by 7 months of below-average flows.

Although there was a bimodal pattern in total flows (see Figure 2), there were no statistically significant trends ($P>0.05$) in either mean or total monthly Susquehanna River flows over either 12 or 7 months, over 8 years, or the first and last 4 years, using the seasonal Kendall tests. This means that interannual changes in flow were probably not responsible for any of the significant water quality trends observed. The levels of some of the water quality parameters probably were related to interannual changes in flow, but not in a simple fashion.

The complexity of the relationships between Susquehanna River flow and upper Chesapeake Bay water quality is shown by the correlations in Table 1. If there was a simple relationship between nutrients and flow, nutrients would show positive correlations with flow, with the strongest correlations in segment CB1 (Susquehanna Flats), especially in surface samples. Correlations should generally be stronger for nitrogen than for phosphorus because nitrogen, especially nitrate, is more soluble in water than phosphorus, and the lagged correlations should be stronger in segments farther from the fall line because it takes water from the fall line longer to reach these segments.

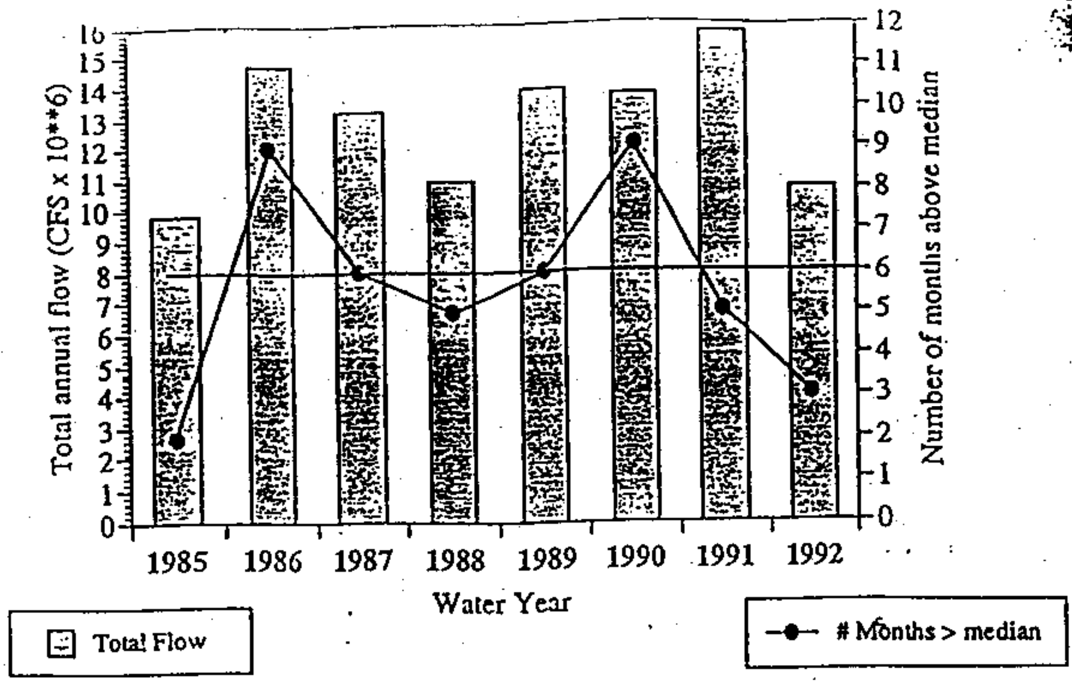


Figure 2. Total annual Susquehanna River flow (bars) and number of months above median flow line (water years 1985 to 1992).

Table 1. Correlations between log mean monthly Susquehanna River flow and mean monthly concentrations of water quality parameters (with *P* values in parentheses).

Parameter	Months	With	CB1	CB2	CB3	CB4	CB5
TP	12	Flow	NS	NS	−0.294 (0.0037)	−0.426 (0.0001)	−0.538 (0.0001)
TP	12	Lag	NS	NS	−0.260 (0.0109)	−0.314 (0.0019)	−0.394 (0.0001)
DIP	12	Flow	NS	−0.290 (0.0042)	−0.361 (0.0003)	−0.485 (0.0001)	−0.554 (0.0001)
DIP	12	Lag	NS	−0.310 (0.0022)	−0.484 (0.0001)	−0.359 (0.0004)	−0.360 (0.0003)
DIP	7	Flow	NS	NS	−0.372 (0.0048)	−0.468 (0.0003)	−0.540 (0.0001)
DIP	7	Lag	NS	−0.277 (0.0404)	−0.463 (0.0004)	NS	NS
TN	12	Flow	0.394 (0.0001)	0.651 (0.0001)	0.737 (0.0001)	0.618 (0.0001)	0.547 (0.0001)
TN	12	Lag	0.285 (0.0051)	0.545 (0.0001)	0.672 (0.0001)	0.715 (0.0001)	0.673 (0.0001)
DIN	12	Flow	0.432 (0.0001)	0.660 (0.0001)	0.775 (0.0001)	0.737 (0.0001)	0.678 (0.0001)

Table 1. Correlations between log mean monthly Susquehanna River flow and mean monthly concentrations of water quality parameters (with *P* values in parentheses) (Continued).

Parameter	Months	With	CB1	CB2	CB3	CB4	CB5
DIN	12	Lag	0.310 (0.0022)	0.561 (0.0001)	0.663 (0.0001)	0.753 (0.0001)	0.690 (0.0001)
DIN	7	Flow	0.568 (0.0001)	0.791 (0.0001)	0.813 (0.0001)	0.772 (0.0001)	0.697 (0.0001)
DIN	7	Lag	0.333 (0.0130)	0.476 (0.0002)	0.360 (0.0070)	0.386 (0.0036)	0.384 (0.0038)
Secchi Depth	12	Flow	–0.418 (0.0001)	–0.382 (0.0001)	–0.222 (0.0300)	NS	NS
Secchi Depth	12	Lag	–0.315 (0.0019)	–0.404 (0.0001)	–0.319 (0.0017)	NS	NS
Secchi Depth	7	Flow	–0.736 (0.0001)	–0.578 (0.0001)	–0.334 (0.0119)	NS	NS
Secchi Depth	7	Lag	–0.274 (0.0426)	–0.340 (0.0112)	NS	NS	NS
DO	4	Flow	0.398 (0.0242)	0.448 (0.0102)	NS	NS	NS
DO	4	Lag	0.361 (0.0461)	NS	NS	NS	NS
DO Delta	4	Flow	NS	NS	NS	NS	NS
DO Delta	4	Lag	0.368 (0.0418)	NS	NS	–0.361 (0.0461)	NS
DO Deficit	4	Flow	NS	NS	NS	NS	NS
DO Deficit	4	Lag	0.368 (0.0418)	NS	NS	–0.361 (0.0461)	NS

Legend and note:
NS—Not statistically significant ($P>0.05$).
Months: Number of months data used: 12—all year (No. of months—96); 7—April through October (No. of months—56); 4—June through September (No. of months—32). With: Flow—Log mean monthly flow (log of mean of daily flows); Lag—Log mean monthly flow of previous month.

The results (see Table 1) do show stronger positive correlations for nitrogen than for phosphorus, but the nitrogen correlations with flow were always strongest in CB3 (unlagged) or CB4 (lagged) and weakest in CB1. Both forms of phosphorus had negative correlations with flow in all of the segments with significant correlations, even though a positive correlation is expected for TP. Particulate phosphorus, part of TP, is often attached to sediment, and higher flow usually increases sediment loads. Thus, reasons for these negative correlations of phosphorus with flow are not clear.

Only Secchi depth showed the expected pattern of the strongest correlations in CB1 (or CB2 for lagged flow). This may be because Secchi depth has only one measurement per station, while the values for the other water quality parameters were averaged over results from two or four depths. The correlations of flow with Secchi depth were negative, presumably because higher flow brings more sediment, which reduces water clarity. Correlations with unlagged flow were stronger during April through October than during the whole year.

Some of the DO metrics showed positive correlations with flow or lagged flow in CB1 and CB2, but the conflicting nature of the correlations means they were probably not meaningful. The correlations suggest that higher flow is associated both with higher DO concentrations in the current and following months (improvement), possibly due to increased aeration, but also with higher DO delta and deficit a month later (degradation).

PHOSPHORUS

Total Phosphorus

Results show a statistically significant downward trend (improvement, $P<0.01$) baywide, in upper Chesapeake Bay segment CB2, and in lower Chesapeake Bay segments CB6 and CB8 (see Table 2 and Figure 3). There were also marginally significant improvements ($P<0.05$) in upper Chesapeake Bay segments CB1 and CB3 and lower Chesapeake Bay segment CB7 (see Table 2 and Figure 3). One segment with a significant trend (CB2) had a barely significant seasonal heterogeneity: the χ^2 value was 20.6, slightly more than the critical value of 19.7. However, since only 3 months had increasing trends (November, January, and February), the overall decline in CB2 appeared to be valid.

Changes in TP detection limits had little effect on the trend results. An interpolator run with any values below 0.01 mg/L raised to that value had significant trends in the same segments, with very similar slopes.

Figure 4 shows average monthly TP and DIP concentrations for each segment. DIP (thin line) is shown for comparison to TP levels; it was also graphed separately. Segments with statistically significant or marginally significant TP trends have a trend line connecting the 1984 to 1985 mean and the 1991 to 1992 projection based on the seasonal Kendall slope.

The median baywide percent change in TP over 8 years (1984 to 1992), based on the seasonal Kendall slope, was 16 percent plus or minus 8 percent (90 percent confidence interval). This is slightly less than the previous baywide percent change estimate for TP, which was 19 percent.[3] One reason for the lower percent change is that March 1985 TP data, which were included in the previous analysis, were subsequently deleted from the data base due to quality assurance problems and were not used in this analysis. Percent change values for individual segments are listed in Table 2.

The declines (improvements) in TP in upper Chesapeake Bay segments CB1, CB2, and CB3 were probably related to declines in Susquehanna River fall line concentrations. There were statistically significant ($P<0.1$) declines in flow-adjusted TP concentrations at the Susquehanna River fall line between 1984 and 1990, using both parametric regressions and seasonal Kendall trend tests.*

*B. Dobler, Maryland Department of the Environment (MDE), unpublished analyses.

Table 2. Trend results for interpolated monthly mean total phosphorus by segment (12 months).

Segment (CBP)	Slope mg/L/yr	Z Trend	P	χ^2 Seasonal	P	% Change
All	−0.00067	−2.72	0.0066	3.28	>0.95	16
CB1	−0.001	−2.15	0.032	15.64	>0.1	16
CB2	−0.002	−2.87	0.0042	20.63	<0.05	29
CB3	−0.001	−2.48	0.013	13.59	>0.2	17
CB4	–	–	NS	–	–	–
CB5	–	–	NS	–	–	–
CB6	−0.00092	−3.33	≤0.001	8.67	>0.5	21
CB7	−0.0008	−2.53	0.011	8.5	>0.5	19
CB8	−0.0024	−4.86	≤0.0001	7.88	>0.7	36
WE4	–	–	NS	–	–	–
EE3	–	–	NS	–	–	–

Legend and note:
The total number of months (*N*) for all segments was 96 (October 1984 through September 1992); all depths; results shown for segments with significant (P<0.01, underlined) trends and marginally significant (P<0.05) trends only. A negative (down) trend shows improvement (less phosphorus); NS—Not significant (P>0.05). X^2 seasonal and its P value (last two columns) are a test for homogeneity of the trend over different months. A P value of more than 0.05 indicates the trends were homogeneous; the trend in CB2 appeared to be valid even though P<0.05.

Possible causes of the declines (improvements) in lower Chesapeake Bay segments CB6, CB7, and CB8 are less clear. None of the tributaries draining into these main stem segments (Rappahannock, York, and James Rivers) had declining trends in TP over the period 1984 to 1991.[13] In fact, all three rivers had some segments and seasons with significant increases (degradation) in TP, including the segment at the mouths of the Rappahannock and James Rivers.[13] The mouth of Chesapeake Bay (segment CB8) had both the highest concentrations (see Figure 4) and the largest percent change (see Table 2) of these three segments, suggesting that the TP declines in that segment might be related to changes in oceanic concentrations.

The downward trends in TP concentrations are consistent with TP load reductions over the whole watershed. Point source loads of TP were reduced by 40 percent between 1985 and 1990, while controllable nonpoint source loads fell 8 percent between 1985 and 1991, based on watershed model load estimates.[1] Point sources of phosphorus comprise 34 percent of the watershed total loads and 42 percent of the controllable loads (excluding atmospheric deposition). Nonpoint sources of phosphorus comprise 60 percent of the watershed total loads and 58 percent of the controllable loads.[1]

Dissolved Inorganic Phosphorus (Orthophosphate)

Reductions in MDL appeared to have a major impact on trend results for DIP. For this reason, DIP trends were analyzed with four different MDL treatments to eliminate

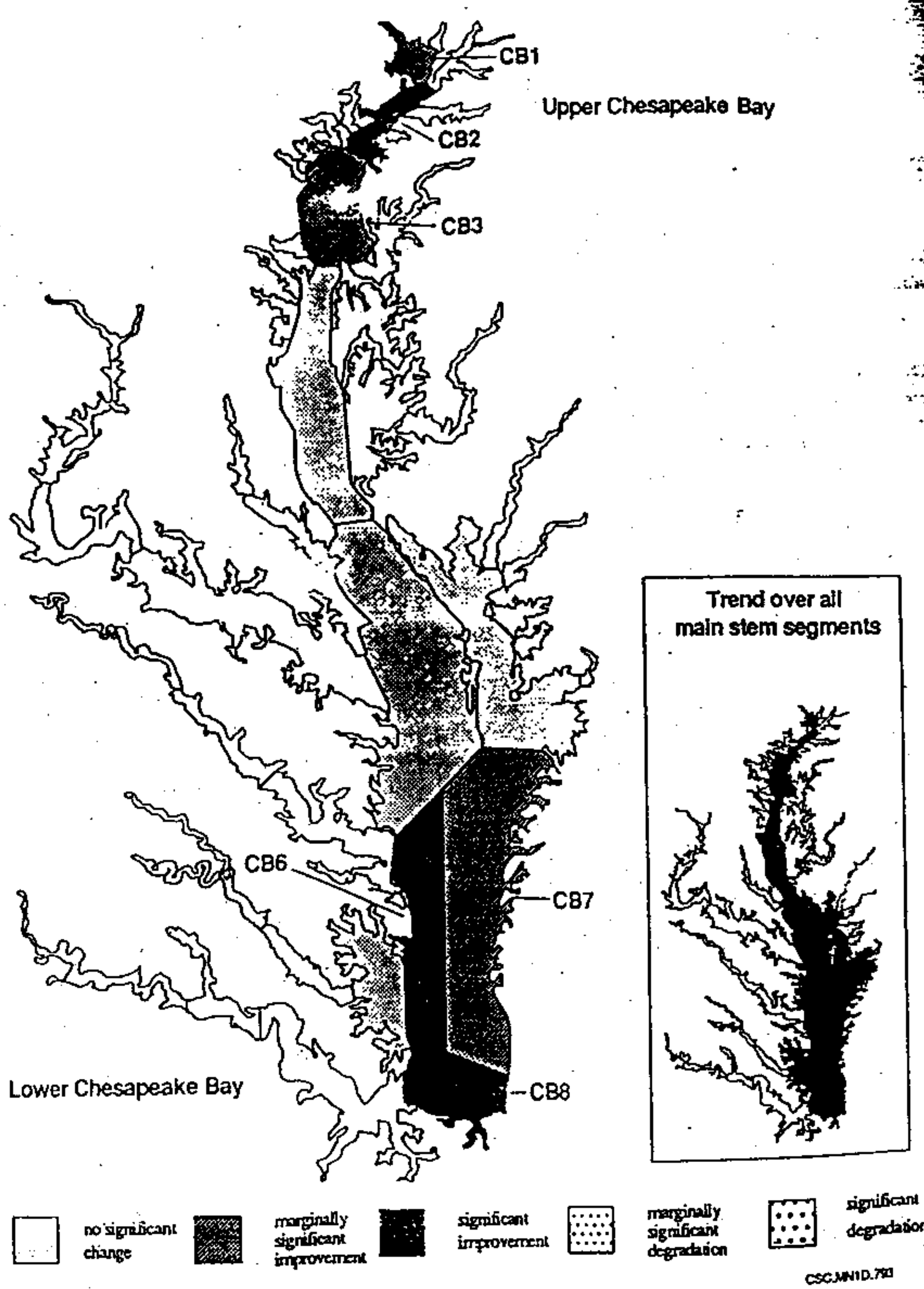


Figure 3. Total phosphorus trends in Chesapeake Bay main stem segments (October 1984 through September 1992).

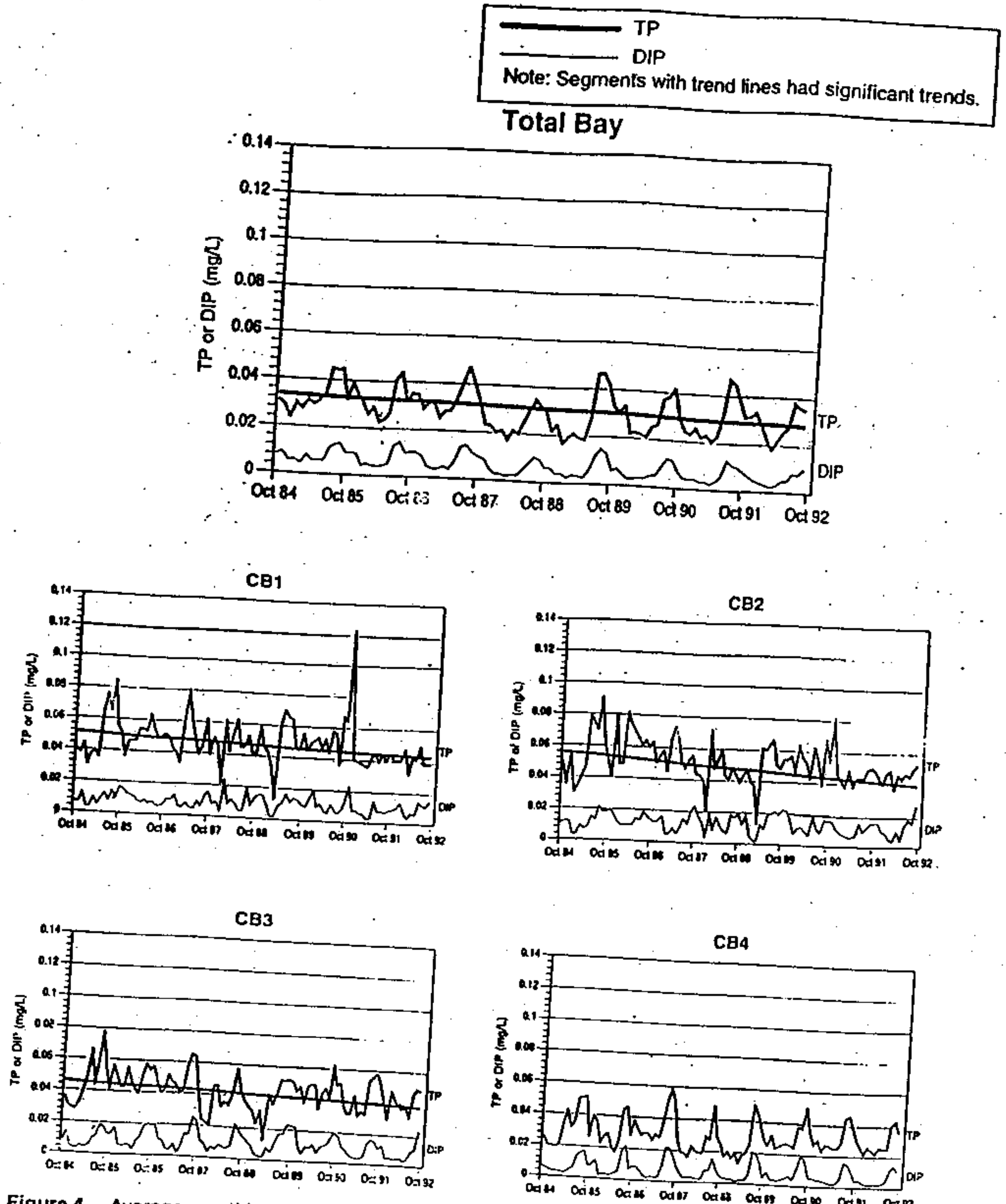


Figure 4. Average monthly concentrations of total phosphorus and dissolved inorganic phosphorus (1984 to 1992).

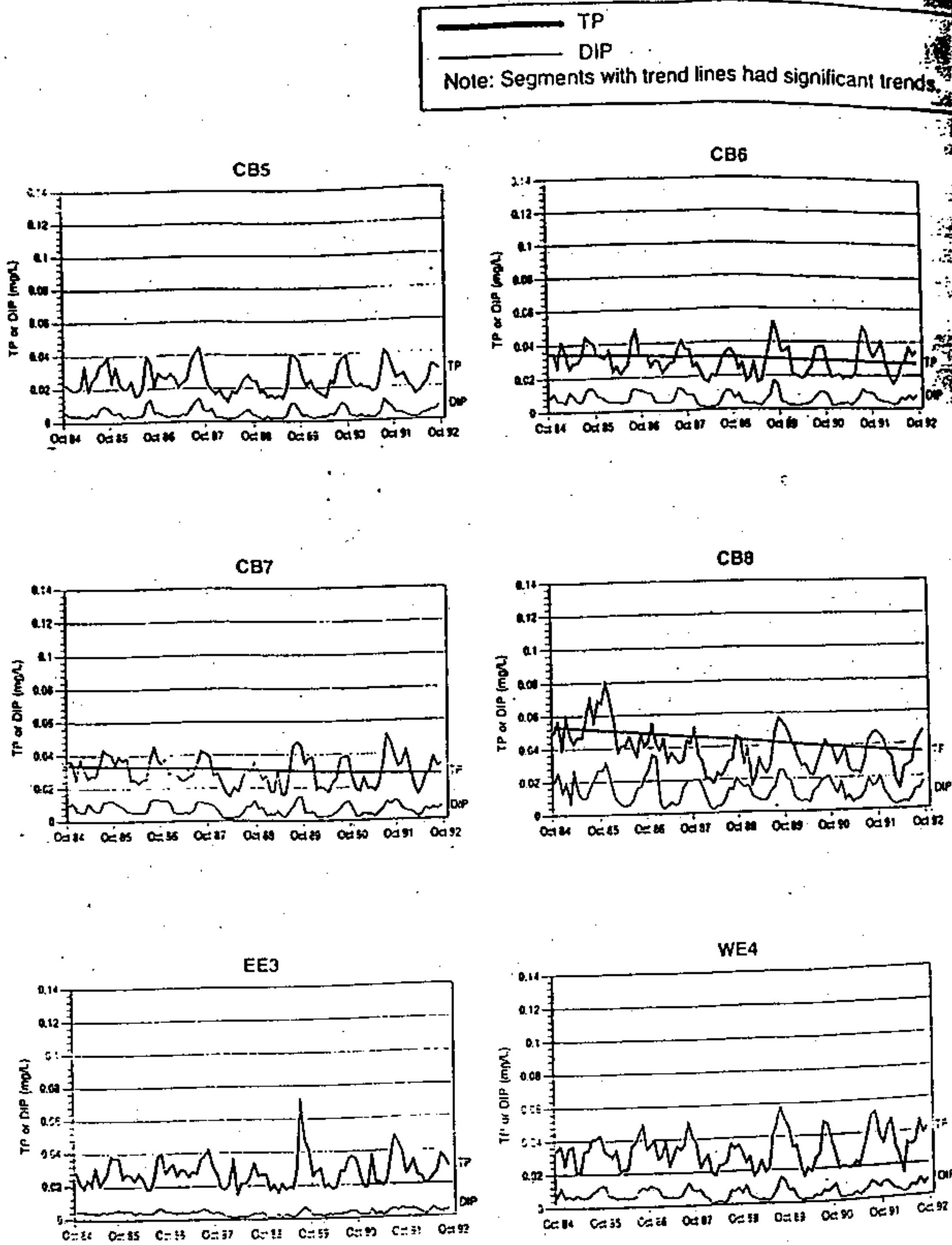


Figure 4. Average monthly concentrations of total phosphorus and dissolved inorganic phosphorus (1984 to 1992) (continued).

trends that were caused by MDL changes. Table 3 lists the results of these treatments over 12 months and over the 7-month SAV growing season, for a total of eight sets of analyses. Two trends that appeared to be real occurred over 12 months in CB8 and 7 months in CB4 (both improvements) and are shown in Figure 5. Baywide, the trend was not significant (see inset, Figure 5).

Table 3. Trend results for interpolated monthly mean levels of dissolved inorganic phosphorus by segment, using four different method detection limit treatments.

Table 3a. BDL data set to one-half.

No. of Months	No. of Years	Main Stem CBP Segments										
		All	CB1	CB2	CB3	CB4	CB5	CB6	CB7	CB8	WE4	EE3
12	8	I	–	–	–	I	I	I	I	I*	I	I
12	4	–	–	–	–	–	–	–	–	I*	DM	–
7	8	I	–	–	–	I*	IM	I	I	IM	–	I
7	4	–	–	IM	I	–	–	–	–	IM	–	–

Table 3b. BDL data set to zero.

No. of Months	No. of Years	Main Stem CBP Segments										
		All	CB1	CB2	CB3	CB4	CB5	CB6	CB7	CB8	WE4	EE3
12	8	–	–	–	–	–	DM	–	–	IM*	D	D
12	4	–	–	–	–	–	–	–	–	I*	–	DM
7	8	–	–	–	–	IM*	–	–	–	–	D	D
7	4	–	–	IM	I	–	–	–	–	IM	–	–

Legend and note:
I—Significant improvement ($P<0.01$).
IM—Marginally significant improvement ($P<0.05$).
D—Significant degradation ($P<0.01$).
DM—Marginally significant degradation ($P<0.05$).
Dash—No significant trend ($P>0.05$).
*Trends that appear to be real, i.e., not caused by declining detection limits.
7 months—April through October only, SAV growing season in lower salinity zones.

Figure 6 shows average monthly DIP concentrations for each segment, with BDL values set to one-half the MDL (thick line) and to zero (thin line). Segments with statistically significant trends have two trend lines connecting the 1984 to 1985 mean and the 1991 to 1992 projection based on the seasonal Kendall slope, one for BDL set to one-half (thick line) and one for BDL set to zero (thin line). In one segment these lines overlap (CB4).

Details of the trend results from Table 3 that appeared to be real are summarized in Tables 4 and 5. Percent change was near 30 percent in both CB4 and CB8. Results over 4

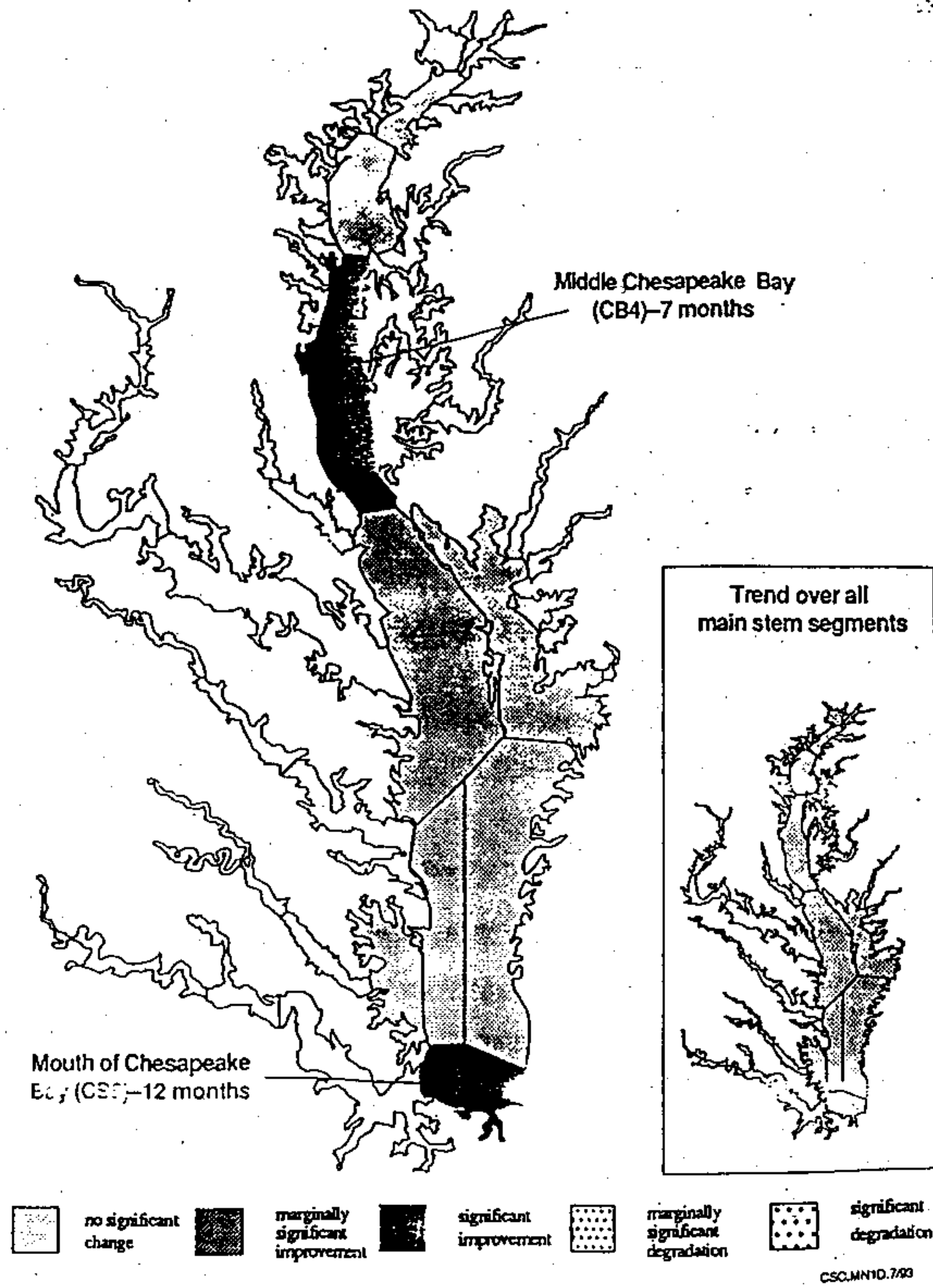


Figure 5. Dissolved inorganic phosphorus trends in Chesapeake Bay main stem segments (October 1984 through September 1992).

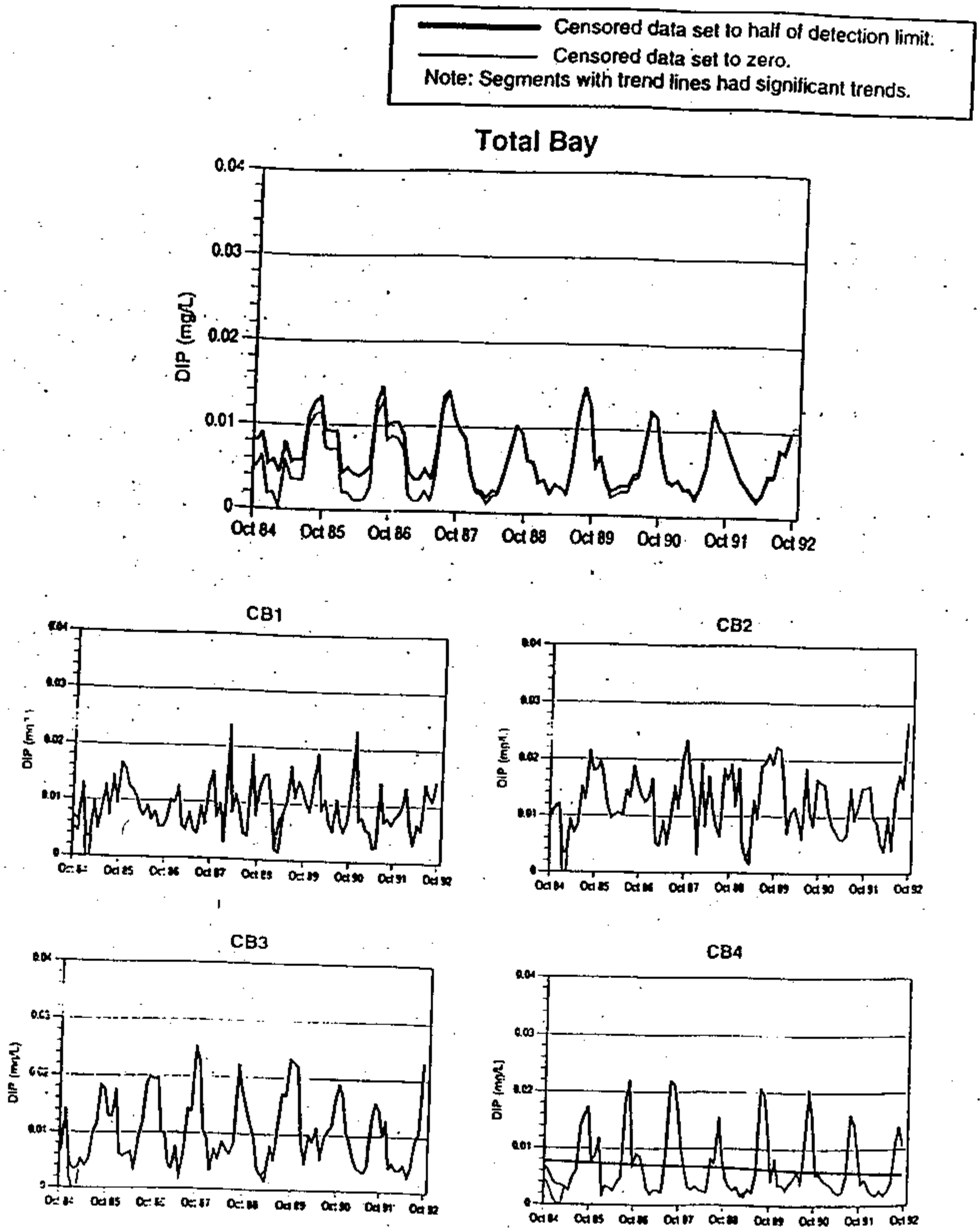


Figure 6. Average monthly concentrations of dissolved inorganic phosphorus (1984 to 1992).

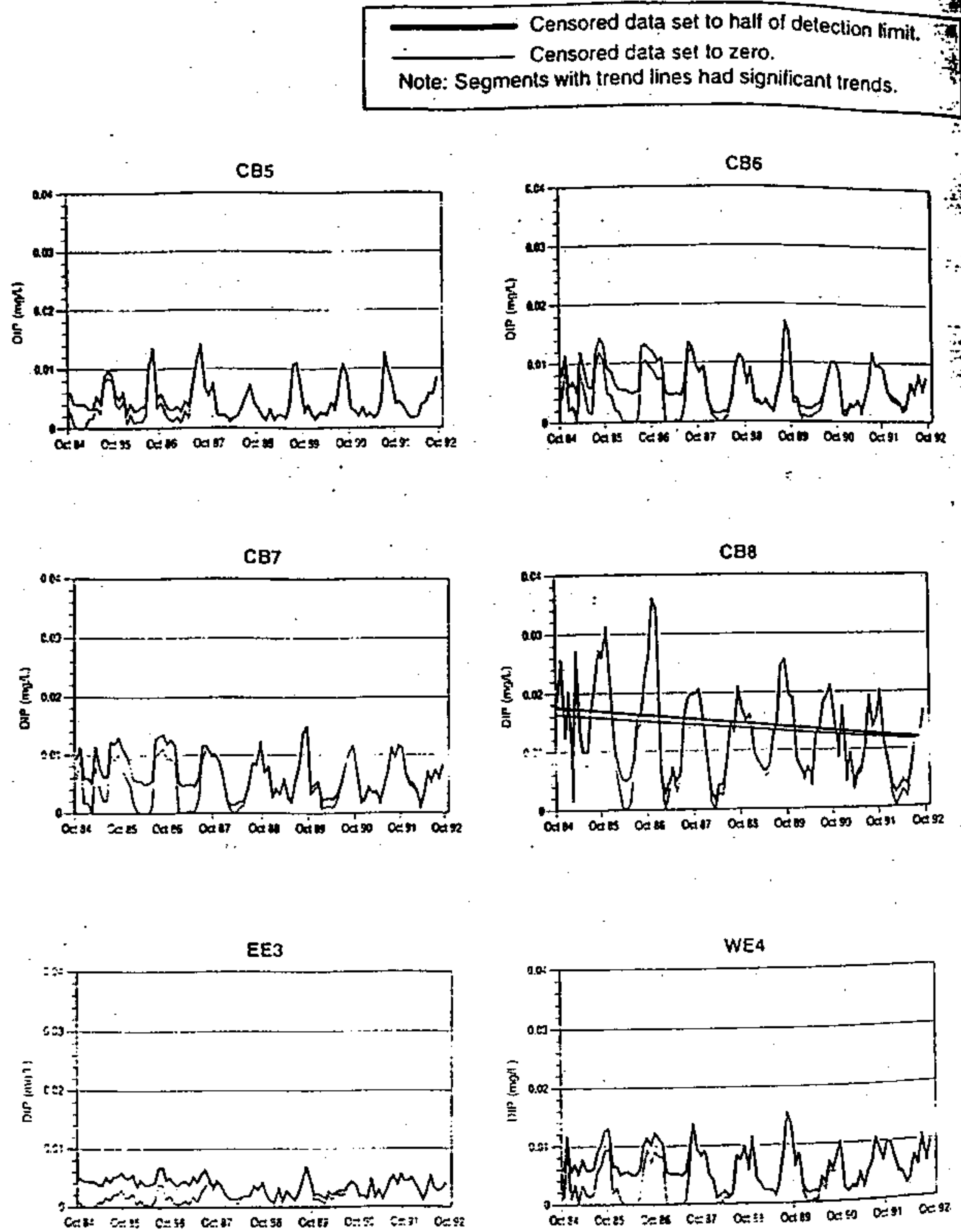


Figure 6. Average monthly concentrations of dissolved inorganic phosphorus (1984 to 1992) (continued).

years are not shown since those analyses were only performed to assess the effects of changing detection limits.

Table 4. Trend results for interpolated monthly mean dissolved inorganic phosphorus by segment (12 months).

Segment (CBP)	BDL Treatment	Slope mg/L/yr	*Z* Trend	*P*	χ^2 Seasonal	*P*	% Change
All	–	–	–	NS	–	–	–
CB1	–	–	–	NS	–	–	–
CB2	–	–	–	NS	–	–	–
CB3	–	–	–	NS	–	–	–
CB4	–	–	–	NS	–	–	–
CB5	–	–	–	NS	–	–	–
CB6	–	–	–	NS	–	–	–
CB7	–	–	–	NS	–	–	–
CB8	1/2	–0.00069	–3.75	<u>0.00018</u>	7.62	>0.7	31
CB8	0	–0.00059	–2.36	0.018	11.77	>0.3	29
WE4	–	–	–	NS	–	–	–
EE3	–	–	–	NS	–	–	–

Legend and note:
The total number of months (*N*) for all segments was 96 (October 1984 through September 1992); all depths; results shown for segments with significant (P<0.01, underlined) trends and marginally significant (P<0.05) trends only. A negative (down) trend shows improvement (less phosphorus); NS—Not significant (P>0.05). χ^2 seasonal and its *P* value (last two columns) are a test for homogeneity of the trend over different months. A *P* value of more than 0.05 indicates the trends were homogeneous. Where there are two slopes for the same segment, they "bracket" the true slope.

Possible reasons for the declines (improvements) in DIP in middle Chesapeake Bay (segment CB4) and the mouth of Chesapeake Bay (segment CB8) are not clear. DIP trends have not been analyzed in tributary segments, mainly due to high MDL. The trend in the mouth of Chesapeake Bay (segment CB8) may be related to changes in oceanic concentrations; as was found for TP, CB8 had higher concentrations than nearby segments CB6 and CB7 (see Figure 6).

The ecological significance of these trends in terms of SAV restoration appears to be be minimal because both of the segments that had significant down trends had already achieved the SAV habitat requirement for DIP (0.01 mg/L in mesohaline regions and 0.02 mg/L in other salinity regimes[5]). The areas where DIP levels need to be reduced to permit SAV growth are in tributary segments.*

*"Water Quality Restoration Priorities for Living Resources Report," (draft), CBP, Annapolis, Md. (1993).

Table 5. Trend results for interpolated monthly mean dissolved inorganic phosphorus by segment (7 months, April through October).

Segment (CBP)	BDL Treatment	Slope mg/L/yr	*Z* Trend	*P*	χ^2 Seasonal	*P*	% Change
All	–	–	–	NS	–	–	–
CB1	–	–	–	NS	–	–	–
CB2	–	–	–	NS	–	–	–
CB3	–	–	–	NS	–	–	–
CB4	1/2	–0.0003	–2.81	<u>0.005</u>	1.37	>0.95	31
CB4	0	–0.000267	–2.21	0.027	2.33	>0.8	28
CB5	–	–	–	NS	–	–	–
CB6	–	–	–	NS	–	–	–
CB7	–	–	–	NS	–	–	–
CB8	–	–	–	NS	–	–	–
WE4	–	–	–	NS	–	–	–
EE3	–	–	–	NS	–	–	–

Legend and note:
The total number of months (*N*) for all segments was 56 (April 1985 through September 1992); all depths; results shown for segments with significant ($P<0.01$, underlined) trends and marginally significant ($P<0.05$) trends only. A negative (down) trend shows improvement (less phosphorus); NS—Not significant ($P>0.05$). χ^2 seasonal and its *P* value (last two columns) are a test for homogeneity of the trend over different months. A *P* value of more than 0.05 indicates the trends were homogeneous. Where there are two slopes for the same segment, they "bracket" the true slope.

NITROGEN

Total Nitrogen

There was no significant trend baywide for TN (see Table 6 and inset, Figure 7). There was a marginally significant increase (degradation, $P=0.027$) in segment WE4, which includes the mouth of the York River (see Figure 7).

Figure 8 shows average monthly TN and DIN concentrations for each segment. DIN (thin line) is shown for comparison to TN levels, it was also graphed separately. Segments with marginally significant or statistically significant TN trends have a trend line connecting the 1984 to 1985 mean and the 1991 to 1992 projection based on the seasonal Kendall slope.

The lack of any TN trend in upper Chesapeake Bay is consistent with the flow-adjusted TN loads at the Susquehanna River fall line. Data from this station showed no significant changes in loads ($P>0.1$) between 1984 and 1990.*

*B. Dore[illegible], [illegible], unpublished analyses

Table 6. Trend results for interpolated monthly mean total nitrogen by segment.

Segment (CBP)	Slope mg/L/yr	Z Trend	P	χ^2 Seasonal	P	% Change
All	–	–	NS	–	–	–
CB1	–	–	NS	–	–	–
CB2	–	–	NS	–	–	–
CB3	–	–	NS	–	–	–
CB4	–	–	NS	–	–	–
CB5	–	–	NS	–	–	–
CB6	–	–	NS	–	–	–
CB7	–	–	NS	–	–	–
CB8	–	–	NS	–	–	–
WE4	0.006	2.21	0.027	5.74	>0.8	10
EE3	–	–	NS	–	–	–

Legend and note:
The total number of months (*N*) for all segments was 96 (October 1984 through September 1992); all depths; results shown for marginally significant ($P<0.05$) trends only. A negative (down) trend shows improvement (less nitrogen); NS—Not significant ($P>0.05$). χ^2 seasonal and its *P* value (last two columns) are a test for homogeneity of the trend over different months. A *P* value of more than 0.05 indicates the trends were homogeneous.

The increase (degradation) in Mobjack Bay (segment WE4) is probably related to increases in nearby tributary segments. York River tributary segments LE4, RET4, and TF4 also showed significant TN increases (degradation).* Trend analyses by the Virginia Department of Environmental Quality found increasing trends in both TN and chlorophyll *a* in all of the tidal sections of the York River.[13]

The general lack of significant trends in TN concentrations is consistent with TN point source load reductions over the whole watershed, which have been smaller than point source load reductions for TP. Point source loads of TN were reduced by only 6 to 7 percent between 1985 and 1990, while controllable nonpoint source nitrogen loads fell 12 percent between 1985 and 1991, based on watershed model load estimates.[1] Point sources of nitrogen comprise 23 percent of the watershed total loads and 46 percent of the controllable loads (excluding atmospheric deposition). Nonpoint sources of nitrogen comprise 68 percent of the watershed total loads and 54 percent of the controllable loads.[1]

Dissolved Inorganic Nitrogen

As was found for DIP, reductions in MDL appeared to have a major impact on trend results for DIN. For this reason, DIN trends were also analyzed four different ways:

1. Over all 8 years;

*"Water Quality Characterization Report for the 1991 Re-Evaluation of the Chesapeake Bay Nutrient Reduction Strategy," (draft). CBP, Annapolis, Md. (1991).

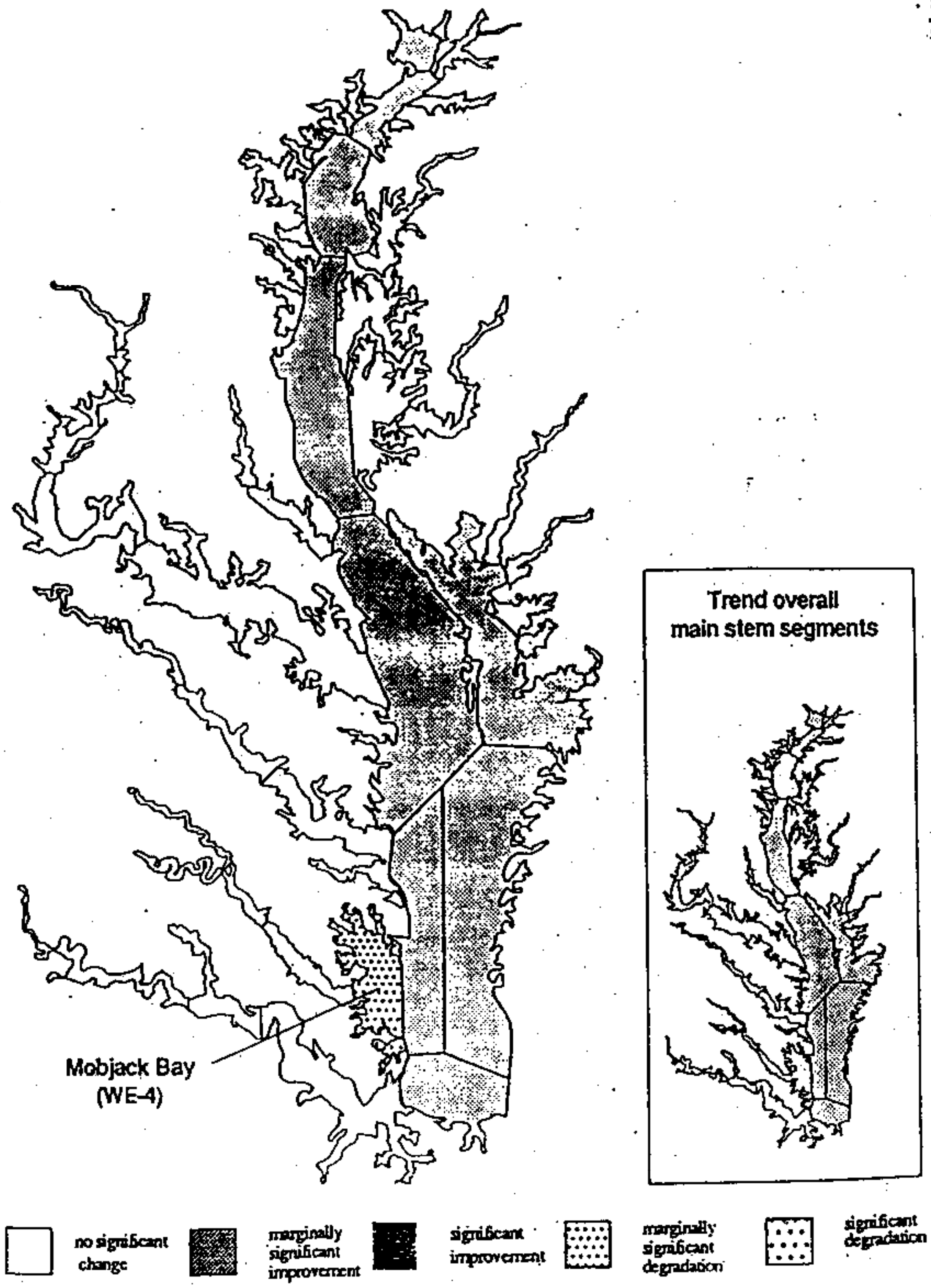


Figure 7. Total nitrogen trends in Chesapeake Bay main stem segments (October 1984 through September 1992).

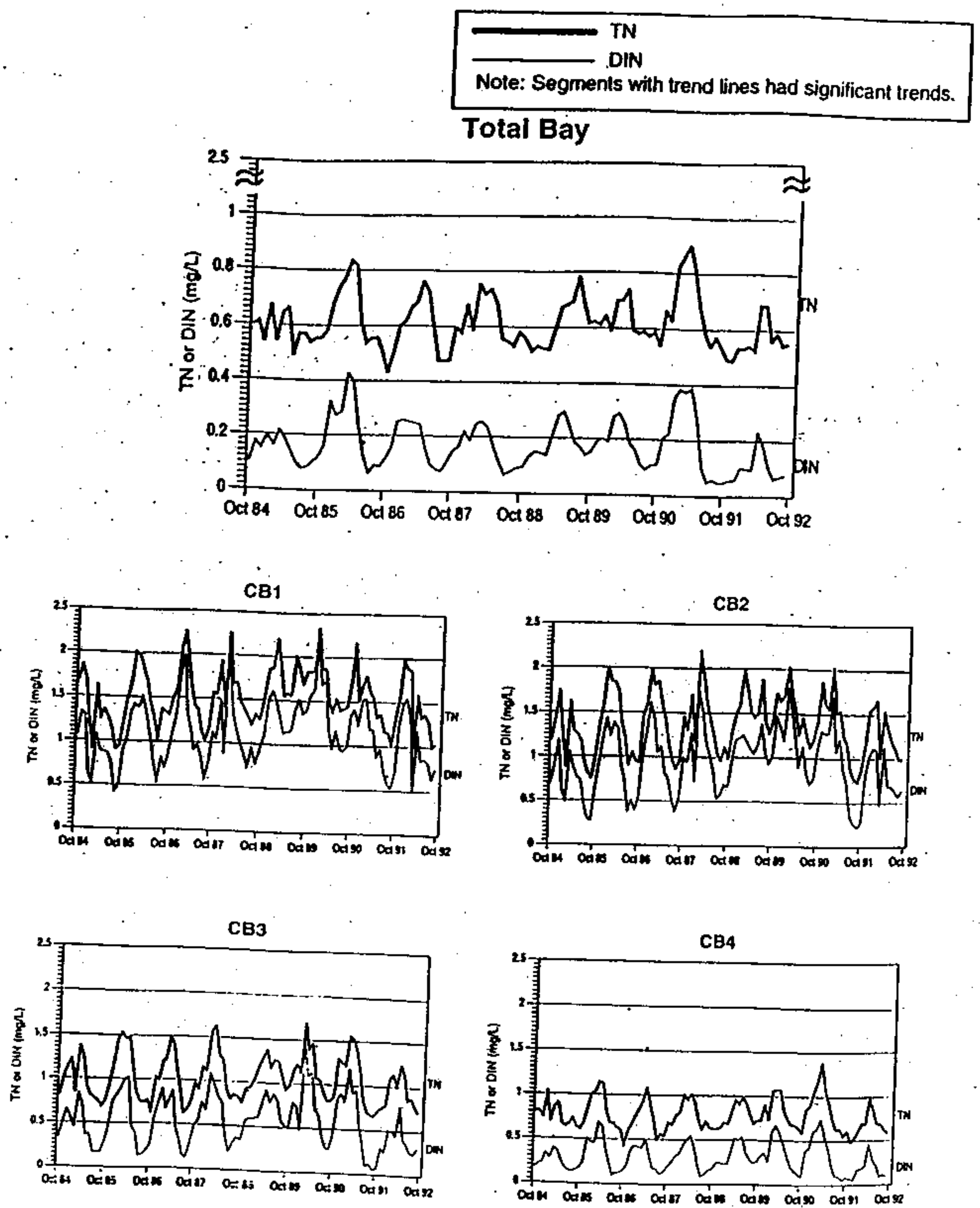


Figure 8. Average monthly concentrations of total nitrogen and dissolved inorganic nitrogen (1984 to 1992).

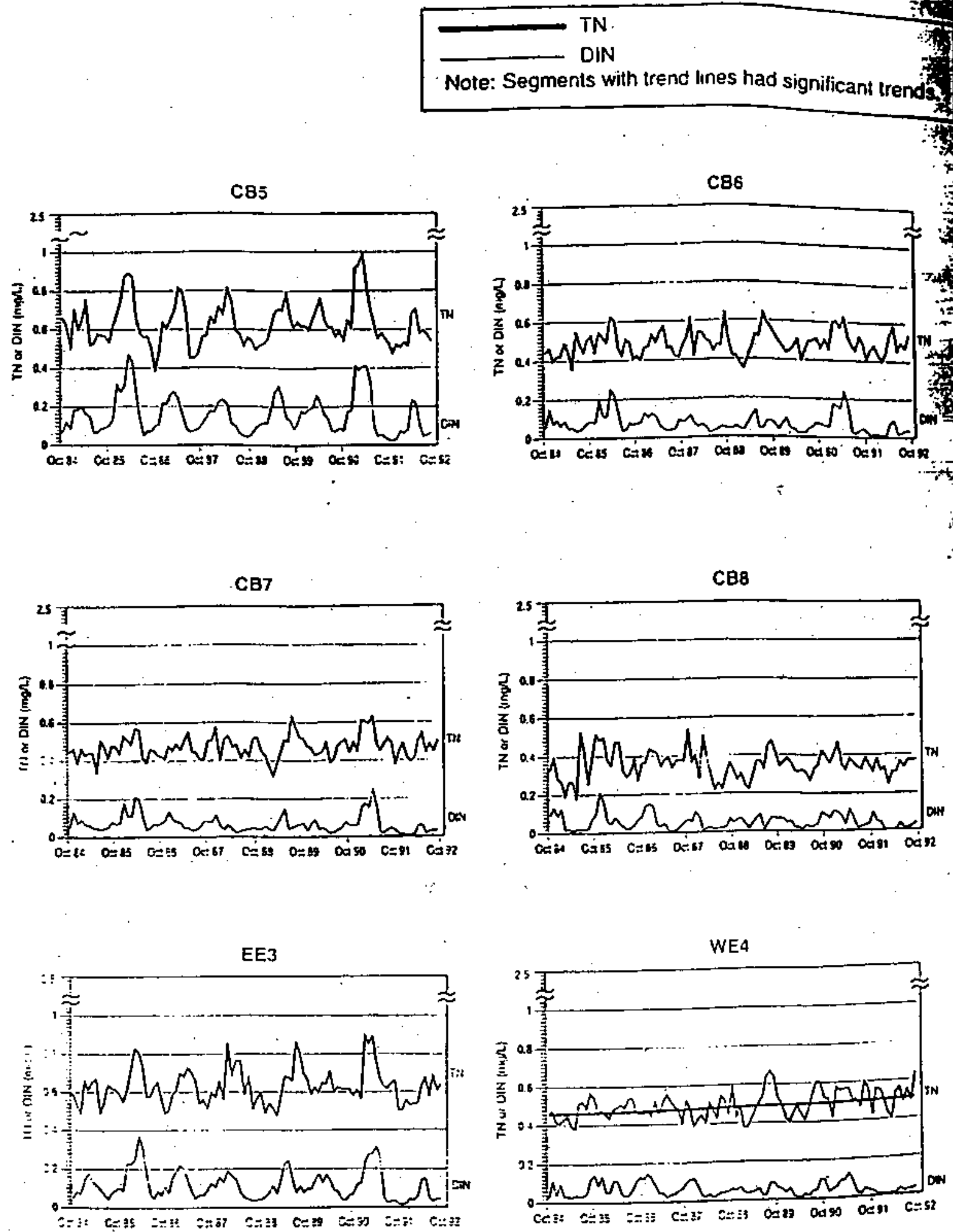


Figure 8. Average monthly concentrations of total nitrogen and dissolved inorganic nitrogen (1984 to 1992, (continued).

2. Over the last 4 years;
3. Starting in October 1988, when most detection limits were lowered;
4. With BDL set to either one-half the MDL or set to zero to assess the effects of BDL data on trends.

There was no significant trend baywide over the 8-year period (see Table 7 and inset, Figure 9). None of the significant trend results in Table 7 appeared to be real; the significant trends in lower Chesapeake Bay segments CB6, CB7, WE4, and EE3 could be caused by declining detection limits. The significant improvements in total (baywide) and other segments only appeared over 4 years (see Table 7), so they were eliminated as probable results of nonmonotonic trends.

Figure 10 shows average monthly DIN concentrations for each segment, with BDL values set to one-half the MDL (thick line) and to zero (thin line). These lines usually overlap, and the thin line is only visible in a few segments. There is a pattern of increasing concentrations followed by decreasing concentrations in the three upper Chesapeake Bay segments (CB1, CB2, and CB3) that are closest to the Susquehanna River and, thus, most affected by its flow. This pattern was not apparent in any other segments.

SECCHI DEPTH

Results show no significant trend baywide (see inset, Figure 11) or for any segment over 12 months (see Figure 11). There were marginally significant upward trends (improvements) in upper Chesapeake Bay segments CB1 and CB2 over the 7-month SAV growing season (April through October) (see Table 8 and Figure 11). CB2 includes the turbidity maximum in Chesapeake Bay.

Figure 12 shows average monthly Secchi depths for each segment. Segments with significant or marginally significant trends have a trend line connecting the 1984 to 1985 mean and the 1991 to 1992 projection based on the seasonal Kendall slope. The SAV habitat requirement for light attenuation (KD), which is related to Secchi depth, was often not met in segment CB2. The requirement was usually met in years with low flow and not met in years with high flow. The KD requirement for this area (2.0 m^{-1}), is equivalent to a Secchi depth of 0.73 m (using Secchi=1.45/KD[5]). In CB2, the KD/Secchi requirement was met in 3 of the last 8 years (38 percent attainment). It was met in 1988 and 1992, both low flow years, also in 1991, a year with high total flow but a below average number of months (5) above median flow (see Figure 2). The KD/Secchi requirement was not met in 5 years (1985 through 1987 and 1989 and 1990). Four of these years had high Susquehanna River flow, but 1985 had relatively low flow (see Figure 2).

Table 7. Trend results for interpolated monthly mean levels of dissolved inorganic nitrogen by segment using four different method detection limit treatments.

Table 7a. Below detection limit data set to one-half.

		Main Stem CBP Segments										
No. of Months	No. of Years	All	CB1	CB2	CB3	CB4	CB5	CB6	CB7	CB8	WE4	EE3
12	8	–	–	–	–	–	–	I+	I+	IM	I+	IM+
12	4	IM	IM	I	I	I	IM	IM+	IM+	–	IM+	–
7	8	–	–	–	–	–	–	IM	I	–	IM	–
7	4	I	IM	I	I	I	IM	IM	I	–	–	IM

Table 7b. Below detection limit data set to zero.

		Main Stem CBP Segments										
No. of Months	No. of Years	All	CB1	CB2	CB3	CB4	CB5	CB6	CB7	CB8	WE4	EE3
12	8	–	–	–	–	–	–	I+	I+	–	IM+	IM+
12	4	IM	I	I	I	I	IM	IM+	IM+	–	–	–
7	8	–	–	–	–	–	–	–	–	–	–	–
7	4	I	IM	I	I	I	IM	IM	I	–	–	IM

Legend and note:
I—Significant improvement ($P<0.01$).
IM—Marginally significant improvement ($P<0.05$).
Dash—No significant trend ($P>0.05$).
+These trends were not identified as real because detection limits in these segments continued to decline until July 1990; therefore, the marginally significant 4-year trends could be caused by declining detection limits.
7 months—April through October only, SAV growing season in lower salinity zones.

The annual pattern of attainment of the KD requirement suggests an inverse correlation between Susquehanna River flow and Secchi depth in these segments, which was found (see Table 1). However, the lack of a significant monotonic trend in flow over this period means that the marginally significant trends in Secchi depth in upper Chesapeake Bay were not a simple consequence of a trend in flow.

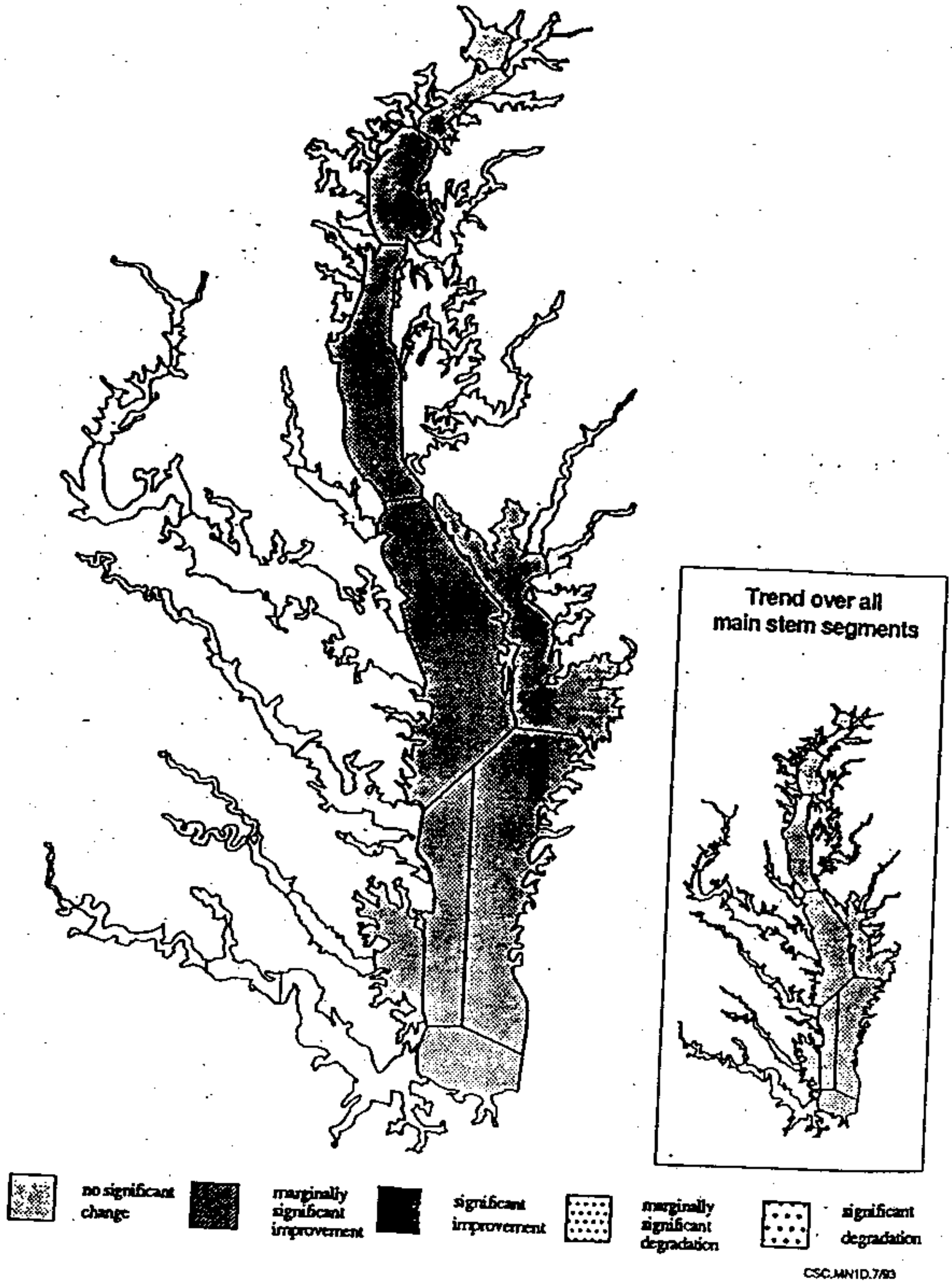


Figure 9. Dissolved inorganic nitrogen trends in Chesapeake Bay main stem segments (October 1984 through September 1992).

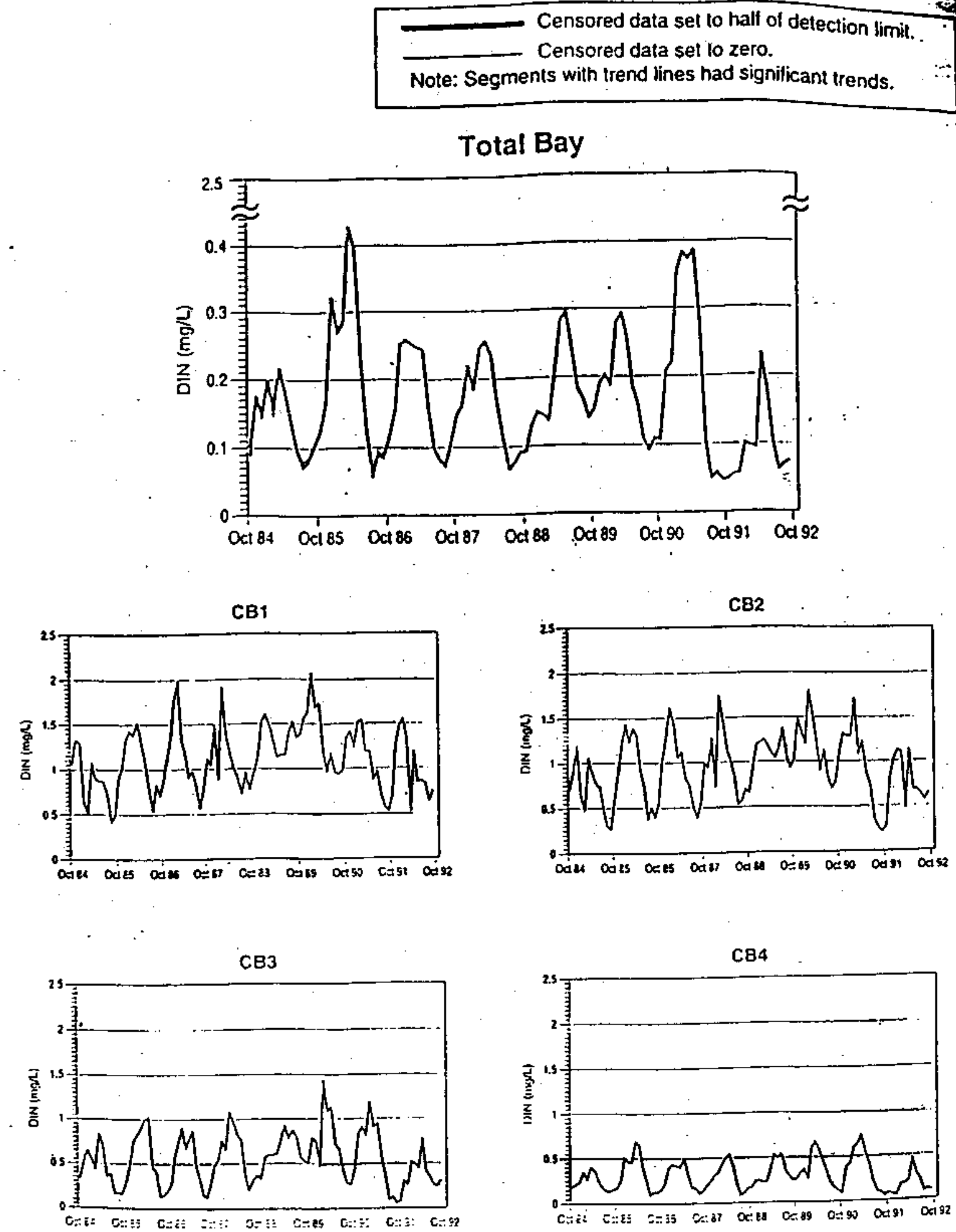


Figure 10. Average monthly concentrations of dissolved inorganic nitrogen (1984 to 1992).

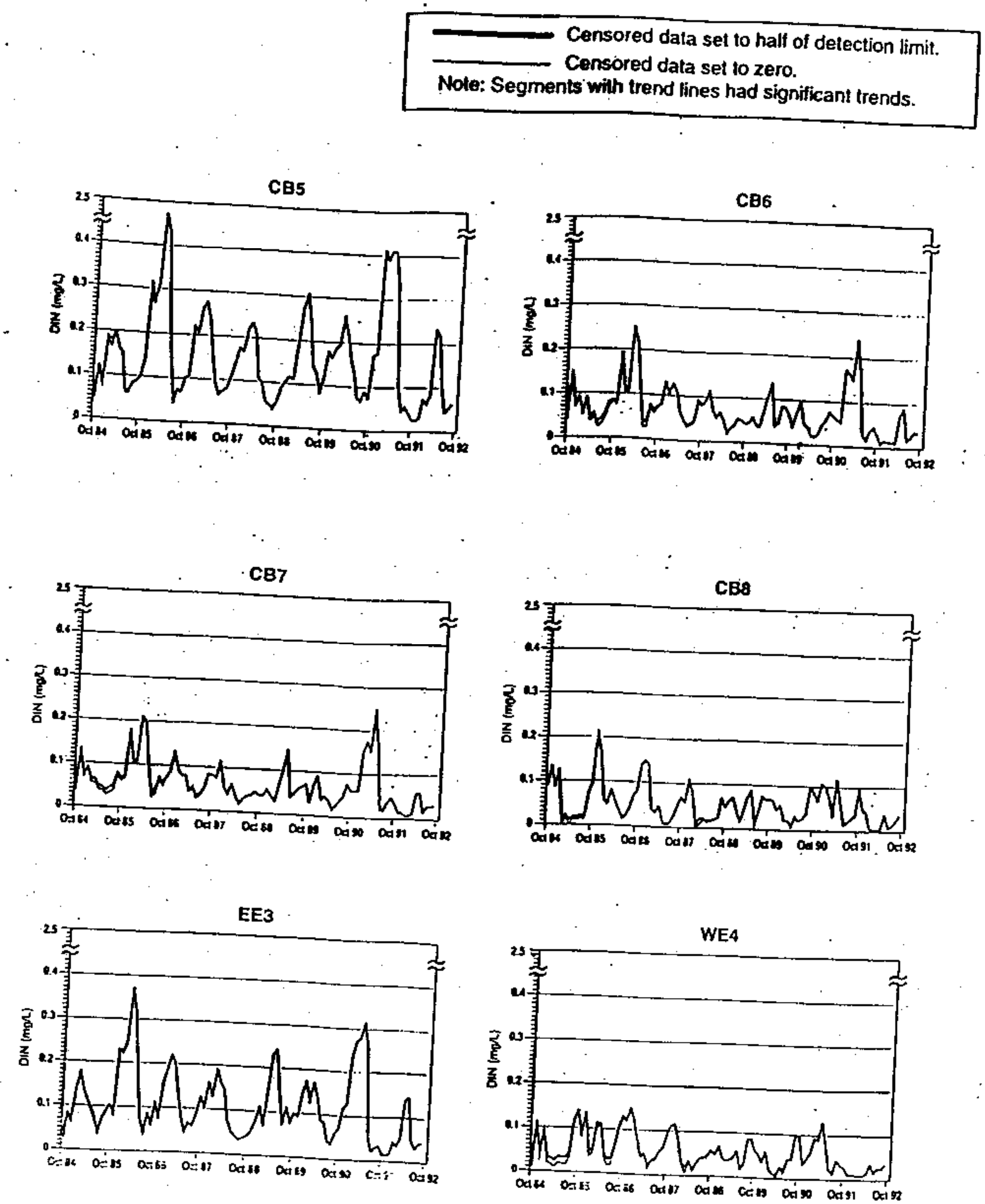


Figure 10. Average monthly concentrations of dissolved inorganic nitrogen (1984 to 1992) (continued).

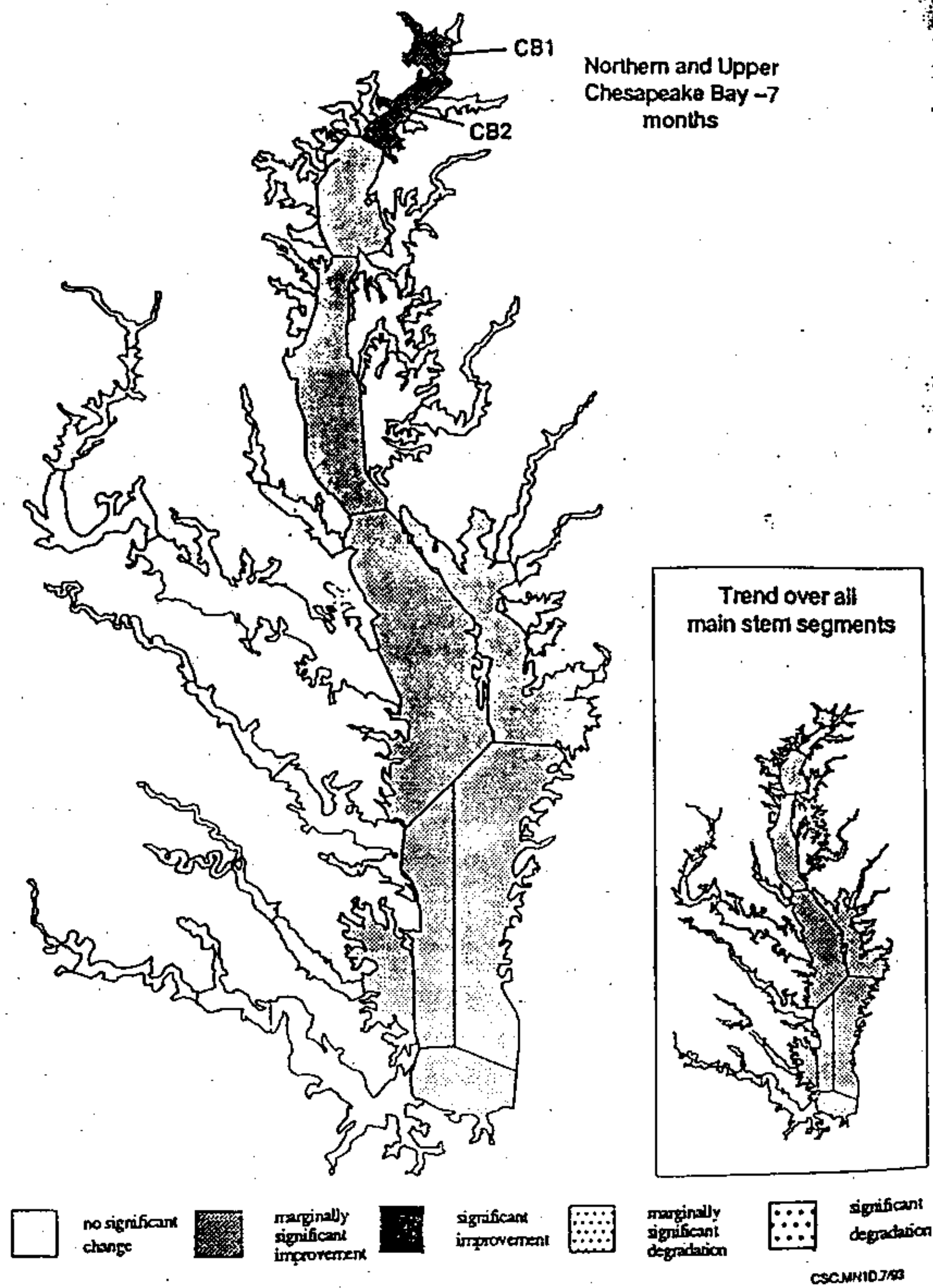


Figure 11. Secchi depth trends in Chesapeake Bay main stem segments (October 1984 through September 1992).

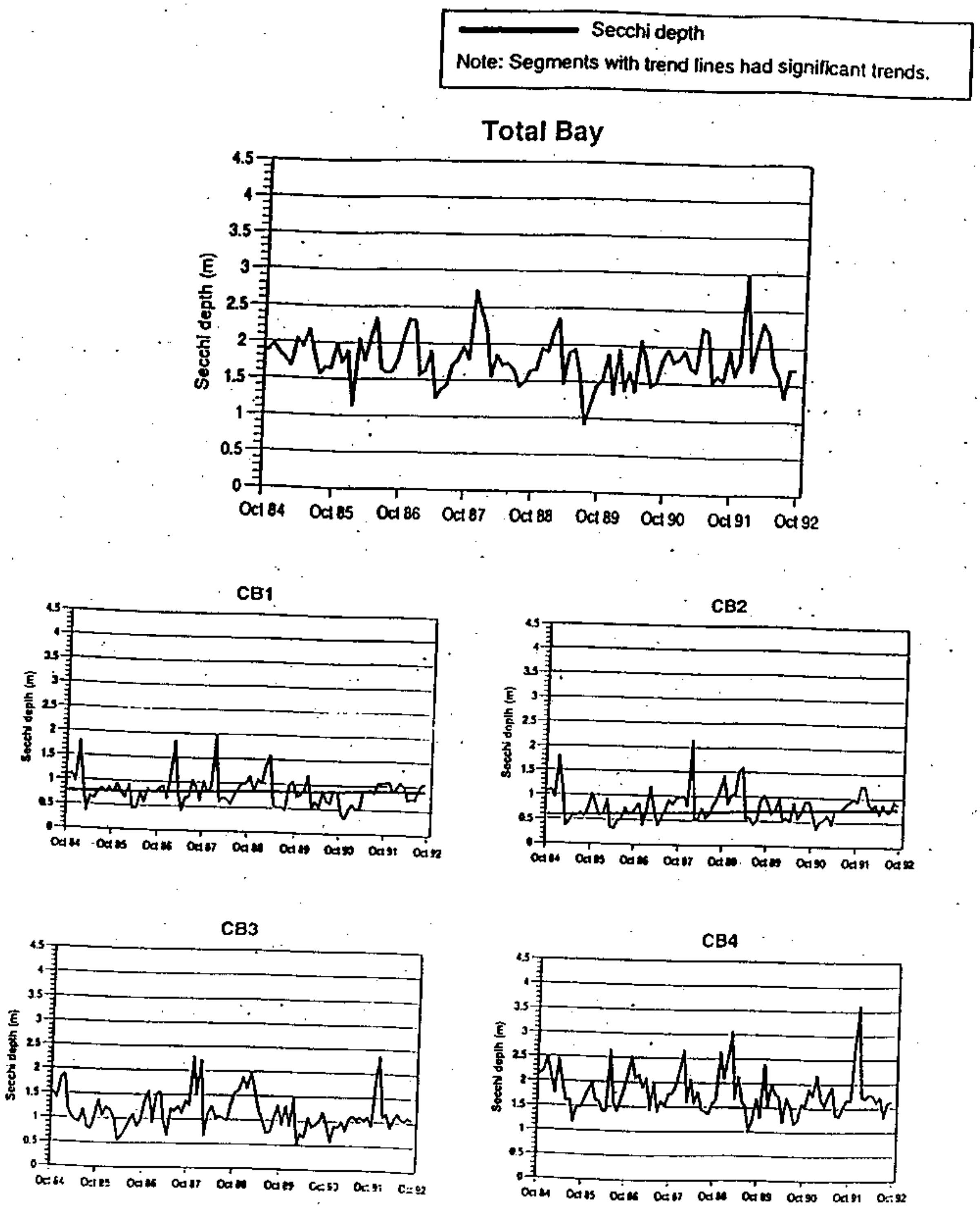


Figure 12. Average monthly Secchi depths (1984 to 1992).

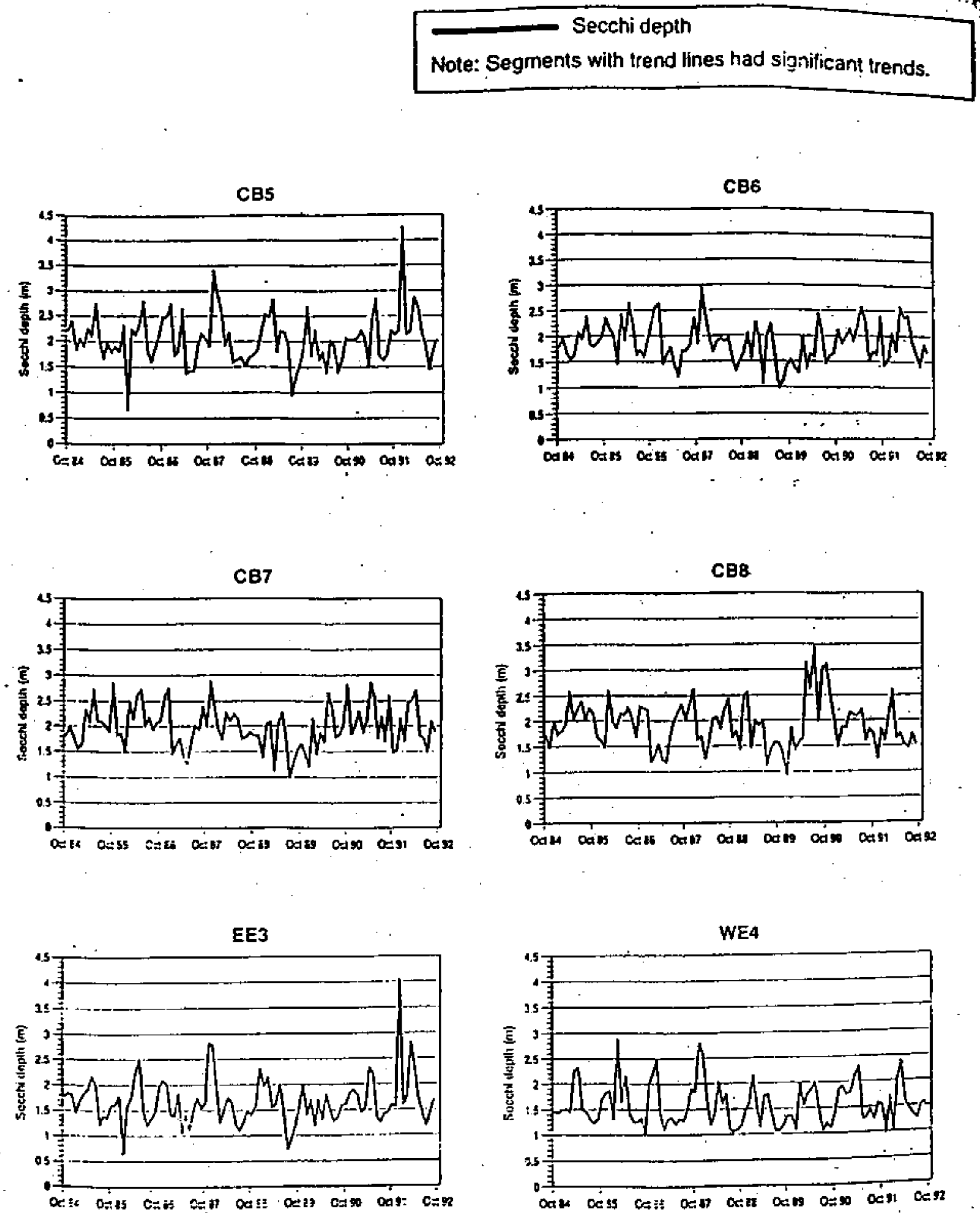


Figure 12. Average monthly Secchi depths (1984 to 1992) (continued).

Table 8. Trend results for interpolated monthly mean Secchi depth by segment (7 months, April through October).

Segment (CBP)	Slope m/yr	Z Trend	P	χ^2 Seasonal	P	% Change
All	–	–	NS	–	–	–
CB1	0.017	1.97	<0.05	4.92	<0.7	18
CB2	0.025	2.38	<0.017	8.46	>0.2	34
CB3	–	–	NS	–	–	–
CB4	–	–	NS	–	–	–
CB5	–	–	NS	–	–	–
CB6	–	–	NS	–	–	–
CB7	–	–	NS	–	–	–
CB8	–	–	NS	–	–	–
WE4	–	–	NS	–	–	–
EE3	–	–	NS	–	–	–

Legend and note:
The total number of months (*N*) for all segments was 56 (April 1985 through September 1992); all depths; results shown for marginally significant ($P<0.05$) trends only. No segments had significant trends over 12 months. A positive (up) trend shows improvement (clearer water); NS—Not significant ($P>0.05$). χ^2 seasonal and its *P* value (last two columns) are a test for homogeneity of the trend over different months. A *P* value of more than 0.05 indicates the trends were homogeneous.

Secchi depth is not measured in the Susquehanna River, so it is not known whether there were trends in Secchi depth there. Total suspended solids and turbidity data collected at the Susquehanna River fall line station (CB1.0) showed no significant trends over the 1984-to-1991 period ($P>0.1$*).

DISSOLVED OXYGEN

Trend results for the two DO metrics that had significant trends are shown in Tables 9 and 10. Table 9 shows results for DO delta, and Table 10 shows results for DO deficit, both over the warm weather period (June through September). Trend results for DO concentration and the four metrics for volumes below specific concentrations are not shown because no trends were statistically significant for those parameters. Segment CB8 showed marginally significant degradation in both DO delta and DO deficit (see Figure 13).

*B. Dobler, MDE, unpublished analyses.

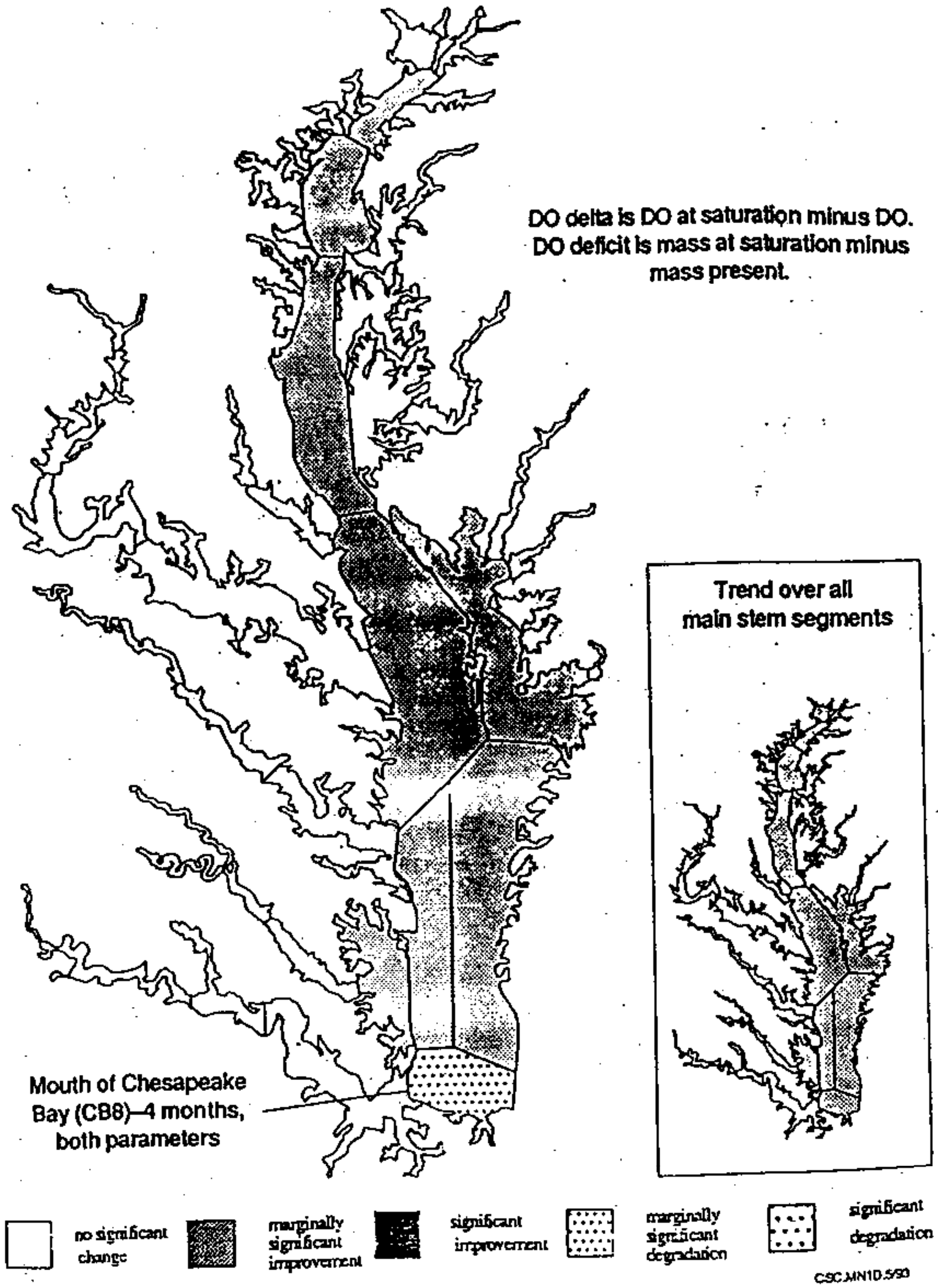


Figure 13. Dissolved oxygen delta and dissolved oxygen deficit trends in Chesapeake Bay main stem segments (October 1984 through September 1992).

Table 9. Trend results for interpolated monthly mean dissolved oxygen delta by segment (4 warm weather months, June through September).

Segment (CBP)	Slope mg/L/yr	Z Trend	P	χ^2 Seasonal	P	% Change
All	–	–	NS	–	–	–
CB1	–	–	NS	–	–	–
CB2	–	–	NS	–	–	–
CB3	–	–	NS	–	–	–
CB4	–	–	NS	–	–	–
CB5	–	–	NS	–	–	–
CB6	–	–	NS	–	–	–
CB7	–	–	NS	–	–	–
CB8	0.038	2.50	0.012	0.57	0.9	77
WE4	–	–	NS	–	–	–

Legend and note:

The total number of months (*N*) for all segments was 32 (June 1985 through September 1992); all depths; results shown for marginally significant ($P<0.05$) trends only. A positive (up) trend shows less desirable conditions (degradation); NS—Not significant ($P>0.05$). χ^2 seasonal and its *P* value (last two columns) are a test for homogeneity of the trend over different months. A *P* value of more than 0.05 indicates the trends were homogeneous. DO data were not analyzed in EE3.

Figure 14 shows average monthly DO and DO delta concentrations for each segment. As DO (upper line) goes down in the summer, DO delta (lower line) goes up, especially in segment CB4. Segments with marginally significant trends (DO delta in CB8) have a trend line connecting the 1984 to 1985 mean and the 1991 to 1992 projection based on the seasonal Kendall slope. Although some segments appear to have declining trends in DO concentration, e.g., total segments and segment CB8, these were not statistically significant when tested over the warm weather period only (June through September).

Figure 15 shows the total volumes of water in each segment with DO below four concentrations: 0.2, 1, 3, and 5 mg/L, summed over all 4 months of the warm weather period (June through September). Hypoxia/anoxia is a problem during late spring and summer in the deeper waters of middle Chesapeake Bay (primarily segments CB4 and CB5). Reducing the volume of anoxic water in Chesapeake Bay is a major goal of nutrient reduction strategies. The trend results for anoxic volume and the volumes of water at the other target concentrations were not significant in any segment; in segments CB4 and CB5 (segments with relatively large total volumes), the volumes at the higher concentration categories were fairly consistent from year to year, with some shifting between the less than 0.2 and 0.2-to-1 mg/L categories. Lower Chesapeake Bay segments CB6 and CB7, also relatively large segments, had almost no anoxic water and had more variability in the volumes of water in the other categories. A low flow year, 1988 (see Figure 2),

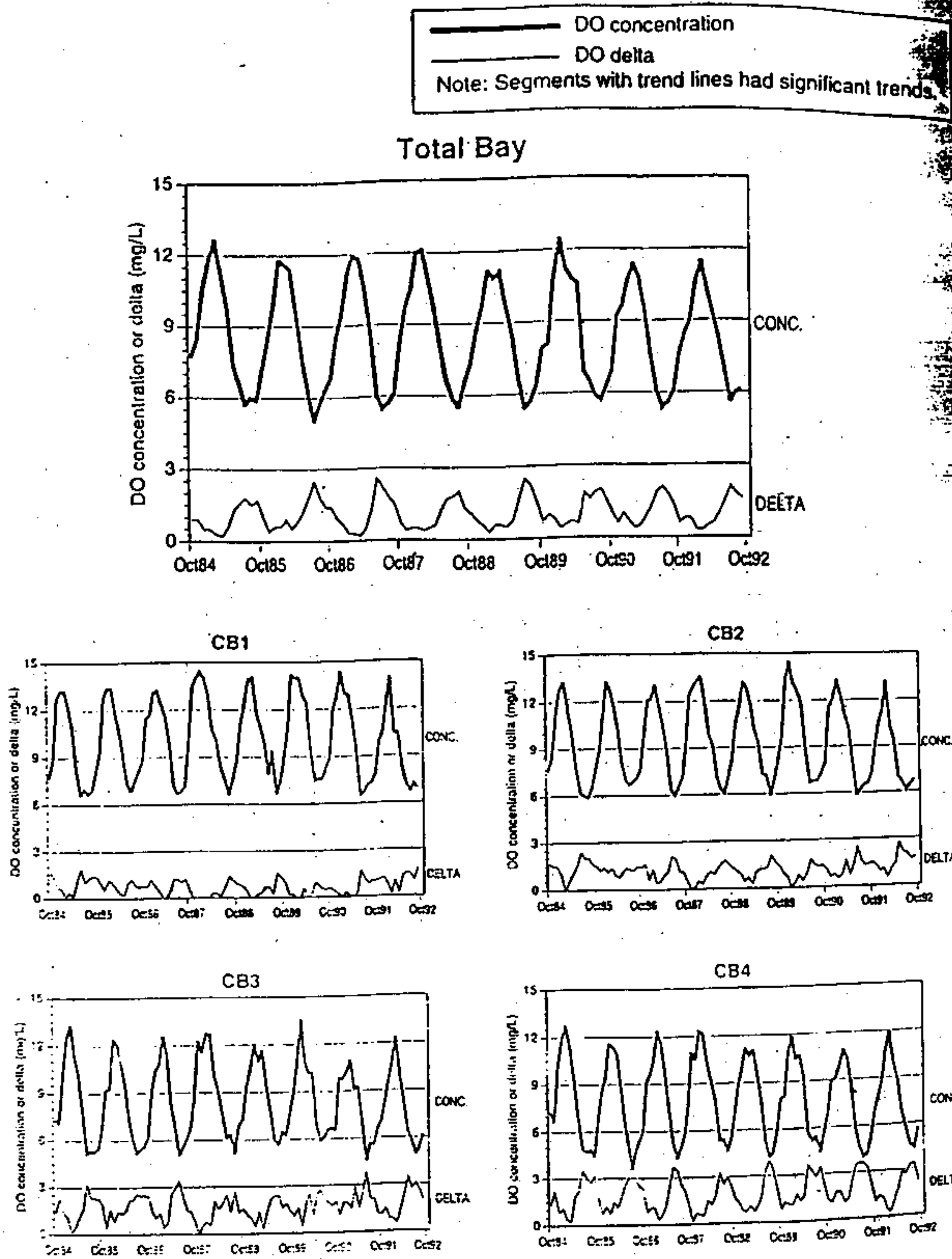


Figure 14. Average monthly concentrations of dissolved oxygen and dissolved oxygen delta (1984 to 1992,

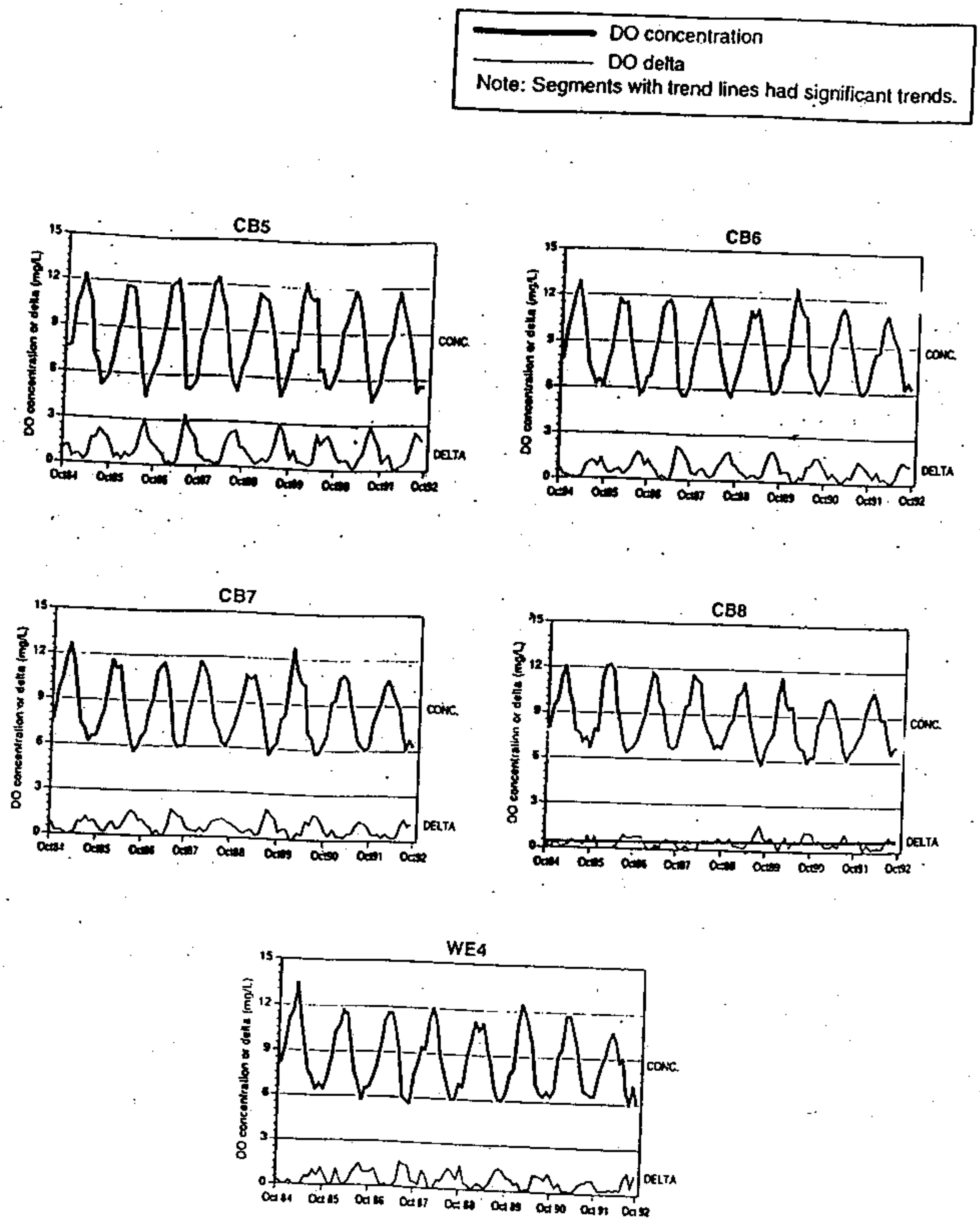


Figure 14. Average monthly concentrations of dissolved oxygen and dissolved oxygen delta (1984 to 1992) (continued).

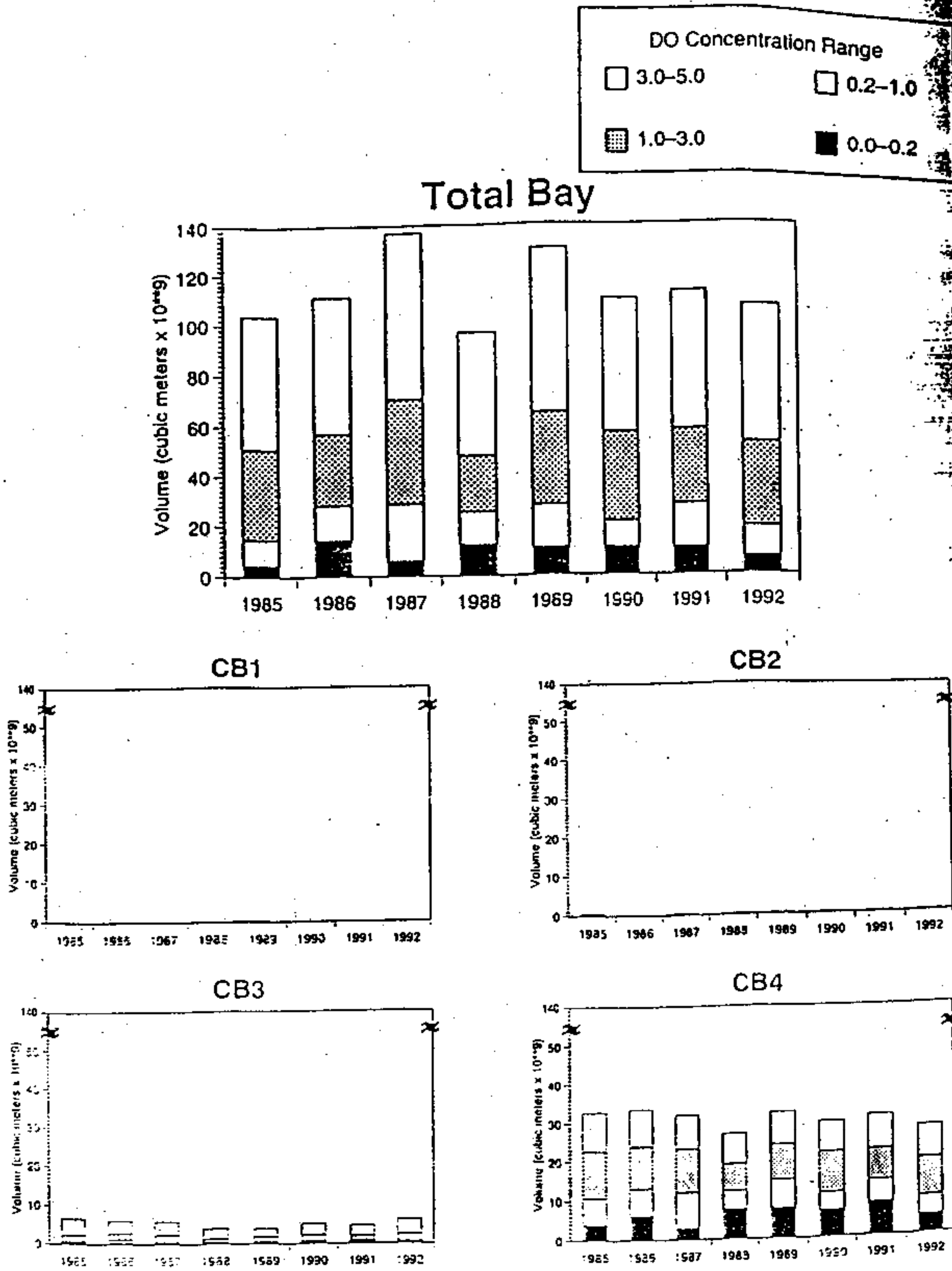


Figure 15. Total volumes of water with dissolved oxygen concentrations below 0.2, 1, 3, and 5 mg/L (June through September, 1985 to 1992).

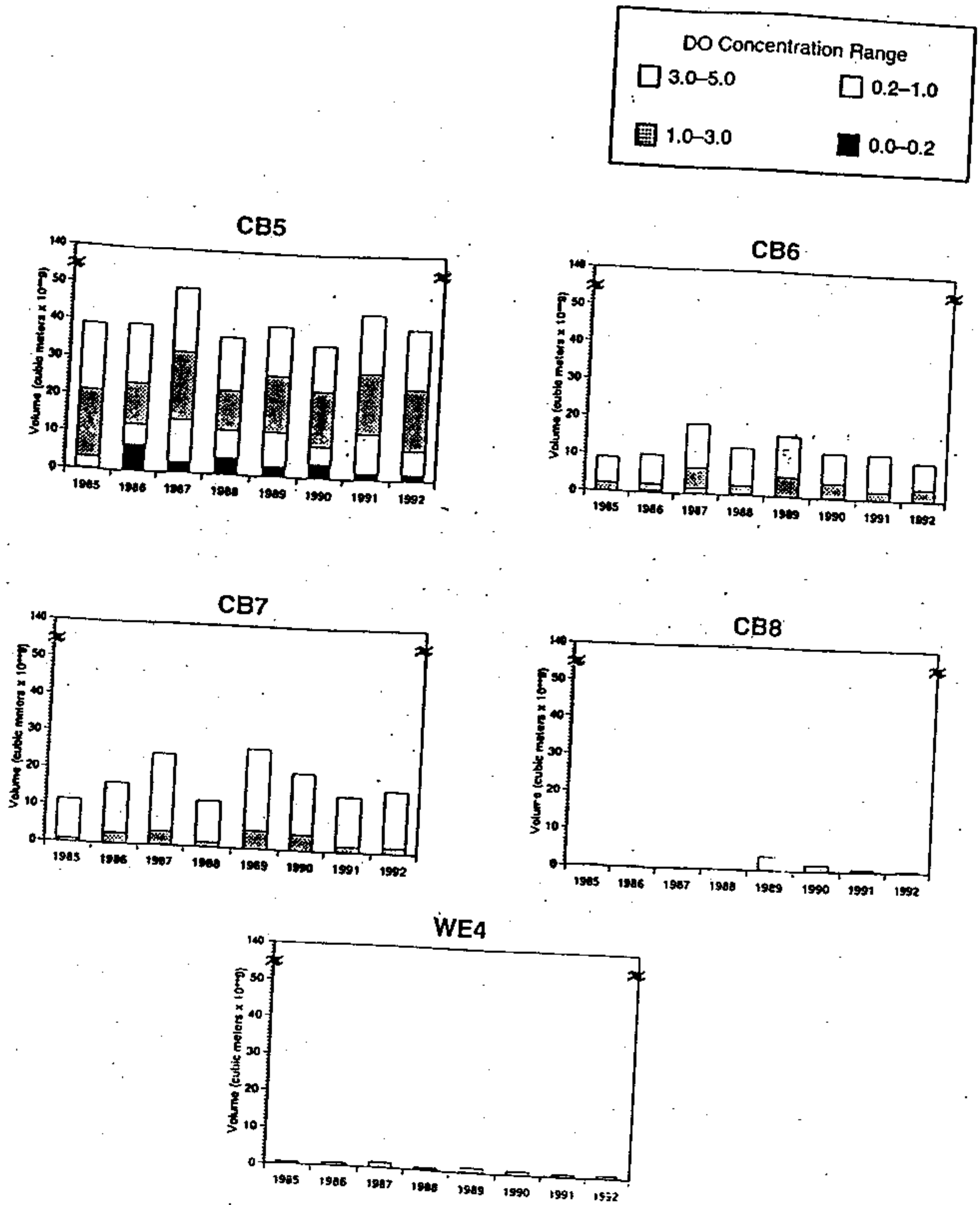


Figure 15. Total volumes of water with dissolved oxygen concentrations below 0.2, 1, 3, and 5 mg/L (June through September, 1985 to 1992) (continued).

usually had the lowest total volume of water below 5 mg/L. This is probably due to reduced stratification in low flow years.

Table 10. Trend results for interpolated monthly mean dissolved oxygen deficit by segment (4 warm weather months, June through September).

Segment (CBP)	Slope kg/yr*	*Z* Trend	*P*	χ^2 Seasonal	*P*	% Change
All	–	–	NS	–	–	–
CB1	–	–	NS	–	–	–
CB2	–	–	NS	–	–	–
CB3	–	–	NS	–	–	–
CB4	–	–	NS	–	–	–
CB5	–	–	NS	–	–	–
CB6	–	–	NS	–	–	–
CB7	–	–	NS	–	–	–
CB8	143.4	2.04	0.041	0.17	0.98	88
WE4	–	–	NS	–	–	–

*Units are kg × 10^{11}.

Legend and note:

Dissolved oxygen deficit is dissolved oxygen delta converted to a mass of oxygen. The total number of months (*N*) for all segments was 32 (June 1985 through September 1992); all depths; results shown for marginally significant ($P<0.05$) trends only. A positive (up) trend shows a movement toward less desirable conditions (degradation); NS—Not significant ($P>0.05$). χ^2 seasonal and its *P* value (last two columns) are a test for homogeneity of the trend over different months. A *P* value of more than 0.05 indicates the trends were homogeneous. DO data were not analyzed in EE3.

The marginally significant trends in two DO metrics at the mouth of Chesapeake Bay (segment CB8) have no obvious potential causes. DO concentrations are generally high in CB8 (see Figure 14) and DO delta is quite low, so these trends are unlikely to have any negative impact on living resources in CB8. The high percent change values (77 and 88 percent) appear to be partly due to abnormally low values in the 1985 WY.

PLANS FOR FUTURE TREND ANALYSES

INTERPOLATING ABOVE AND BELOW PYCNOCLINE LAYERS AND SURFACE AND BOTTOM LAYERS SEPARATELY

Several enhancements to the trend analysis methods are planned for the next trend analysis update. The enhancements that may be implemented include interpolating above and below pycnocline layers and surface and bottom layers separately. This will make it possible to perform trend analyses of water quality in separate water layers. Trend analyses of DO concentrations will focus on the bottom layer and the region below the pycnocline, where almost all of the low DO concentrations occur. Trends in nutrient parameters affecting SAV growth, DIN, and DIP will focus on the surface mixed layer, since SAV habitat requirements are defined only for surface concentrations.

ACCOUNTING FOR INTERANNUAL CHANGES IN FLOW

The seasonal Kendall test accounts for seasonal changes in flow within years, but not for changes in flow between years. Interannual flow differences could be estimated from fall line flow data; however, this is difficult in the main stem, where the fall line may be quite far from the segment and flow from more than one river affects some segments. Flow effects will probably be estimated indirectly from the degree of stratification within each main stem segment, especially for DO.

ADDING PARAMETRIC TREND TESTS

Software is currently being developed to streamline the autoregressive parametric trend tests that were used in two of the previous trend reports.[3, 4] The advantages of these tests are that they account for serial correlation in the data; therefore, the significance levels are more accurate and they can account for changes in detection limits.

ADDING TREND TESTS ON INTERPOLATED TRIBUTARY DATA

The volumetric interpolator does not currently operate in the tributaries, but there are plans to develop this capability. This would permit the analysis of tributary water quality trends using the same methods and time periods used to analyze main stem trends.

SUMMARY

The trend results for phosphorus, nitrogen, Secchi depth, and DO are summarized in Table 11. Because eutrophication is one of the main causes of low DO in Chesapeake Bay, there should be improvements in DO where there are improvements (declines) in nutrient levels. Improving trends in DO would increase the amount of living resource habitat in Chesapeake Bay. Table 11 shows that there were statistically significant declines (improvements) in TP and DIP in some segments but no corresponding improvements in any of the DO metrics. This lack of improving trends in DO could be due to two factors:

1. The nutrient declines, although statistically significant, may not have been large enough to improve DO conditions or they may not have affected enough of Chesapeake Bay. Also, nitrogen has not shown significant improvements in any segments. Summer hypoxia and anoxia may be more affected by the freshet and its nitrogen supply than by phosphorus levels.
2. There has not been enough time for DO responses. There may be a time lag between nutrient reductions and DO improvements. Nutrients stored in sediments from previous years may promote DO depletion,[8] although some authors have argued that the timing and extent of summer anoxia are governed mainly by climatic conditions in that year.[14] Upbay and downbay transfer of nutrients, organic matter, and DO also complicate any responses of DO levels to nutrient reductions.

Improving trends in dissolved inorganic nutrients and Secchi depths can also lead to attainment of SAV habitat requirements if the requirements are not currently met. This should promote SAV restoration. Both of the segments that had improving trends in DIP are already in attainment for those requirements, so these trends should have little impact on SAV restoration. However, the improving trend in Secchi depth in one upper Chesapeake Bay segment (CB2) may lead to an increased frequency of attainment of the Secchi depth requirement in that segment in the future.

Table 11. Summary of trend results (October 1984 through September 1992).

Parameter	No. of Months	Main Stem CBP Segments										
		All	CB1	CB2	CB3	CB4	CB5	CB6	CB7	CB8	WE4	EE3
TP	12	I	IM	I	IM	–	–	I	IM	I	–	–
DIP	12	–	–	–	–	–	–	–	–	I	–	–
DIP	7	–	–	–	–	I	–	–	–	–	–	–
TN	12	–	–	–	–	–	–	–	–	–	DM	–
DIN	12	–	–	–	–	–	–	+	+	–	+	+
DIN	7	–	–	–	–	–	–	+	+	–	+	+
Secchi Depth	12	–	–	–	–	–	–	–	–	–	–	–
Secchi Depth	7	–	IM	IM	–	–	–	–	–	–	–	–
DO Concentration	4	–	–	–	–	–	–	–	–	–	–	–
DO Delta	4	–	–	–	–	–	–	–	–	DM	–	–
DO Deficit	4	–	–	–	–	–	–	–	–	DM	–	–
DO<0.2	4	–	–	–	–	–	–	–	–	–	–	–
DO<1.0	4	–	–	–	–	–	–	–	–	–	–	–
DO<3.0	4	–	–	–	–	–	–	–	–	–	–	–
DO<5.0	4	–	–	–	–	–	–	–	–	–	–	–

Legend and note:
I—Significant improvement ($P<0.01$).
IM—Marginally significant improvement ($P<0.05$).
DM—Marginally significant degradation.
Dash—No significant trend ($P>0.05$).
+—DIN trends could not be assessed in these segments because detection limits did not stop declining until July 1990.
7 months—April through October only, same as SAV growing season in lower salinity zones; 4 months—June through September only, used as period of anoxia in three-dimensional model analyses.
DO data were not analyzed in EE3.
See text for explanation of DO delta, DO deficit, and DO volumes below the four concentrations.

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APPENDIX

FREQUENCIES OF BELOW DETECTION LIMIT VALUES FOR DISSOLVED INORGANIC PHOSPHORUS AND DISSOLVED INORGANIC NITROGEN

Table A.1: Percent of observations with below detection limit values for dissolved inorganic phosphorus by segment, laboratory, and water year.

Segment	Laboratory	Year	% BDL	Mean MDL
CB1	CRL/CBL	85	19.4	0.0055
CB1	CRL/CBL	86	0	–
CB1	CRL/CBL	87	7.9	0.0016
CB1	CRL/CBL	88	0	–
CB1	CRL/CBL	89	0	–
CB1	CRL/CBL	90	0	–
CB1	CRL/CBL	91	0	–
CB1	CRL/CBL	92	0	–
CB2	CRL/CBL	85	3.8	0.007
CB2	CRL/CBL	86	0	–
CB2	CRL/CBL	87	0	–
CB2	CRL/CBL	88	0	–
CB2	CRL/CBL	89	0	–
CB2	CRL/CBL	90	0	–
CB2	CRL/CBL	91	0	–
CB2	CRL/CBL	92	0	–
CB3	CRL/CBL	85	8.6	0.007
CB3	CRL/CBL	86	1.3	0.0016
CB3	CRL/CBL	87	2.5	0.0016
CB3	CRL/CBL	88	0	–
CB3	CRL/CBL	89	0	–
CB3	CRL/CBL	90	0	–
CB3	CRL/CBL	91	0	–
CB3	CRL/CBL	92	0	–
CB4	CRL/CBL	85	22.2	0.006
CB4	CRL/CBL	86	6.8	0.0016
CB4	CRL/CBL	87	11.4	0.0016
CB4	CRL/CBL	88	0.1	0.0006
CB4	CRL/CBL	89	0	–
CB4	CRL/CBL	90	0	–
CB4	CRL/CBL	91	0.6	0.0006
CB4	CRL/CBL	92	0	–
CB5	CRL/CBL	85	30.7	0.0061
CB5	CRL/CBL	86	21.5	0.0016

Segment	Laboratory	Year	% BDL	Mean MDL
CB5	CRL/CBL	87	15.2	0.0016
CB5	CRL/CBL	88	0.9	0.0006
CB5	CRL/CBL	89	0.6	0.0006
CB5	CRL/CBL	90	0	–
CB5	CRL/CBL	91	0	–
CB5	CRL/CBL	92	0.3	0.0006
CB5	VIMS	85	81.8	0.01
CB5	VIMS	86	89.4	0.0105
CB5	VIMS	87	75.6	0.0101
CB5	VIMS	88	37.6	0.0016
CB5	VIMS	89	27.4	0.002
CB5	VIMS	90	62	0.0028
CB5	VIMS	91	18.1	0.0006
CB5	VIMS	92	7.8	0.0006
CB6	VIMS	85	85.1	0.01
CB6	VIMS	86	85.4	0.0105
CB6	VIMS	87	70.8	0.0104
CB6	VIMS	88	37.8	0.0016
CB6	VIMS	89	30.5	0.002
CB6	VIMS	90	62.5	0.0027
CB6	VIMS	91	18.1	0.0006
CB6	VIMS	92	10.5	0.0006
CB7	VIMS	85	83.5	0.01
CB7	VIMS	86	83.8	0.0105
CB7	VIMS	87	75.8	0.01
CB7	VIMS	88	34.2	0.0016
CB7	VIMS	89	25	0.0022
CB7	VIMS	90	55.6	0.0028
CB7	VIMS	91	19.5	0.0006
CB7	VIMS	92	10.6	0.0006
EE3	VIMS	85	100	0.01
EE3	VIMS	86	100	0.0105
EE3	VIMS	87	94.9	0.0094
EE3	VIMS	88	36.1	0.0019
EE3	VIMS	89	47.4	0.0016
EE3	VIMS	90	69.4	0.0024

Segment	Laboratory	Year	% BDL	Mean MDL
EE3	VIMS	91	27.8	0.0006
EE3	VIMS	92	5.6	0.0006
WE4	VIMS	85	90.7	0.0099
WE4	VIMS	86	84.9	0.0105
WE4	VIMS	87	71.7	0.0109
WE4	VIMS	88	40.3	0.0016
WE4	VIMS	89	28.3	0.0022
WE4	VIMS	90	58.3	0.0028
WE4	VIMS	91	11.9	0.0006
WE4	VIMS	92	2.8	0.0006
CB6	ODU	85	36.2	0.01
CB6	ODU	86	63.3	0.01
CB6	ODU	87	50	0.0053
CB6	ODU	88	47.2	0.005
CB6	ODU	89	25.7	0.005
CB6	ODU	90	36.1	0.005
CB6	ODU	91	44.4	0.005
CB6	ODU	92	58.3	0.005
CB7	ODU	85	32.3	0.01
CB7	ODU	86	52.7	0.01
CB7	ODU	87	46.7	0.0052
CB7	ODU	88	32.7	0.005
CB7	ODU	89	17.8	0.005
CB7	ODU	90	23.1	0.005
CB7	ODU	91	23.6	0.005
CB7	ODU	92	44.4	0.005
CB8	ODU	85	16.1	0.01
CB8	ODU	86	39.9	0.01
CB8	ODU	87	29.2	0.0051
CB8	ODU	88	26.1	0.005
CB8	ODU	89	9	0.005
CB8	ODU	90	7.2	0.005
CB8	ODU	91	15	0.005
CB8	ODU	92	35.8	0.005

Table A.2. Percent of observations with below detection limit values for dissolved inorganic nitrogen by segment, laboratory, constituent parameter, and water year.

Segment	Laboratory	Parameter	Year	% BDL	Mean MDL	% of DIN
CB1	CRL/CBL	Both	85	0	–	–
CB1	CRL/CBL	NH_4	85	13.9	0.0166	1.3
CB1	CRL/CBL	NO_{23}	85	0	–	–
CB1	CRL/CBL	Both	86	0	–	–
CB1	CRL/CBL	NH_4	86	2.8	0.003	0.3
CB1	CRL/CBL	NO_{23}	86	0	–	–
CB1	CRL/CBL	Both	87	0	–	–
CB1	CRL/CBL	NH_4	87	0	–	–
CB1	CRL/CBL	NO_{23}	87	0	–	–
CB1	CRL/CBL	Both	88	0	–	–
CB1	CRL/CBL	NH_4	88	5.3	0.003	0.5
CB1	CRL/CBL	NO_{23}	88	0	–	–
CB1	CRL/CBL	Both	89	0	–	–
CB1	CRL/CBL	NH_4	89	10.5	0.003	0.2
CB1	CRL/CBL	NO_{23}	89	0	–	–
CB1	CRL/CBL	Both	90	0	–	–
CB1	CRL/CBL	NH_4	90	5	0.003	0.3
CB1	CRL/CBL	NO_{23}	90	0	–	–
CB1	CRL/CBL	Both	91	0	–	–
CB1	CRL/CBL	NH_4	91	15.4	0.003	0.3
CB1	CRL/CBL	NO_{23}	91	0	–	–
CB1	CRL/CBL	Both	92	0	–	–
CB1	CRL/CBL	NH_4	92	2.5	0.003	0.3
CB1	CRL/CBL	NO_{23}	92	0	–	–
CB2	CRL/CBL	Both	85	0	–	–
CB2	CRL/CBL	NH_4	85	0	–	–
CB2	CRL/CBL	NO_{23}	85	0	–	–
CB2	CRL/CBL	Both	86	0	–	–
CB2	CRL/CBL	NH_4	86	0.9	0.003	1.4
CB2	CRL/CBL	NO_{23}	86	0	–	–
CB2	CRL/CBL	Both	87	0	–	–
CB2	CRL/CBL	NH_4	87	0	–	–
CB2	CRL/CBL	NO_{23}	87	0	–	–
CB2	CRL/CBL	Both	88	0	–	–

Segment	Laboratory	Parameter	Year	% BDL	Mean MDL	% of DIN
CB2	CRL/CBL	NH_4	88	0.9	0.005	0.7
CB2	CRL/CBL	NO_{23}	88	0	–	–
CB2	CRL/CBL	Both	89	0	–	–
CB2	CRL/CBL	NH_4	89	0.9	0.003	0.2
CB2	CRL/CBL	NO_{23}	89	0	–	–
CB2	CRL/CBL	Both	90	0	–	–
CB2	CRL/CBL	NH_4	90	5	0.003	0.3
CB2	CRL/CBL	NO_{23}	90	0	–	–
CB2	CRL/CBL	Both	91	0	–	–
CB2	CRL/CBL	NH_4	91	3.3	0.003	0.9
CB2	CRL/CBL	NO_{23}	91	0	–	–
CB2	CRL/CBL	Both	92	0	–	–
CB2	CRL/CBL	NH_4	92	1.7	0.003	0.3
CB2	CRL/CBL	NO_{23}	92	0	–	–
CB3	CRL/CBL	Both	85	0	–	–
CB3	CRL/CBL	NH_4	85	2.9	0.0257	6.7
CB3	CRL/CBL	NO_{23}	85	0	–	–
CB3	CRL/CBL	Both	86	0	–	–
CB3	CRL/CBL	NH_4	86	0	–	–
CB3	CRL/CBL	NO_{23}	86	0	–	–
CB3	CRL/CBL	Both	87	0	–	–
CB3	CRL/CBL	NH_4	87	0	–	–
CB3	CRL/CBL	NO_{23}	87	0	–	–
CB3	CRL/CBL	Both	88	0	–	–
CB3	CRL/CBL	NH_4	88	0	–	–
CB3	CRL/CBL	NO_{23}	88	0	–	–
CB3	CRL/CBL	Both	89	0	–	–
CB3	CRL/CBL	NH_4	89	3.9	0.003	0.5
CB3	CRL/CBL	NO_{23}	89	0	–	–
CB3	CRL/CBL	Both	90	0	–	–
CB3	CRL/CBL	NH_4	90	4.4	0.003	0.7
CB3	CRL/CBL	NO_{23}	90	0	–	–
CB3	CRL/CBL	Both	91	0	–	–
CB3	CRL/CBL	NH_4	91	4.3	0.003	7.6
CB3	CRL/CBL	NO_{23}	91	0	–	–
CB3	CRL/CBL	Both	92	0	–	–

Segment	Laboratory	Parameter	Year	% BDL	Mean MDL	% of DIN
CB3	CRL/CBL	NH_4	92	2.5	0.0097	1.7
CB3	CRL/CBL	NO_{23}	92	0	–	–
CB4	CRL/CBL	Both	85	0	–	–
CB4	CRL/CBL	NH_4	85	7.5	0.0293	19.2
CB4	CRL/CBL	NO_{23}	85	3.8	0.04	22
CB4	CRL/CBL	Both	86	0	–	–
CB4	CRL/CBL	NH_4	86	0.7	0.003	0.6
CB4	CRL/CBL	NO_{23}	86	0.1	0.0009	0.3
CB4	CRL/CBL	Both	87	0	–	–
CB4	CRL/CBL	NH_4	87	0	–	–
CB4	CRL/CBL	NO_{23}	87	0.1	0.0009	0.3
CB4	CRL/CBL	Both	88	0	–	–
CB4	CRL/CBL	NH_4	88	5.7	0.0046	25.9
CB4	CRL/CBL	NO_{23}	88	0	–	–
CB4	CRL/CBL	Both	89	0	–	–
CB4	CRL/CBL	NH_4	89	7.8	0.003	2.3
CB4	CRL/CBL	NO_{23}	89	0	–	–
CB4	CRL/CBL	Both	90	0	–	–
CB4	CRL/CBL	NH_4	90	10.3	0.003	4.8
CB4	CRL/CBL	NO_{23}	90	0	–	–
CB4	CRL/CBL	Both	91	0	–	–
CB4	CRL/CBL	NH_4	91	13.9	0.003	13.1
CB4	CRL/CBL	NO_{23}	91	0	–	–
CB4	CRL/CBL	Both	92	0	–	–
CB4	CRL/CBL	NH_4	92	11	0.003	13.4
CB4	CRL/CBL	NO_{23}	92	0	–	–
CB5	CRL/CBL	Both	85	3.8	0.06	–
CB5	CRL/CBL	NH_4	85	10	0.0242	30
CB5	CRL/CBL	NO_{23}	85	14.1	0.04	34
CB5	CRL/CBL	Both	86	0	–	–
CB5	CRL/CBL	NH_4	86	0.6	0.003	0.9
CB5	CRL/CBL	NO_{23}	86	0	–	–
CB5	CRL/CBL	Both	87	0	–	–
CB5	CRL/CBL	NH_4	87	0	–	–
CB5	CRL/CBL	NO_{23}	87	0	–	–
CB5	CRL/CBL	Both	88	0	–	–

Segment	Laboratory	Parameter	Year	% BDL	Mean MDL	% of DIN
CB5	CRL/CBL	NH_4	88	14.7	0.0043	22
CB5	CRL/CBL	NO_{23}	88	0	–	–
CB5	CRL/CBL	Both	89	0	–	–
CB5	CRL/CBL	NH_4	89	15.9	0.003	5.2
CB5	CRL/CBL	NO_{23}	89	0	–	–
CB5	CRL/CBL	Both	90	0	–	–
CB5	CRL/CBL	NH_4	90	13.8	0.003	11.2
CB5	CRL/CBL	NO_{23}	90	0	–	–
CB5	CRL/CBL	Both	91	0	–	–
CB5	CRL/CBL	NH_4	91	20.6	0.003	20.7
CB5	CRL/CBL	NO_{23}	91	0	–	–
CB5	CRL/CBL	Both	92	0	–	–
CB5	CRL/CBL	NH_4	92	14.7	0.003	22.8
CB5	CRL/CBL	NO_{23}	92	0	–	–
CB5	VIMS	Both	85	22.3	0.0397	–
CB5	VIMS	NH_4	85	25.9	0.0198	19.1
CB5	VIMS	NO_{23}	85	33.1	0.0199	22.8
CB5	VIMS	Both	86	18.1	0.0418	–
CB5	VIMS	NH_4	86	35.7	0.0215	13
CB5	VIMS	NO_{23}	86	16.6	0.0198	26.7
CB5	VIMS	Both	87	8.1	0.0254	–
CB5	VIMS	NH_4	87	12.1	0.0155	14.7
CB5	VIMS	NO_{23}	87	31.8	0.0104	21.2
CB5	VIMS	Both	88	4.2	0.0161	–
CB5	VIMS	NH_4	88	12.2	0.0133	53.5
CB5	VIMS	NO_{23}	88	9.5	0.0033	9.6
CB5	VIMS	Both	89	6.5	0.0121	–
CB5	VIMS	NH_4	89	28.8	0.012	23
CB5	VIMS	NO_{23}	89	1.6	0.0021	7.2
CB5	VIMS	Both	90	5.6	0.0075	–
CB5	VIMS	NH_4	90	36.3	0.0094	23.5
CB5	VIMS	NO_{23}	90	6.1	0.0024	19.9
CB5	VIMS	Both	91	7.9	0.0045	–
CB5	VIMS	NH_4	91	9.6	0.0038	8
CB5	VIMS	NO_{23}	91	14.7	0.0024	24.5
CB5	VIMS	Both	92	5	0.0046	–

Segment	Laboratory	Parameter	Year	% BDL	Mean MDL	% of DIN
CB5	VIMS	NH_4	92	16.7	0.0039	31.2
CB5	VIMS	NO_{23}	92	6.7	0.0023	31.2
CB6	VIMS	Both	85	28.9	0.04	–
CB6	VIMS	NH_4	85	24.5	0.0193	25
CB6	VIMS	NO_{23}	85	29.6	0.0199	29
CB6	VIMS	Both	86	16.8	0.042	–
CB6	VIMS	NH_4	86	33.5	0.0215	14.9
CB6	VIMS	NO_{23}	86	19.2	0.0198	26.6
CB6	VIMS	Both	87	8.8	0.0212	–
CB6	VIMS	NH_4	87	11.3	0.0119	12.8
CB6	VIMS	NO_{23}	87	36.8	0.0112	24.5
CB6	VIMS	Both	88	6.3	0.0162	–
CB6	VIMS	NH_4	88	10	0.0124	56.1
CB6	VIMS	NO_{23}	88	14.3	0.0047	16
CB6	VIMS	Both	89	9	0.0121	–
CB6	VIMS	NH_4	89	28.1	0.0121	26.2
CB6	VIMS	NO_{23}	89	2	0.0021	8.1
CB6	VIMS	Both	90	19.6	0.0102	–
CB6	VIMS	NH_4	90	28.4	0.0096	36.2
CB6	VIMS	NO_{23}	90	3.5	0.0024	22
CB6	VIMS	Both	91	8.7	0.005	–
CB6	VIMS	NH_4	91	11.1	0.0038	9.6
CB6	VIMS	NO_{23}	91	11.8	0.0024	28.7
CB6	VIMS	Both	92	7	0.0046	–
CB6	VIMS	NH_4	92	25.5	0.0039	43.6
CB6	VIMS	NO_{23}	92	8	0.0023	34.6
CB7	VIMS	Both	85	28.4	0.0398	–
CB7	VIMS	NH_4	85	23.3	0.0197	27.4
CB7	VIMS	NO_{23}	85	31.5	0.02	25.2
CB7	VIMS	Both	86	16.3	0.0415	–
CB7	VIMS	NH_4	86	32.9	0.0215	18.5
CB7	VIMS	NO_{23}	86	20.8	0.0199	30
CB7	VIMS	Both	87	10.8	0.0202	–
CB7	VIMS	NH_4	87	9.2	0.0147	25.5
CB7	VIMS	NO_{23}	87	39.6	0.0106	21.5
CB7	VIMS	Both	88	6.8	0.0183	–

Segment	Laboratory	Parameter	Year	% BDL	Mean MDL	% of DIN
CB7	VIMS	NH_4	88	10.5	0.0129	67.9
CB7	VIMS	NO_{23}	88	16.4	0.0068	20.4
CB7	VIMS	Both	89	7.2	0.0122	–
CB7	VIMS	NH_4	89	31.4	0.0121	37.3
CB7	VIMS	NO_{23}	89	0.9	0.0021	8.1
CB7	VIMS	Both	90	14.4	0.0103	–
CB7	VIMS	NH_4	90	28.2	0.0092	45
CB7	VIMS	NO_{23}	90	4.2	0.0023	12.9
CB7	VIMS	Both	91	9.3	0.0053	–
CB7	VIMS	NH_4	91	7.4	0.0036	9.1
CB7	VIMS	NO_{23}	91	9.3	0.0024	27.6
CB7	VIMS	Both	92	7.4	0.0045	–
CB7	VIMS	NH_4	92	25.9	0.0039	48.2
CB7	VIMS	NO_{23}	92	8.3	0.0023	40.5
EE3	VIMS	Both	85	37.1	0.0398	–
EE3	VIMS	NH_4	85	5.7	0.02	30.8
EE3	VIMS	NO_{23}	85	25.7	0.02	28
EE3	VIMS	Both	86	21.1	0.0407	–
EE3	VIMS	NH_4	86	44.7	0.0214	23.1
EE3	VIMS	NO_{23}	86	2.6	0.021	28
EE3	VIMS	Both	87	7.7	0.02	–
EE3	VIMS	NH_4	87	2.6	0.021	21.2
EE3	VIMS	NO_{23}	87	43.6	0.0099	26.6
EE3	VIMS	Both	88	2.8	0.023	–
EE3	VIMS	NH_4	88	13.9	0.013	77.2
EE3	VIMS	NO_{23}	88	19.4	0.0054	18.9
EE3	VIMS	Both	89	13.5	0.0126	–
EE3	VIMS	NH_4	89	27	0.0121	50.4
EE3	VIMS	NO_{23}	89	0	–	–
EE3	VIMS	Both	90	19.4	0.0105	–
EE3	VIMS	NH_4	90	36.1	0.0095	50.3
EE3	VIMS	NO_{23}	90	5.6	0.0024	22.1
EE3	VIMS	Both	91	11.1	0.0049	–
EE3	VIMS	NH_4	91	11.1	0.004	5
EE3	VIMS	NO_{23}	91	25	0.0024	28.5
EE3	VIMS	Both	92	13.9	0.0045	–

Segment	Laboratory	Parameter	Year	% BDL	Mean MDL	% of DIN
EE3	VIMS	NH_4	92	11.1	0.004	62.6
EE3	VIMS	NO_{23}	92	11.1	0.0024	40.5
WE4	VIMS	Both	85	59.7	0.0397	–
WE4	VIMS	NH_4	85	8.1	0.02	39.1
WE4	VIMS	NO_{23}	85	19.5	0.02	31.1
WE4	VIMS	Both	86	29.5	0.0412	–
WE4	VIMS	NH_4	86	32.5	0.022	30
WE4	VIMS	NO_{23}	86	15.1	0.0198	29.3
WE4	VIMS	Both	87	18.9	0.0236	–
WE4	VIMS	NH_4	87	5	0.0124	27.7
WE4	VIMS	NO_{23}	87	44	0.01	24.3
WE4	VIMS	Both	88	12.1	0.0226	–
WE4	VIMS	NH_4	88	2.8	0.0129	79.6
WE4	VIMS	NO_{23}	88	21.5	0.0073	21
WE4	VIMS	Both	89	10.8	0.0124	–
WE4	VIMS	NH_4	89	31.8	0.0124	48.4
WE4	VIMS	NO_{23}	89	4.7	0.0021	12.1
WE4	VIMS	Both	90	33.3	0.0113	–
WE4	VIMS	NH_4	90	16.7	0.01	62.3
WE4	VIMS	NO_{23}	90	14.6	0.0023	16.2
WE4	VIMS	Both	91	16.7	0.0052	–
WE4	VIMS	NH_4	91	7.6	0.004	14.2
WE4	VIMS	NO_{23}	91	20.1	0.0024	24.3
WE4	VIMS	Both	92	5.6	0.0045	–
WE4	VIMS	NH_4	92	22.9	0.0039	60.1
WE4	VIMS	NO_{23}	92	12.5	0.0022	29.3
CB6	ODU	Both	85	20.8	0.0174	–
CB6	ODU	NH_4	85	14.6	0.01	24.6
CB6	ODU	NO_{23}	85	47.9	0.01	28.1
CB6	ODU	Both	86	10	0.0106	–
CB6	ODU	NH_4	86	3.3	0.0056	6
CB6	ODU	NO_{23}	86	18.3	0.0064	24.7
CB6	ODU	Both	87	33.8	0.0106	–
CB6	ODU	NH_4	87	5.6	0.0056	36.8
CB6	ODU	NO_{23}	87	19.7	0.005	17.2
CB6	ODU	Both	88	22.9	0.0101	–

Segment	Laboratory	Parameter	Year	% BDL	Mean MDL	% of DIN
CB6	ODU	NH_4	88	7.1	0.0056	48.1
CB6	ODU	NO_{23}	88	22.9	0.0039	23.3
CB6	ODU	Both	89	8	0.0081	–
CB6	ODU	NH_4	89	10.7	0.0056	28.6
CB6	ODU	NO_{23}	89	6.7	0.0025	19.8
CB6	ODU	Both	90	20.8	0.0081	–
CB6	ODU	NH_4	90	22.2	0.0056	38.1
CB6	ODU	NO_{23}	90	4.2	0.0025	26.8
CB6	ODU	Both	91	6.9	0.0081	–
CB6	ODU	NH_4	91	22.2	0.0056	17.1
CB6	ODU	NO_{23}	91	0	–	–
CB6	ODU	Both	92	34.4	0.0081	–
CB6	ODU	NH_4	92	21.9	0.0056	38.3
CB6	ODU	NO_{23}	92	4.7	0.0025	17
CB7	ODU	Both	85	35.4	0.0172	–
CB7	ODU	NH_4	85	10.8	0.01	26.6
CB7	ODU	NO_{23}	85	36.9	0.01	33.3
CB7	ODU	Both	86	20.4	0.0118	–
CB7	ODU	NH_4	86	4.1	0.0056	6.9
CB7	ODU	NO_{23}	86	30.6	0.0062	28.1
CB7	ODU	Both	87	45.4	0.0106	–
CB7	ODU	NH_4	87	4.6	0.0056	33
CB7	ODU	NO_{23}	87	23.7	0.005	24.8
CB7	ODU	Both	88	29.1	0.01	–
CB7	ODU	NH_4	88	4.1	0.0056	56.1
CB7	ODU	NO_{23}	88	37.2	0.004	21.8
CB7	ODU	Both	89	18.4	0.0081	–
CB7	ODU	NH_4	89	10.5	0.0056	46.1
CB7	ODU	NO_{23}	89	18.4	0.0025	15.3
CB7	ODU	Both	90	31.3	0.0081	–
CB7	ODU	NH_4	90	23.6	0.0056	48.6
CB7	ODU	NO_{23}	90	14.6	0.0025	17.1
CB7	ODU	Both	91	16.7	0.0081	–
CB7	ODU	NH_4	91	22.2	0.0056	26.4
CB7	ODU	NO_{23}	91	6.3	0.0025	19.7
CB7	ODU	Both	92	44.4	0.0081	–

Segment	Laboratory	Parameter	Year	% BDL	Mean MDL	% of DIN
CB7	ODU	NH_4	92	22.3	0.0056	55.3
CB7	ODU	NO_{23}	92	9	0.0025	19.6
CB8	ODU	Both	85	29.7	0.018	–
CB8	ODU	NH_4	85	4.2	0.0094	33.6
CB8	ODU	NO_{23}	85	35.8	0.01	37.9
CB8	ODU	Both	86	11.3	0.0113	–
CB8	ODU	NH_4	86	4	0.0056	13.8
CB8	ODU	NO_{23}	86	26.8	0.0059	23
CB8	ODU	Both	87	29.8	0.0106	–
CB8	ODU	NH_4	87	3.7	0.0056	38.5
CB8	ODU	NO_{23}	87	28.8	0.005	28.3
CB8	ODU	Both	88	25.9	0.0103	–
CB8	ODU	NH_4	88	3.2	0.0056	56.1
CB8	ODU	NO_{23}	88	33	0.0042	25.5
CB8	ODU	Both	89	13.8	0.0081	–
CB8	ODU	NH_4	89	4.2	0.0056	40.4
CB8	ODU	NO_{23}	89	12.2	0.0025	15.7
CB8	ODU	Both	90	19.1	0.0081	–
CB8	ODU	NH_4	90	19.1	0.0056	50
CB8	ODU	NO_{23}	90	9.6	0.0025	19
CB8	ODU	Both	91	13.3	0.0081	–
CB8	ODU	NH_4	91	16.7	0.0056	32.9
CB8	ODU	NO_{23}	91	6.1	0.0025	17.2
CB8	ODU	Both	92	39.9	0.0081	–
CB8	ODU	NH_4	92	12.9	0.0056	53
CB8	ODU	NO_{23}	92	5.6	0.0025	18.6