

Trends in Precipitation Chemistry in the United States, 1983–94—An Analysis of the Effects in 1995 of Phase I of the Clean Air Act Amendments of 1990, Title IV

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INTRODUCTION

Title IV of the Clean Air Act Amendments of 1990 (CAAA-90) (Public Law 101-549) seeks to reduce acidic deposition in the United States through phased reductions in sulfur dioxide and nitrogen oxide emissions. One of the first steps in assessing the effectiveness of emissions reductions is to evaluate spatial and temporal trends in sulfate (SO_4^{2-}), nitrate (NO_3^-), and hydrogen (H^+) ion concentrations in precipitation. Lynch et al. (1995a) reported the most recent comprehensive summary of temporal trends in precipitation chemistry in the United States using data from 58 National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites from 1980 through 1992. Results showed widespread declines in SO_4^{2-} concentrations accompanied by significant decreases in all of the base cations, most noticeably calcium (Ca^{2+}) and magnesium (Mg^{2+}). As a result, only 17 of the 42 sites with significant ($p < 0.05$) decreasing SO_4^{2-} trends had concurrent significant decreasing H^+ trends. Lynch et al. (1995a) cautioned that they found considerable inter- and intra-regional variability in pH trends even among multiple sites within the same state. They speculated that significant site-specific changes in NO_3^- and ammonium (NH_4^+) concentrations, as well as varying magnitudes of SO_4^{2-} and Ca^{2+} changes could help explain much of this variability.

In the National Acid Precipitation Assessment Program (NAPAP) report on deposition monitoring, Sisterson et al. (1990) applied a Kendall seasonal tau test for trend detection in the presence of seasonal cycles (see Hirsch et al., 1982). Seasonal observations were defined as monthly mean precipitation-weighted concentrations or monthly depositions for each site. Data from six North American networks, including NADP/NTN, were used in the analysis. Sen's median slopes (see Hirsch et al., 1982) were calculated to estimate the magnitude of changes in concentrations and depositions for sites meeting predetermined data completeness criteria (Olsen et al., 1990; Sisterson et al., 1990). The NAPAP trends analysis addressed two time periods: a 39-site (24 NADP/NTN sites), 9-year data set (1979-1987) and a 148-site (76 NADP/NTN sites), 6-year data set (1982-1987). Statistically significant ($p < 0.05$) trends were found at a higher proportion of sites for all ions, except NO_3^- , in the 9-year data set than during the 6-year period, suggesting that the largest changes occurred early in the data record from 1979-1982. Except for NO_3^- and potassium (K^+), the absolute magnitudes of the median percent changes were larger for the 9-year period, as well. For the ions that most affected pH (SO_4^{2-} , NO_3^- , NH_4^+ , and Ca^{2+}), the strongest evidence for change was in the base cation, Ca^{2+} . Calcium decreased at 38 of the 39 sites over the 1979-1987 period; at 13 sites these changes, all down, were significant ($p < 0.05$). Sulfate decreased at 35 of the 39 sites; at seven sites these changes, all down, were significant ($p < 0.05$). Nitrate, NH_4^+ , and H^+ ions exhibited a more even split of increasing and decreasing changes (Sisterson et al., 1990, pages 6-154 through 6-163). These results led the authors to conclude that the acidity of precipitation did not decrease because of the concurrent decrease in cation concentrations.

Lynch et al. (1995b) also evaluated trends in precipitation chemistry at NADP/NTN sites for multiple summary periods. This analysis utilized a general, linear least-squares model to evaluate trends for three summary periods: 1980-1993, 1983-1993, and 1985-1993. Major growth in the NADP/NTN occurred between 1980 and 1985 effectively tripling the number of network sites. Choosing successively later start dates allowed comparison of results among larger numbers of sites having greater spatial coverage. It also allowed the assessment of the effect of summary period length on trends. Regardless of the summary period length, the vast majority of NADP/NTN sites exhibited decreasing SO_4^{2-} concentrations. Consistent with

the findings of Sisterson et al. (1990), this analysis also indicated that SO_4^{2-} concentrations decreased more rapidly during the early 1980s and less rapidly thereafter. Nitrate and NH_4^+ concentrations exhibited considerable variability with only a few sites showing statistically significant trends, some positive and some negative. The larger SO_4^{2-} decreases in the early 1980s were similar to sulfur dioxide emissions changes, which decreased more rapidly between 1980 and 1983, then vacillated about a nearly constant rate in many states (Lins, 1987).

Hedin et al. (1994) reported steep declines in base cations in precipitation from Sweden, the Netherlands, and the United States. In the United States, annual volume-weighted mean concentrations of SO_4^{2-} and base cations (defined as the sum of non-sea-salt Ca^{2+} , Mg^{2+} , Na^+ , and K^+) were calculated using data from 32 NADP/NTN sites (1979 or 1980 to 1990), nine Multistate Atmospheric Power Production Pollution Study (MAP3S) sites (1978-1988), and the Hubbard Brook Experimental Forest (HBEF) (1965-1989). A regression of these annual means against time in years yielded trend estimates for SO_4^{2-} and cations (NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+). At the HBEF and at NADP/NTN sites in the Northeast, Southeast, and Midwest, both SO_4^{2-} and base cations decreased and the trends were significant ($p < 0.05$ or $p < 0.001$). At the nine MAP3S sites, SO_4^{2-} decreases were also statistically significant; however, base cations decreased at only five sites, none of which were statistically significant. Hedin et al. (1994) concluded that recent declines in both base cation and SO_4^{2-} concentrations had offset one another in varying proportions in many regions in the Northern Hemisphere.

Other authors have also focused their attention on describing trends in precipitation concentrations or depositions (for eastern North America, see Sirois, 1993 or Oehlert, 1993; for NADP/NTN data, see Baier and Cohn, 1993; for MAP3S data, see Dana and Easter, 1987; for data from the Netherlands, see Ruijgrok and Romer, 1993 or Buishand et al., 1988; for data from Texas, see Kessler et al., 1992; and for data from New York, see Hirsch and Peters, 1988). All have shown general decreasing trends in SO_4^{2-} and base cation concentrations, with small and generally statistically insignificant changes in free acidity. In these studies, both parametric (e.g., Buishand et al., 1988) and nonparametric (e.g., Baier and Cohn, 1993) approaches have been used.

Measuring and reliably quantifying trends in precipitation chemistry are essential tools for assessing the effectiveness of sulfur and nitrogen emissions reductions programs designed to protect the environment. Trend estimation techniques were compared at a recent workshop (Holland et al., 1995). Four approaches were examined, including the linear least-squares model used in this analysis and several modifications of the seasonal Kendall test (Hirsch et al., 1982). In one case, a modification of Sen's slope estimator (Hirsch et al., 1982) was used to estimate the annual percentage change in precipitation-weighted mean concentrations. This comparison indicated that all four approaches were valid and generally yielded similar long-term trend results, although strengths and weaknesses were noted for each approach. The linear least-squares approach provided the added advantage of quantifying seasonal changes in concentration over time.

Phase I of Title IV of the CAAA-90 requires specific reductions in sulfur dioxide emissions on or before 1 January 1995 at selected electric utility plants, the majority of which are located in states east of the Mississippi River. As a result of this legislation, large reductions in sulfur dioxide emissions are likely to have occurred in 1995 which should have affected

SO_4^{2-} and H^+ concentrations, and to a lesser extent NO_3^- concentrations, in precipitation in this region. The purpose of this study was to evaluate this effect, if any, at NADP/NTN sites in the region in 1995. This assessment was based on a comparison of observed 1995 SO_4^{2-} , H^+ , and NO_3^- concentrations at these NADP/NTN sites with estimates obtained from linear least-squares trend models of precipitation chemistry data collected from 1983 through 1994. The 1983 through 1994 summary period was selected for the following reasons: (1) the 1980-1994 record limits the number of sites to 57, too few for meaningful inter- and intra-regional comparisons; (2) the 1985-1994 summary period increases the number of sites to 168, but reduces the strength of the trend models estimates because of the shortness (10 years) of record; (3) the 1983-1994 summary period represents the best compromise between both the spatial and temporal strengths of the analysis; (4) the 1983-1994 summary period avoids potential start-up problems associated with field sampling and laboratory protocols; (5) the 1983-1994 period has stable emissions relative to the early 1980s (Lins, 1987); and (6) the National Trends Network (NTN) became a formal part of NADP in 1983, so many of the sites added in the 1983-1994 summary period over the 1980-1994 period were NTN sites.

METHODS AND RESULTS

Correction of Pre-1994 NADP/NTN Data

Since its inception in 1978, NADP/NTN sampling protocols required site operators to send precipitation samples to the Central Analytical Lab (CAL) at the Illinois State Water Survey in the ~14-liter HDPE (high density polyethylene) buckets used for collection. The bucket lid contained a rubber o-ring, which sealed the lid and bucket, preventing leaks during shipment. This o-ring was found to be a source of many of the same cations and anions measured in precipitation. For most samples, the concentration biases due to o-ring contamination were small and unimportant. Most affected were free H^+ concentrations (pH) at sites in the western states, where pH values are typically above 4.8. Samples lost free acidity due to the o-ring so sample pHs were biased high. Efforts to improve lid cleaning procedures reduced, but could not eliminate, o-ring contamination.

Although o-ring contamination was persistent, occasional changes by the lid manufacturer added to the uncertainty in the size of the bias over time. This had the potential for interfering with long-term trend analyses. Studies had shown that samples sent to the CAL in bottles had much smaller losses of acidity than samples sent in the buckets with the lid o-ring. As a result, the NADP/NTN elected to change its procedures effective 11 January 1994, ending the use of the buckets for sample shipment and eliminating any contact of the sample with the o-ring. After 11 January 1994, a snap-on lid with no o-ring was used to cover the collection bucket during transport from the site to the field laboratory and a one-liter, wide-mouthed, HDPE bottle was used for shipment to the CAL.

A special study was conducted at 11 sites scattered across the network to assess the size and direction of the concentration change of each analyte due to lid o-ring contamination. The results of this study were analyzed with the intent of identifying a set of algorithms that could be used to adjust the pre-1994 data for the effects of o-ring contamination. Side-by-side samples were collected at these sites, one using the old procedure with the bucket and lid

with the o-ring and the other using the new procedure with the bottle. Paired concentration differences were calculated from the two samples at each site. Nonlinear, least squares regressions were performed to evaluate these differences for dependence on sample volume or on pH or on a combination of these factors. CAL experimental results suggested that both factors could be important in explaining the differences between the bucket and bottle samples. Specifically, these results indicated that as the volume increases the o-ring contamination increases, approaching a maximum value. For a fixed volume, the o-ring contamination is large at low and high pH values and small at mid-level pHs. These volume and pH relationships dictated the form of the equations used in the analysis.

Six different models (algorithms) per analyte were evaluated for each of the conservative ions. These included: (1) a constant mass model, (2) a simple linear regression model, (3) a mass difference model as a function of sample volume, (4) a mass difference model as a function of sample volume and pH, (5) a power law model, and (6) hybrids of 2 and 3 or 2 and 4. To select the best algorithms, the root mean square (RMS) bucket/bottle concentration differences and the RMS corrected bucket/bottle concentration differences from the six models were calculated. A sensitivity test of the RMS calculations was performed using a "bootstrap" experiment with 100 repetitions. Following these experiments, the most robust algorithms with the lowest RMS of the corrected bucket/bottle concentration differences were identified. Using the overall "best fit" models for the conservative ions, the pH (H^+) correction was evaluated. This evaluation revealed that the best model was one based on adding the effects of all of the corrections plus an unmeasured cation (probably zinc, which can be leached from the lid seal), then calculating a corrected pH. The equations that best fit the special study results for all measurements are presented in the Appendix (Table A.1). Four of the correction equations (K^+ , NO_3^- , Na^+ , and SO_4^{2-}) incorporate both sample volume and sample pH as predictor variables. For four others (Ca^{2+} , Mg^{2+} , NH_4^+ , and Cl^-), sample volume alone was the best predictor.

A comparison of volume-weighted mean annual concentrations in precipitation for corrected and uncorrected NADP/NTN data from 1983-1993 (Appendix, Table A.2) illustrates the effects the corrections (Appendix, Table A.1) had on NADP/NTN precipitation chemistry data. At all sites, the corrections resulted in lower mean annual concentrations for all ions, except H^+ . Hydrogen ion concentrations increased as reflected in the lower pH values. With a few exceptions, the reductions in pH were less than 0.04 unit in the eastern states; reductions in pH were higher in the West, with some sites experiencing reductions in mean annual pH of more than 0.3 unit. Sulfate concentrations generally decreased from 0.03 mg/L to 0.04 mg/L in the western region of the country; at Eastern sites, SO_4^{2-} concentration decreases were about 0.01 mg/L with concentration changes at some sites exceeding 0.1 mg/L. Decreases in NO_3^- concentrations were fairly uniform across the country and averaged around 0.03 mg/L. Chloride concentrations decreased approximately 0.005 mg/L and did not exhibit significant regional differences. Ammonium concentrations decreased approximately 0.01 mg/L and were considerably more variable in the western than the eastern states. Calcium and Mg^{2+} concentrations decreased between 0.003 and 0.004 mg/L at most sites and exhibited very little spatial variation across the country. A similar pattern and magnitude of change was also evident for K^+ and Na^+ concentrations. Overall, the correction equations did not result in any major aberrations in the data set and are consistent with results from bucket versus bottle comparison studies.

Temporal Trend Analyses

Temporal trend analyses covered the entire NADP/NTN network, included all analytes except orthophosphate, and was based on corrected data through 1993 and 1994 data. Trends in analyte concentrations were examined for the 1983-1994 summary period. Results of this analysis provided a baseline against which 1995 concentrations were contrasted to assess the effects of the CAAA-90, Phase I emissions reductions on precipitation chemistry.

In the trend analysis of the summary period (1983-1994), weekly precipitation volume and corrected chemical observations were accumulated into bi-monthly precipitation totals and volume-weighted mean concentrations of H^+ (from pH), SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Ca^{2+} , Mg^{2+} , K^+ , and Na^+ ions. Orthophosphate was omitted because a large percentage (>80%) of weekly samples have concentrations below the analytical detection limit (0.003 mg/L). Only valid weekly samples with a complete set of analyses were used to calculate bi-monthly volume-weighted mean concentrations. Sites and bi-monthly records were selected for the trend analysis according to the following completeness criteria:

- (1) Only those monitoring sites having weekly precipitation chemistry records from January 1983 through December 1994, were considered. At least 75 percent of the precipitation recorded during this summary period had to have valid chemical analyses in order for the site's data to be accepted for trend analyses.
- (2) For a bi-monthly record to be accepted, a valid analysis for each ion had to be available for at least 75 percent of the bi-monthly precipitation.
- (3) During each bi-monthly period, at least 50 percent of the weekly samples having sufficient volume for analysis (≥ 35 mL) had to have a valid analysis for each ion.

Trends in ionic concentrations in precipitation at each site were evaluated using a two-stage, least-squares general linear model (SAS Inst, 1988). This model was developed by the principal investigators for detecting and quantifying trends in precipitation chemistry data that exhibit strong seasonal patterns (Lynch, et al., 1995a). The form of the model for both stages was

$$\log(C_y) = b_0 + b_y \cdot y + \sum_{s=1}^6 b_s I_s$$

where,

- C_y = estimated concentration of a given ion at time y .
- b_0 = intercept.
- b_y = slope of the long-term log-concentration trend.
- y = mid-point of the bi-monthly observation period expressed as decimal years. For example, y for a May-June 1990 observation was coded as $90+(5/12)$ or 90.4167.
- b_s = adjustment to estimate for bimonthly period, s . The array of 6 b_s coefficients account for the seasonal variation in precipitation chemistry.
- I_s = an element of an array of 6 indicator variables set to 1 for bi-monthly period, s , and set to 0, otherwise.

Log-transformed concentrations were used because the model residuals have a more nearly normal distribution (Lynch et al., 1995a). After initially fitting the model to a site's concentration data (expressed as $\mu\text{eq/L}$) for a given ion, studentized residuals were calculated. Bi-monthly observations having a studentized residual >3.5 in absolute value were eliminated from the data set and a second calculation of model coefficients was performed using the remaining observations. The selected cut-off value applied to the studentized residuals would be exceeded by chance at a rate less than 0.001 under the assumption of normally distributed residuals of constant variance.

A tabular summary of the trend results is presented in Table A.3 (Appendix). This summary table contains information on the direction (b_{year}) and statistical significance (p) of the trend in each analyte for each site that met the above completeness criteria. Sites are identified by their NADP/NTN CAL code. The Mississippi River was used to segregate those sites located in the eastern and western sections of the country. The number of sites exhibiting increasing trends and the number exhibiting decreasing trends are presented in Table 1. These sites are further subdivided by statistical significance ($p < 0.05$).

The direction and statistical significance ($p < 0.05$) of trends for each analyte are also presented graphically in Figures 1-9. Upward or downward pointing triangles indicate the direction of the trend. A solid triangle indicates a statistically significant ($p < 0.05$) trend; an open triangle indicates that the trend is not significant ($p > 0.05$). NADP/NTN sites located in Alaska and Hawaii are not shown on the maps but were included in the analyses if they met the completeness criteria.

Changes in ionic composition of precipitation at each site from the beginning (1983) to the end (1994) of the summary period were calculated as the difference between the average of six bi-monthly mean concentrations ($\mu\text{eq/L}$) estimated from the models for 1983 and 1994. Cation and anion concentration ($\mu\text{eq/L}$) changes and percent changes from 1983 to 1994 are presented in Table 4.A (Appendix). Table 2 lists the mean concentration ($\mu\text{eq/L}$) changes and percent changes for all sites and for only sites with statistically significant ($p < 0.05$) trends. The coincidence of significant ($p < 0.05$) decreasing SO_4^{2-} and H^+ concentrations is summarized in Table 3. Sites are identified by the NADP/NTN CAL code.

Evaluating the Effectiveness of Phase I of the Clean Air Act Amendments of 1990

Phase I of the CAAA-90, Title IV was implemented on 1 January 1995. One-hundred and ten (110) electric utility plants were affected in 21 states, 17 of which are located east of the Mississippi River. Sixty-three (63) of these targeted plants are located in states in the Ohio River Valley. Notwithstanding the effects of trades of emissions allowances, large reductions in sulfur dioxide emissions are likely to have occurred in 1995, particularly in the eastern states. These reductions should have affected precipitation chemistry, particularly SO_4^{2-} and H^+ concentrations, and to a lesser extent NO_3^- concentrations. In order to evaluate this effect, if any, at NADP/NTN sites in the eastern states in 1995, the linear least-squares models discussed above were used to estimate 1995 bi-monthly and annual mean concentrations for each analyte. The model estimates were compared to actual bi-monthly volume-weighted mean concentrations for each NADP/NTN site that met the above completeness criteria. Because the bi-monthly means were summed to obtain annual means, only 109 sites with six valid 1995 bi-monthly means were included in this analysis. For

comparative purposes, separate, identical analyses were conducted for sites located east and west of the Mississippi River. The impact of Phase I emissions reductions in the western states should have been minimal given that only 16 of the affected plants are located in this region (Missouri-8, Iowa-6, Kansas-1, Minnesota-1). As a result, a comparison of predicted with observed concentration means in both regions provides a means of evaluating model performance and the effect of CAAA-90 emissions reductions on precipitation chemistry.

The results of the comparisons of 1995 measured and estimated bi-monthly and annual mean concentrations for individual sites located in eastern and western regions of the country are presented in Tables 4, 5, and 6 for SO_4^{2-} , H^+ , and NO_3^- concentrations, respectively. Similar comparisons for the remaining cations and anions are presented in the Appendix (Tables A.5-A.10). Eastern results are further stratified into Northeast (NE) and Southeast (SE) regions. Table 7 list the frequency of occurrence of observed 1995 cation and anion concentrations that were less than predicted concentrations. Regional mean and percent departures from the trend model estimates are presented in Table 8 for annual and bi-monthly cation and anion concentrations.

One way to assess the statistical significance of the effects of Phase I emissions reductions on precipitation chemistry is to determine the significance of the deviations of the 1995 bi-monthly observations from the trend model estimates derived from the 1983-1994 data. Because only one year (1995) of data is available subsequent to Phase I implementation, quantifying a slope change in the long-term trend is inappropriate. However, the data do permit estimation of changes in the intercept of the trend line coinciding with the implementation of emission reductions. Estimating the change in the intercept is appropriate because it directly quantifies the "step-function" that would occur in precipitation chemistry if emissions were reduced suddenly, i.e., large reductions over a short period of time. The change in intercept for the 1995 data was estimated by adding a binary indicator variable to the seasonal trend models. This indicator variable was given a value of 1 for 1995 observations and a value of 0, otherwise. This variable's estimated coefficients and its significance are presented in Table A.11 (Appendix) which indicates in what direction and at which sites the 1995 data departed from the historical trend. Because there are only six bi-monthly observations in 1995, the power of this statistical test for change is rather low. Nevertheless, the results of this analysis reaffirm the results from the linear least-squares models and illustrate that the 1995 precipitation chemistry data were different from the historical trends at NADP/NTN sites located in the Eastern United States. Sulfate and H^+ concentrations in 1995 at 12 of the 62 sites located east of the Mississippi River were significantly ($p < 0.05$) different when compared to the historical trend models at these sites; for NO_3^- concentrations, only two sites were significantly different, both positive indicating higher concentrations in 1995 than the model estimates.

In addition to the above analyses, 1983-1994 trends for selected sites are presented graphically by plotting observed bi-monthly mean concentrations along with two corresponding estimates of concentration against time. One set of estimates was from the least-squares general linear models described above, the other set was from a LOWESS regression of the observed bi-monthly mean concentrations. The LOWESS smoothing method, described by Cleveland (1979 and 1985), was added because it does not assume a functional relationship between concentration and time and can depict nonlinearities in trends. The LOWESS method was not used to statistically assess concentration trends

because assessment of changes in ionic concentration from one time to another, by definition, involves linear hypotheses and because LOWESS regressions do not provide an overall test of trend or model fit for the data set as a whole. The "moving window" of data points was set at 2 years (12 bi-monthly points) before and after the date to be estimated. The distance weighting function for the LOWESS regressions was,

$$d_i = (1 - p_i^3)^3$$

where,
 $p_i = |x_i - x_t|/W$ for $|x_i - x_t| < W$; otherwise, 1
 x_t = date of point to be estimated in decimal years
 x_i = date of i^{th} sample point in decimal years
 W = width of moving window in each direction (i.e., 2.0 years)

The robustness weights for the second stage of the LOWESS estimation procedure were calculated as,

$$w_i = (1 - p_i^2)^2$$

where,
 $p_i = (|r_i|/R)$ for $|r_i| < R$; otherwise, 1.0
 r_i = studentized residual of i^{th} sample point from the first stage LOWESS regression
 R = Maximum absolute value of studentized residual for sample points to be used in the second stage regression. R was set to 4.

For comparison purposes, a disjunct LOWESS regression line was plotted for the six bi-monthly mean concentrations in 1995. This LOWESS regression was based on 1993-1995 bi-monthly mean observations. It was separated physically from the 1983 through 1994 LOWESS line to emphasize the step-function change in 1995 from the preceding 12-year summary. Six examples of H^+ , SO_4^{2-} , and NO_3^- concentration trends showing the linear model (solid line) and LOWESS regression (dashed line) and the observed bi-monthly mean concentrations (solid circles) are presented in Figures 10-15 for the 1983-94 and 1995 summary periods. Figures 10 and 11 (KY03 and IL63, respectively) illustrate a dramatic change in 1995 bi-monthly mean concentrations relative to the historical trend, while Figures 12 (NC36) and 13 (VT01) illustrate a moderate decrease and Figures 14 (IN34) and 15 (MA08) illustrate no change. The remaining cation and anion comparisons for these six sites appear in the Appendix (Figures A.1-A.12).

Color-scaled raster maps based on surface estimation algorithms are frequently used to display precipitation chemistry data over a region. This approach was used to illustrate the departures of 1995 observed concentrations ($\mu\text{eq/L}$ and percent) from the trend model estimates for 1995. Maps were prepared for the eastern half of the country, where the greatest impact of Phase I emissions reductions was most likely to occur. The differences were plotted using the Multiquadric Equations (MQE) surfacing function described by Hardy (1971) and evaluated as a tool for depicting regional wet deposition by Grimm and Lynch (1991). Also included is a color-scaled raster map showing deviations in 1995 precipitation volumes from the 1983 through 1994 annual average volumes. All four maps are based on

data from the 109 sites included in the analysis of the effectiveness of the CAAA-90 discussed above. Results are presented in Figures 16, 18, 20, and 22 for SO_4^{2-} , H^+ , NO_3^- , and precipitation volume, respectively; percent differences are presented in Figures 17, 19, 21, and 23, respectively. The location of NADP/NTN sites are indicated by a plus (+) sign.

DISCUSSION

Temporal Trends, 1983-94: Magnitude, Direction and Significance

Sulfate concentrations at 92% of the NADP/NTN monitoring sites in the United States have decreased since 1983; the trends are statistically significant ($p < 0.05$) at 38% of the sites (Table 1, Figure 1). No major regional (east vs west) differences in the number and percentage of sites exhibiting decreasing SO_4^{2-} trends are evident. Sites with increasing SO_4^{2-} trends (Table 1) are also uniformly distributed across the country; however, only one of the increasing SO_4^{2-} concentration trends is significant ($p < 0.05$). The mean change in SO_4^{2-} concentrations across the United States from 1983 to 1994 was $-4.80 \mu\text{eq/L}$ (16.4%) compared to $-7.69 \mu\text{eq/L}$ (25.9%) at sites with statistically significant trends (Table 2). Sulfate concentrations have decreased more rapidly in the eastern states ($5.94 \mu\text{eq/L}$ vs $3.71 \mu\text{eq/L}$), although the mean percentage change has been greater in the western states (18.9% vs 13.8%). This pattern is also evident at sites with significant ($p < 0.05$) trends; however, the concentration and percentage decreases are much larger (Table 2).

Nitrate concentration trends do not exhibit a consistent spatial pattern (Figure 2). The number of sites exhibiting increasing trends is nearly equal to the number exhibiting decreasing trends (Table 1). Perhaps of greater importance, a larger percentage of sites with increasing trends (14%) are significant ($p < 0.05$), while only two of the 153 sites included in this analysis have significant decreasing trends. A larger percentage of sites with increasing trends are located in the western states. As expected from these results, the network mean change in NO_3^- concentrations was very small ($< 0.5 \mu\text{eq/L}$) and positive (Table 2). However, the mean NO_3^- concentration at the 23 sites with statistically significant trends (2 decreasing, 21 increasing) increased 51.6% ($3.34 \mu\text{eq/L}$). The largest increases in NO_3^- concentrations occurred in the western states.

Ammonium concentrations increases were larger and more widespread than NO_3^- increases (Table 2, Figure 3). Eighty percent (80%) of the sites in the NADP/NTN exhibited increasing NH_4^+ concentrations since 1983 (Table 1); at 22% of the sites the trends are significant ($p < 0.05$). Only one of the sites has a statistically significant decreasing trend. Although regional patterns are similar, the largest number of sites with significantly increasing trends are located in the western states. The average increase in NH_4^+ concentrations at these sites is $6.40 \mu\text{eq/L}$, an increase of 86.6% over 1983 levels. The network-wide increase in NH_4^+ concentrations since 1983 is $2.33 \mu\text{eq/L}$ (28.2%). Clearly, nitrogen concentrations (both NO_3^- and NH_4^+) in precipitation have increased in the United States since 1983.

Calcium (Figure 4), Mg^{2+} (Figure 5), and K^+ (Figure 6) concentrations decreased markedly in the United States since 1983. Very few sites exhibited increasing concentrations (Table 1): Ca^{2+} (9 sites), Mg^{2+} (2 sites), and K^+ (21 sites); only two of these trends (both K^+) are

significant ($p < 0.05$). Decreasing trends are significant at 52% of the sites for Ca^{2+} , 77% for Mg^{2+} , and 38% for K^+ . A higher percentage of these sites is located in the eastern states. Mean percentage decreases in these cations are fairly consistent across the United States, 23.5% for K^+ , 27.9% for Ca^{2+} and 39.7% for Mg^{2+} (Table 2). Despite regional similarities in percent decreases, the concentration ($\mu\text{eq/L}$) changes have been consistently larger in the western portion of the country for all three cations. These same patterns are evident when only sites with significant trends are compared, although the percent and $\mu\text{eq/L}$ changes are larger. Clearly, base cation concentrations have decreased over the past 12 years. Similar results have been reported by Lynch et al., (1995a, 1995b); Hedin et al., (1994); and Sisterson et al., (1990).

Sodium and Cl^- concentrations generally decreased across the country (Figures 7 and 8); trends are significant ($p < 0.05$) at 20% of the sites for Na^+ and 37% for Cl^- (Table 1). Regional differences in both Na^+ and Cl^- trends are evident, with slightly more significant Cl^- and Na^+ trends in the western than eastern region of the country. Across the United States, Na^+ and Cl^- concentrations decreased approximately 20% on average since 1983 (Table 2). At sites with significant trends, Na^+ and Cl^- concentrations are 36.8% to 32.3% lower. On a concentration basis, both Na^+ and Cl^- decreased 1.5 $\mu\text{eq/L}$ since 1983.

Like SO_4^{2-} concentrations, the majority of sites (81%) exhibited decreases in H^+ concentrations from 1983 through 1994 (Table 1, Figure 9). However, only 39 sites (25%) have statistically significant H^+ decreases, 20 in the western states and 19 in the eastern states. Of the 29 sites exhibiting H^+ increases, only one is significant. Free acidity in precipitation across the United States decreased by 2.68 $\mu\text{eq/L}$ (13.4%) on average since 1983, with the largest concentration (smallest percentage) changes occurring in the East (Table 2). This same pattern is evident when only sites with significant trends are compared, although both the percentage and concentration decreases are more than twice as large. The lack of consistency between sites with both significant decreasing SO_4^{2-} and H^+ concentrations (Table 3) suggests that concurrent changes in other ions have offset varying amounts of the SO_4^{2-} decrease. As a result, commensurate reductions in H^+ did not occur. A similar hypothesis has been suggested by Lynch et al., (1995a); Hedin et al., (1994); and Sisterson et al., (1990). The ions most frequently offsetting the SO_4^{2-} reductions are the acid neutralizing cations, Ca^{2+} and Mg^{2+} . However, at some sites, increasing NO_3^- concentrations have offset SO_4^{2-} reductions leaving small changes in free acidity (Lynch et al., 1995a).

Comparison of Predicted and Observed 1995 Concentrations

Sulfate and H^+ concentrations in the eastern states in 1995 were considerably lower than predicted from the trend models for the 1983-1994 reference summary period (Tables 4 and 5); NO_3^- concentrations remained relatively unchanged (Table 6). Two examples each of relatively large decreases (KY03 and IL63), moderately large decreases (NC36 and VT01), and little to no change (IN34 and MA08) in 1995 bi-monthly mean SO_4^{2-} and H^+ concentrations, compared to the 1983-1994 trend models, are shown in Figures 10-15, respectively. Site selection was based on change in SO_4^{2-} concentrations in 1995 relative to the historical trend at each site. A LOWESS regression line (dashed line) is included to illustrate the step-function change in SO_4^{2-} and H^+ concentrations that occurred in 1995. Corresponding base cation and Cl^- concentrations at these sites are shown in Figures A.1-A.12 in the Appendix.

Mean annual H^+ and SO_4^{2-} concentrations in 1995 were below predicted values at 88.7% and 79.0%, respectively, of the 109 sites that met the data completeness criteria (Table 7). By comparison, only 31.9% and 36.2%, respectively, of the Western sites were below modeled estimates. On average, 1995 measured SO_4^{2-} concentrations in the eastern states were 4.01 $\mu\text{eq/L}$ (9.8%) below modeled estimates (Table 8). The SO_4^{2-} decreases were substantially larger than 4 $\mu\text{eq/L}$ in much of the Northeast. In contrast, at sites west of the Mississippi River 1995 SO_4^{2-} concentrations averaged 1.37 $\mu\text{eq/L}$ (7.5%) higher than the modeled estimates (Table 8). The spatial pattern of H^+ decreases in the East was virtually the same as the pattern of SO_4 decreases, although the magnitude of the concentration and percentage decreases were even larger than SO_4^{2-} decreases (Table 8).

Unlike SO_4^{2-} and H^+ concentrations, NO_3^- concentrations in 1995 were above predicted concentrations at the majority of sites located in both regions of the country (Table 7). Approximately 61% of the sites in the East recorded higher NO_3^- concentrations in 1995 than predicted from the 1983-1994 models; 57% of the western sites were above model predictions (Table 7). Nitrate concentrations in 1995 were 0.97 $\mu\text{eq/L}$ (4.6%) and 0.76 $\mu\text{eq/L}$ (3.8%) above modeled estimates in the eastern and western states, respectively (Table 8). In addition, there was no evidence of sharp drops in the Northeast as there was for SO_4^{2-} . These results suggest that nitrogen oxides emissions were not significantly affected by Phase I of the CAAA-90, Title IV in 1995, at least not on a broad regional basis.

Color-scaled raster maps of the changes in SO_4^{2-} , H^+ , and NO_3^- concentrations are shown in Figures 16, 18, and 20, respectively; percent changes in these ions are presented in Figures 17, 19, and 21, respectively. The largest reductions in SO_4^{2-} and H^+ concentrations occurred along the Ohio River Valley and in states located immediately downwind of this region. Although no emissions data are presented in this analysis, this region was clearly targeted for major reductions in sulfur dioxide emissions by Phase I of the CAAA-90, Title IV. In fact, of the 110 plants affected by Title IV, 63 are located in this region. Downwind of the Ohio River Valley, e.g., New England or the southeastern states., decreases in both SO_4^{2-} and H^+ concentrations in 1995 were smaller. There are only six affected sources in New England and 18 in the Southeast that were targeted for reductions in emissions in Phase I of the CAAA-90, Title IV. Another important feature of these maps is that the SO_4^{2-} reductions in the eastern states are roughly matched in magnitude and location by H^+ reductions. The largest decreases occur in the Ohio River Valley and the northern portion of the Mid-Atlantic region.

To examine whether the sharp drop in SO_4^{2-} and H^+ concentrations in 1995 were due to precipitation anomalies, a comparison of bi-monthly and annual precipitation volumes at each site with their 1983-1994 means was undertaken. Results of this analysis are listed for each site in Table A.12 (Appendix). A summary of these results is presented in Figures 21 and 22, which depict departures of 1995 annual precipitation from the mean annual volume during 1983 through 1994. A comparison of the precipitation volume color-scaled map (Figure 21) with the SO_4^{2-} (Figure 16) and H^+ (Figure 18) concentration maps reveals that where 1995 SO_4^{2-} and H^+ concentrations were higher than trend model estimates (e.g., the southwestern portion of the Eastern United States and a region south and east of Lake Michigan), 1995 volumes were below the 1983-94 averages. Ionic concentrations in weekly NADP/NTN samples depend on precipitation volume (Baier and Cohn, 1993). Low precipitation volumes are associated with high concentrations and vice versa. When these factors are taken into consideration, the actual reductions in SO_4^{2-} and H^+ concentrations across much of Pennsylvania, Western New York, and the southern portion of New England in 1995 would have been greater had a more "average" amount of precipitation occurred in these regions.

A comparison of the differences in 1995 annual and bi-monthly mean concentrations for those cations (NH_4^+ , Ca^{2+} , Mg^{2+} , K^+ , and Na^+) and Cl^- that would not have been substantially affected by Phase I sulfur dioxide reductions (Tables A.5-A.10, Appendix), supports the argument that the changes in SO_4^{2-} and H^+ concentrations in 1995 were not the result of lower precipitation volume. Precipitation volumes would not selectively affect H^+ and SO_4^{2-} concentrations; all ionic concentrations would be affected. A review of the individual site data in Tables A.5-A.10 (Appendix) and observed differences in NO_3^- concentrations (Figure 20) and percent changes (Figure 21) support this statement. It is not apparent that NO_3^- concentrations were affected over the eastern states by Phase I emissions reductions, only that NO_3^- was affected by the below average precipitation volumes. For example, regions with higher than predicted 1995 NO_3^- concentrations had below average precipitation and regions with lower concentrations in 1995 generally had above average precipitation. Although nitrogen emissions may have been affected by the CAAA-90, Title IV, the reductions would have been much smaller than the sulfur dioxide reductions. In addition, since Phase I, Title IV of the CAAA-90 targeted only stationary (utilities) sources and since these sources contribute only one-third of the total United States nitrogen oxide emissions (Placet, 1990), it is highly unlikely that large regions of the East would experience major reductions in nitrate concentrations in 1995.

CONCLUSIONS

Clearly, implementation of Phase I of the CAAA-90, Title IV (Public Law 101-549), has resulted in lower sulfate concentrations in precipitation in the Eastern United States, particularly along the Ohio River Valley and in the Mid-Atlantic region. Concurrent with these sulfate reductions have been similar (nearly one for one) reductions in hydrogen ion concentrations. In contrast, nitrate concentrations, as well as chloride and base cations, were not affected. Although emissions data were not included in this analysis, maximum reductions in sulfate and hydrogen ion concentrations occurred in the same area as and immediately downwind of most of the major stationary sources targeted by Phase I of the CAAA-90, Title IV. Precipitation deviations from the long-term (1983-1994) average cannot explain the observed decreases in sulfate and hydrogen ion concentrations in 1995. For one, precipitation volumes would not selectively reduce only sulfate and hydrogen ions. Other ions would be similarly affected, but they were not. For another, lower precipitation volumes are associated with higher concentrations, and most of the eastern states had below average precipitation volumes in 1995. Indeed, the lower volumes resulted in higher 1995 concentrations for virtually all ions except sulfate and hydrogen. These two ions dropped independent of precipitation volume. These results clearly support the conclusion that Phase I of the CAAA-90, Title IV, has reduced acid deposition (acid rain) in the Eastern United States.

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Figure 1

National Atmospheric Deposition Program / National Trends Network

Trends in Sulfate Ion Concentration

1983 through 1994

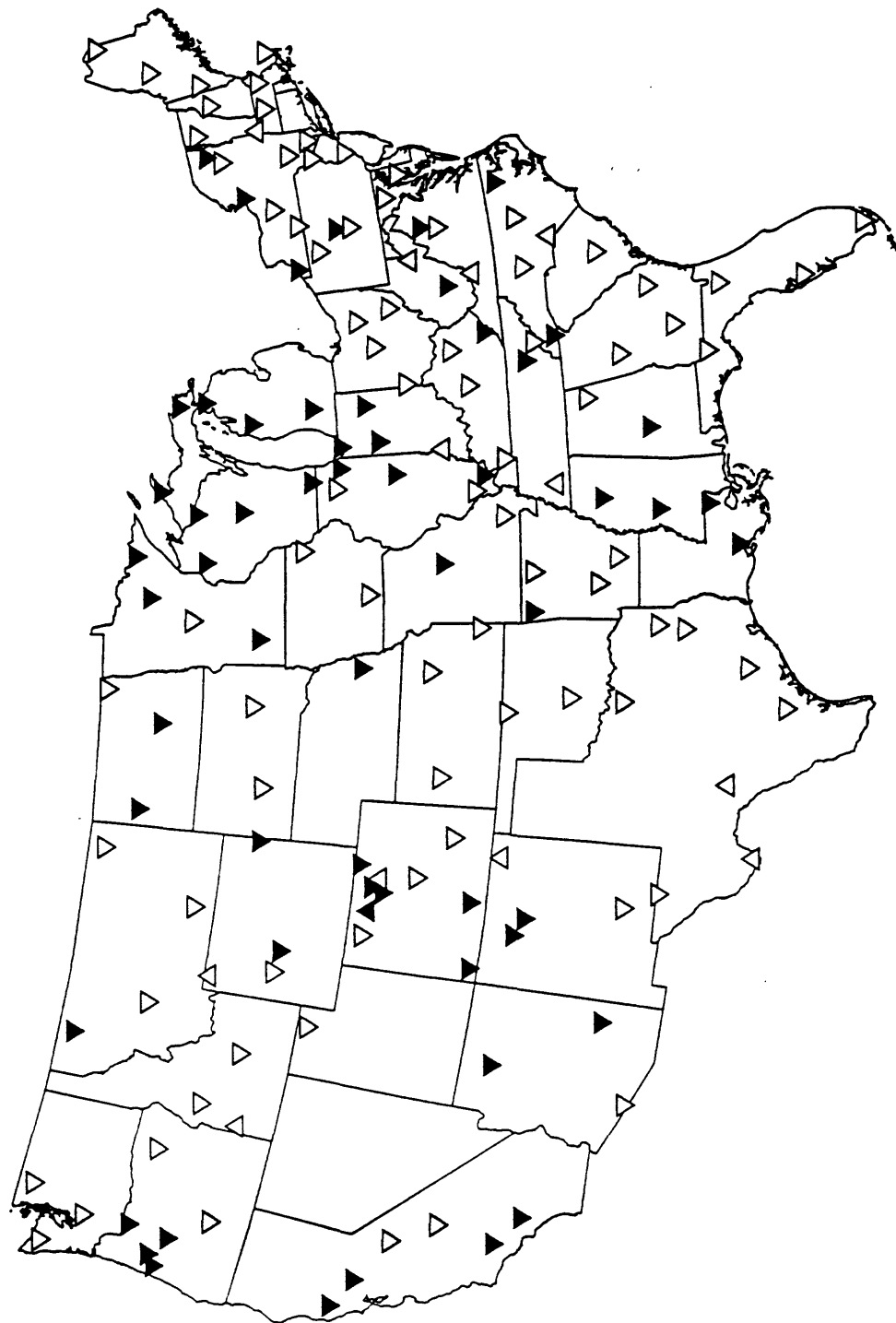


Figure 2
National Atmospheric Deposition Program / National Trends Network
Trends in Nitrate Ion Concentration
1983 through 1994

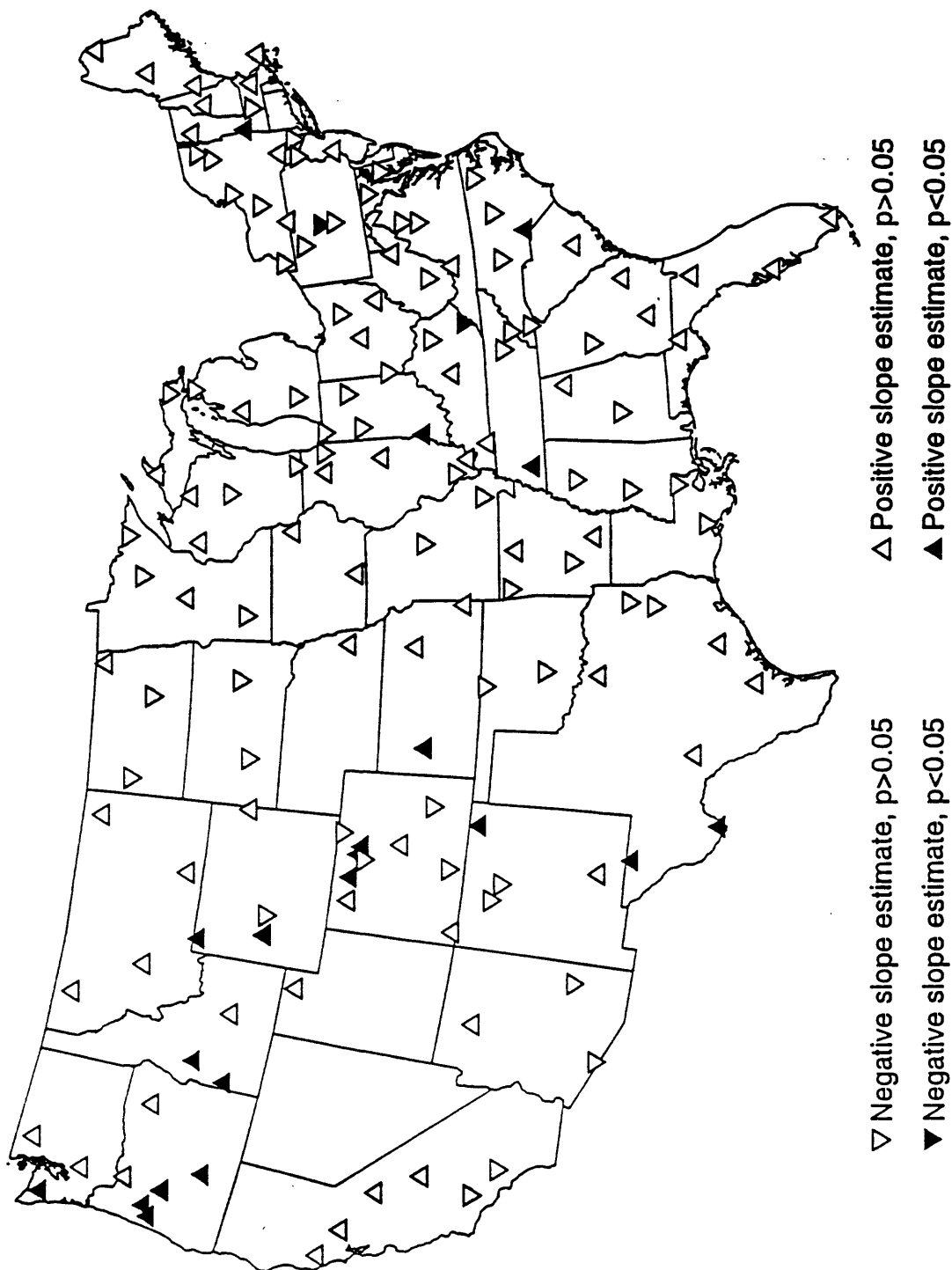


Figure 3
National Atmospheric Deposition Program / National Trends Network
Trends in Ammonium Ion Concentration
1983 through 1994

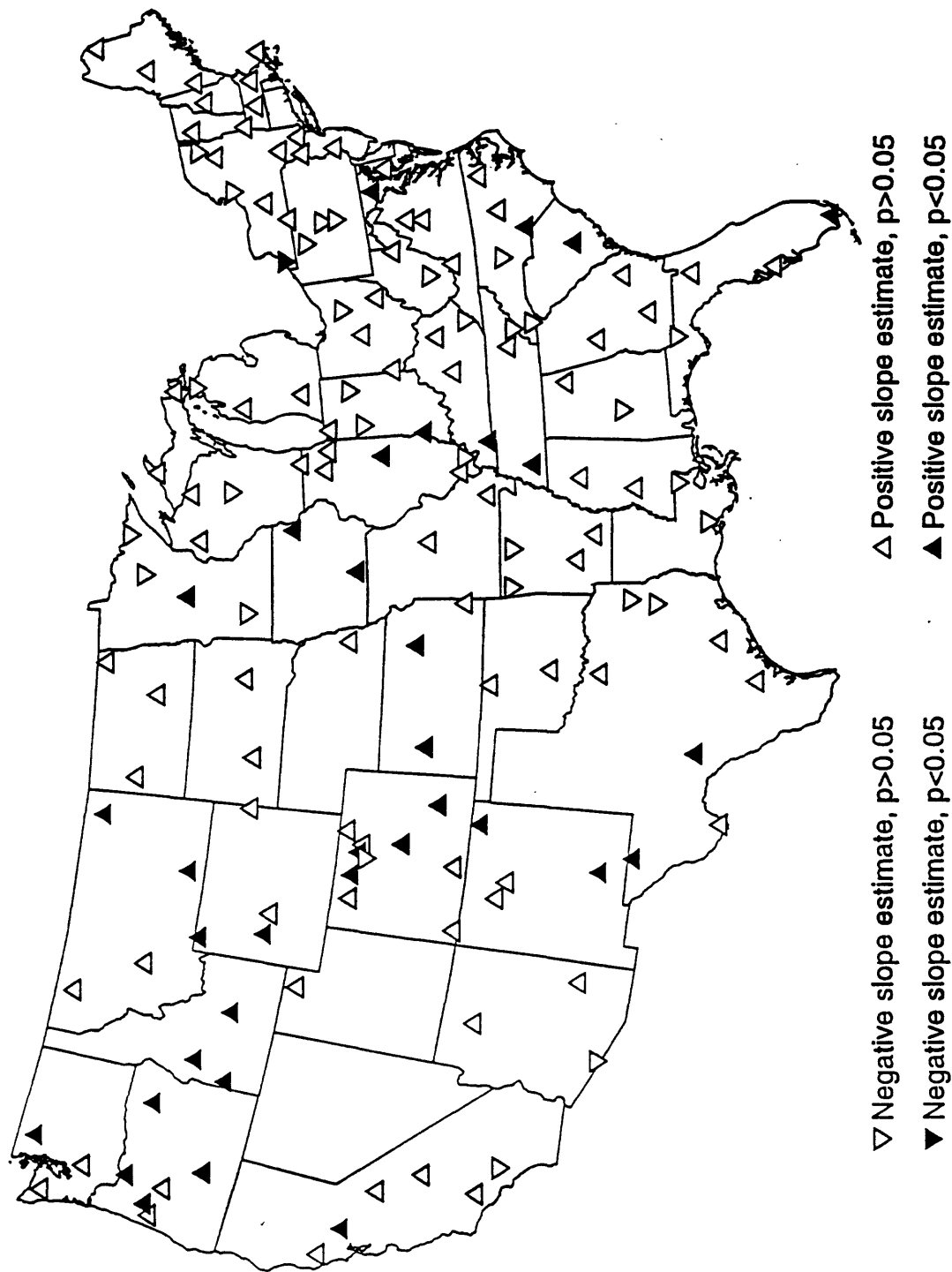


Figure 4
National Atmospheric Deposition Program / National Trends Network
Trends in Calcium Ion Concentration
1983 through 1994

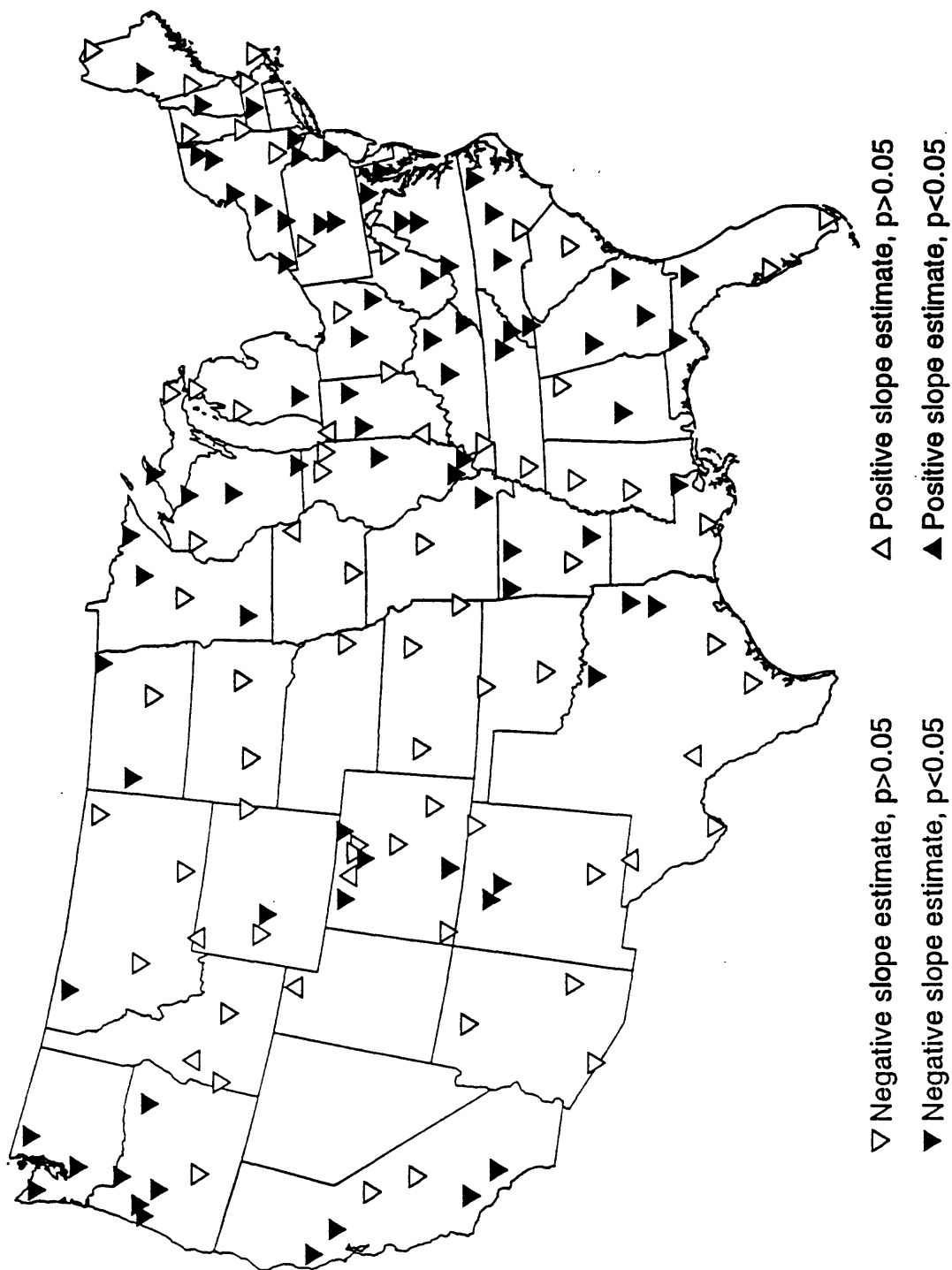


Figure 5

National Atmospheric Deposition Program / National Trends Network

Trends in Magnesium Ion Concentration

1983 through 1994

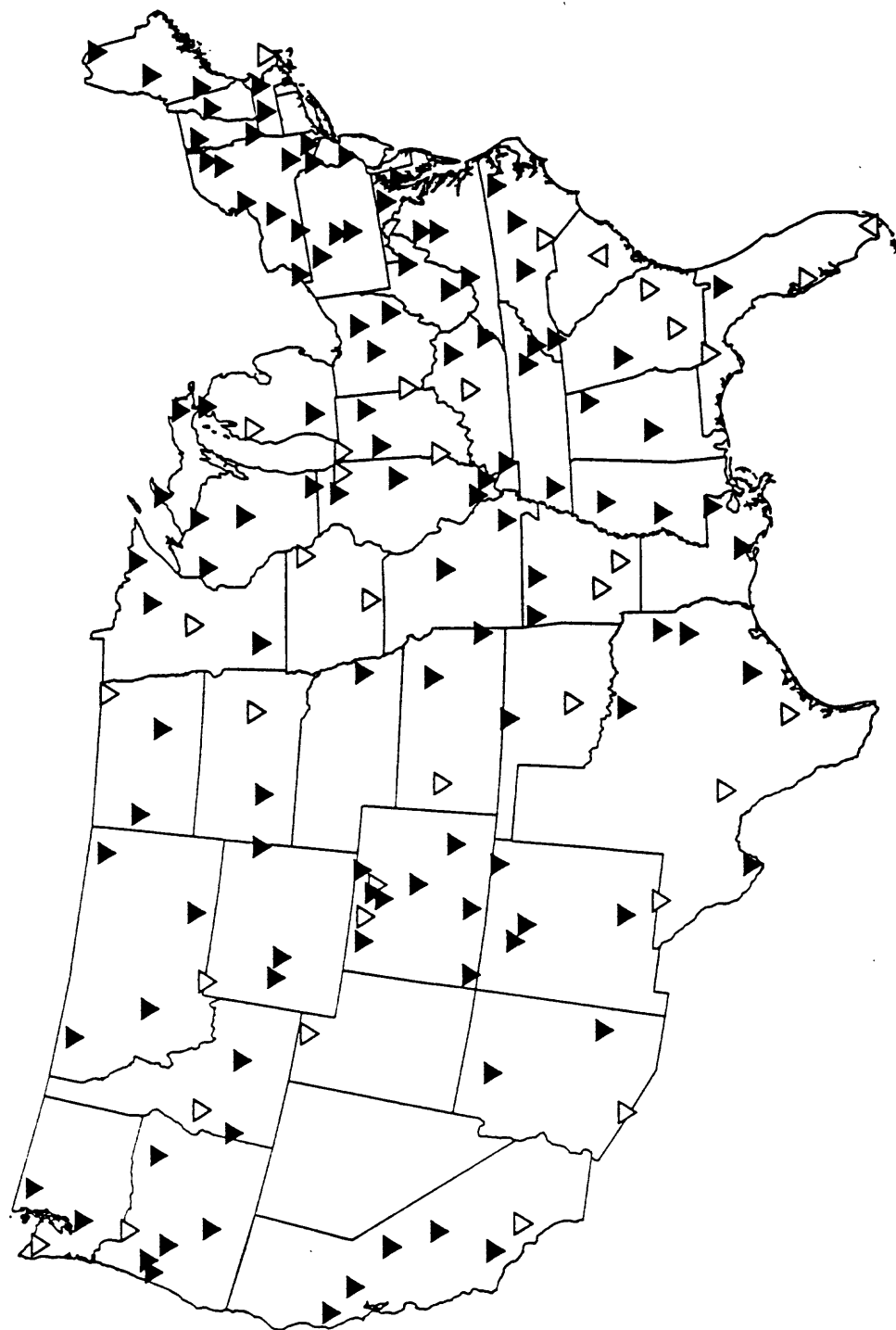


Figure 6

National Atmospheric Deposition Program / National Trends Network

Trends in Potassium Ion Concentration

1983 through 1994

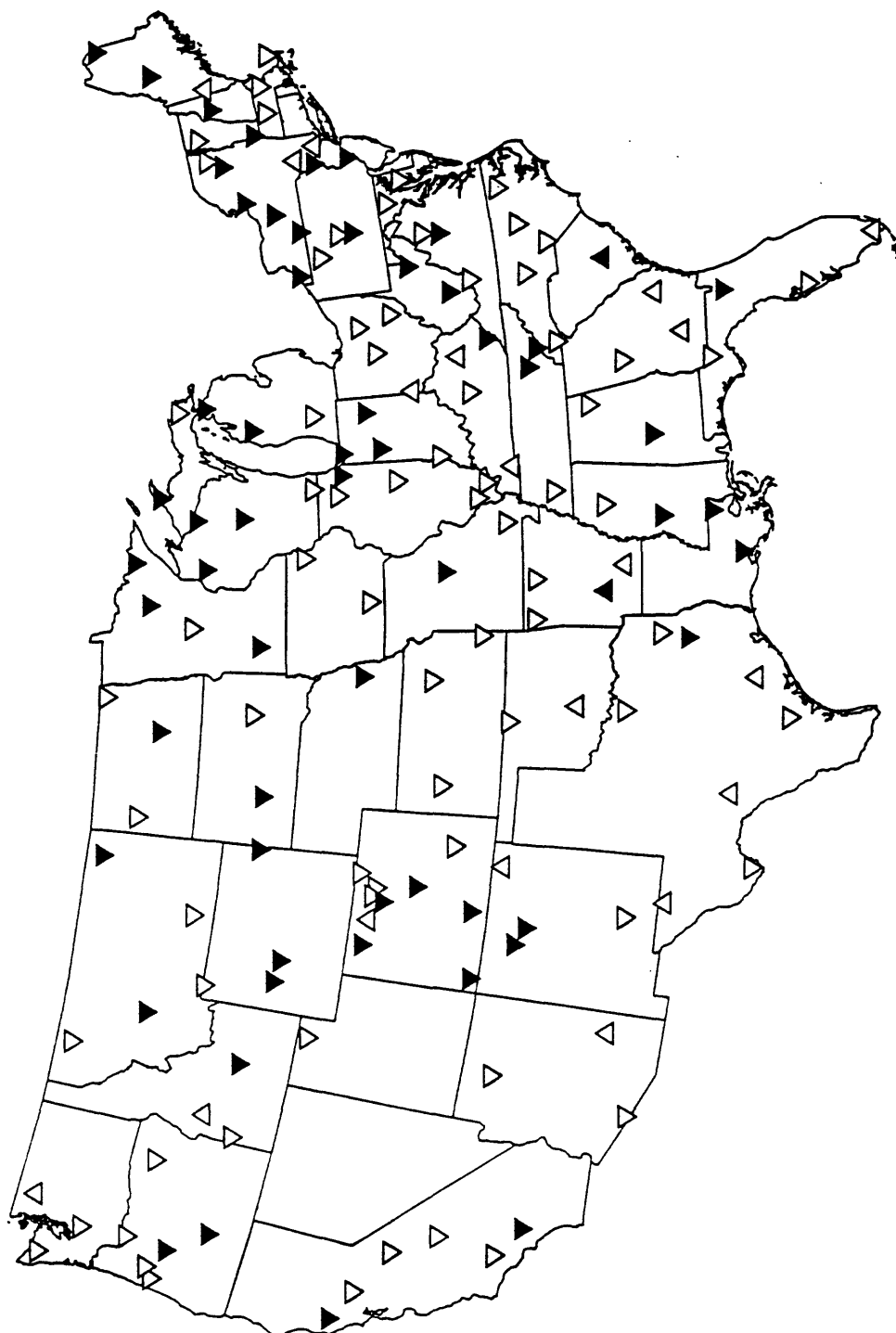
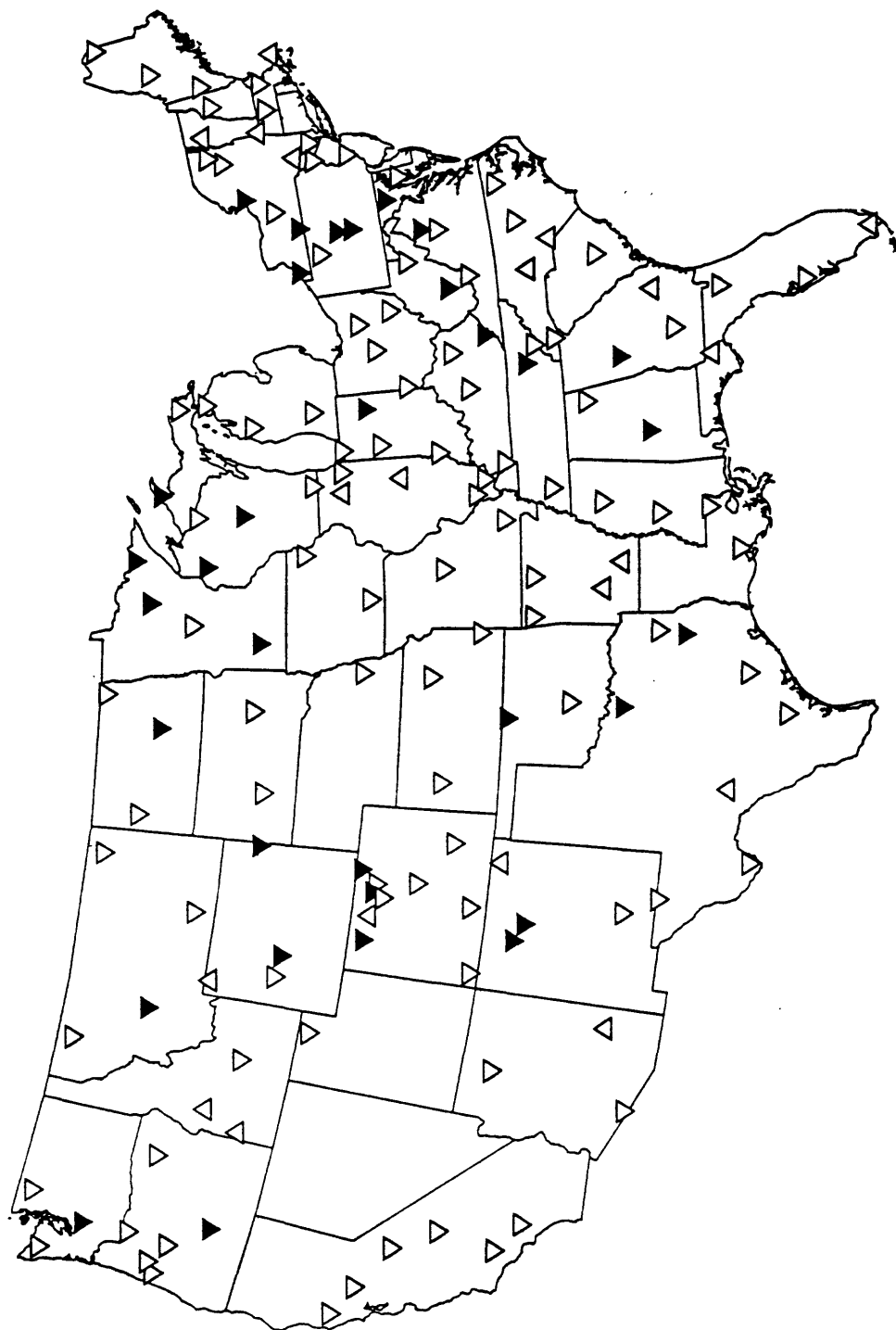


Figure 7

National Atmospheric Deposition Program / National Trends Network

Trends in Sodium Ion Concentration

1983 through 1994



▽ Negative slope estimate, $p > 0.05$

▼ Negative slope estimate, $p < 0.05$

△ Positive slope estimate, $p > 0.05$

▲ Positive slope estimate, $p < 0.05$

Figure 8

National Atmospheric Deposition Program / National Trends Network

Trends in Chloride Ion Concentration

1983 through 1994

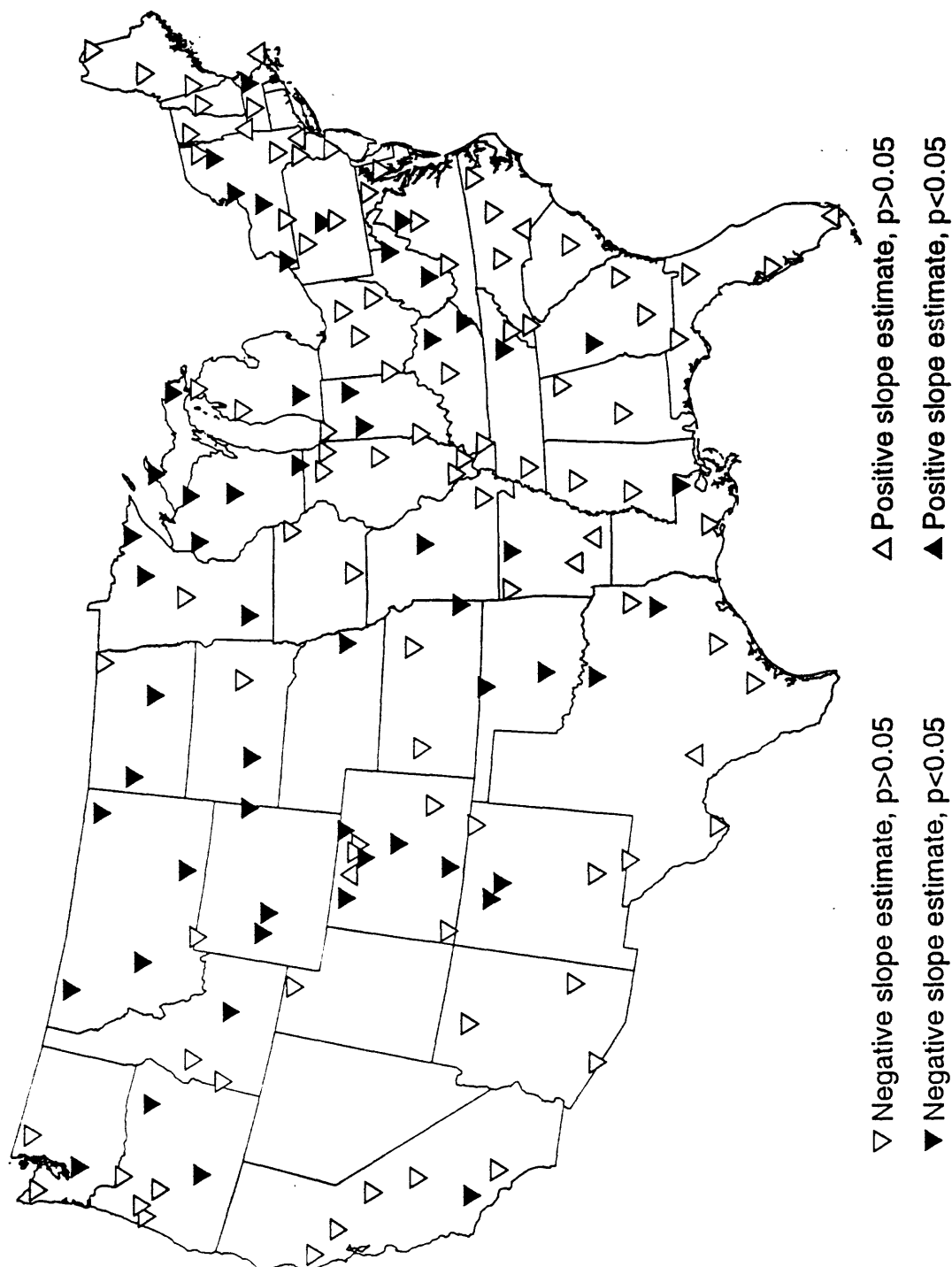
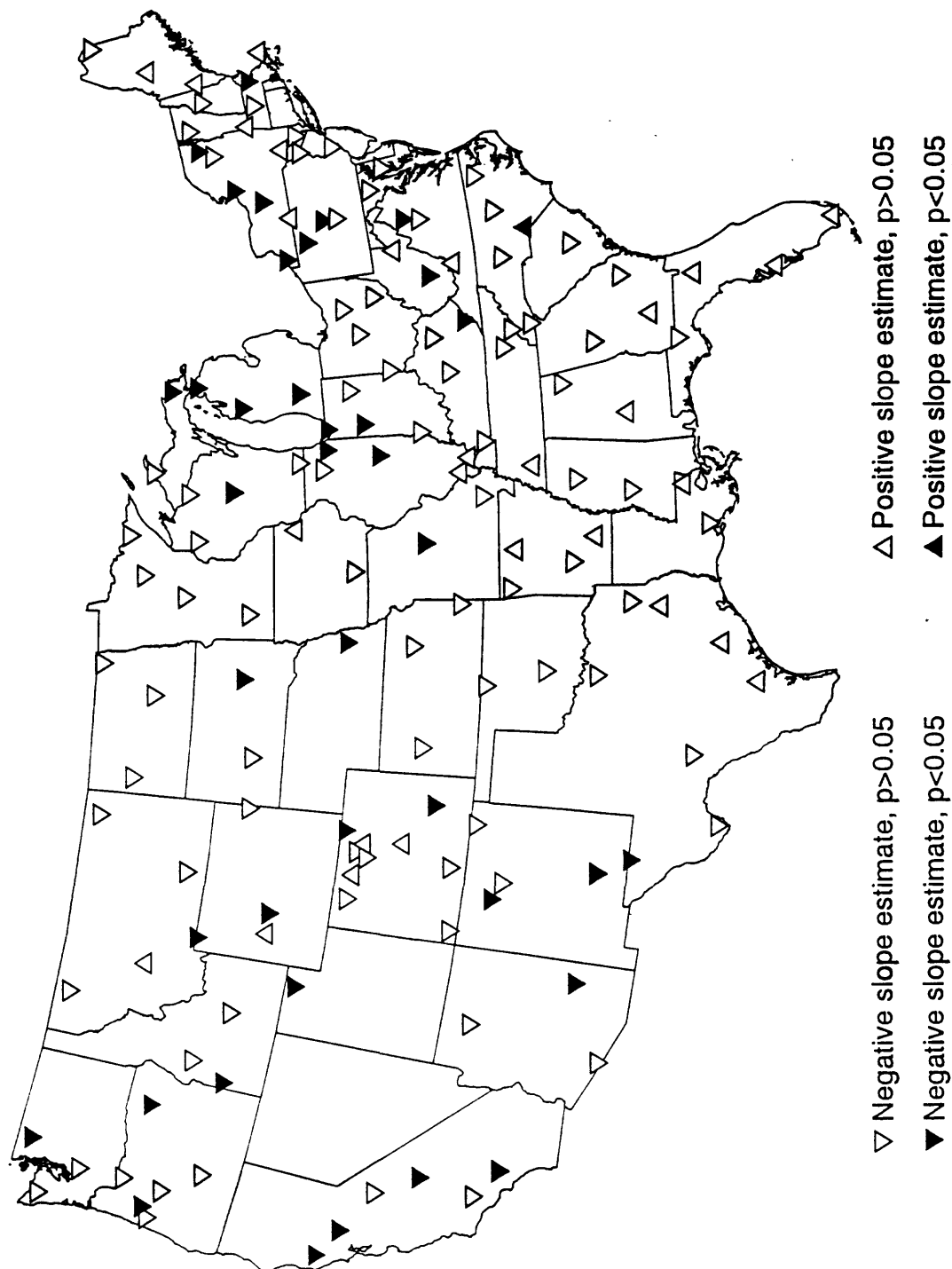


Figure 9

National Atmospheric Deposition Program / National Trends Network
Trends in Hydrogen Ion Concentration
1983 through 1994



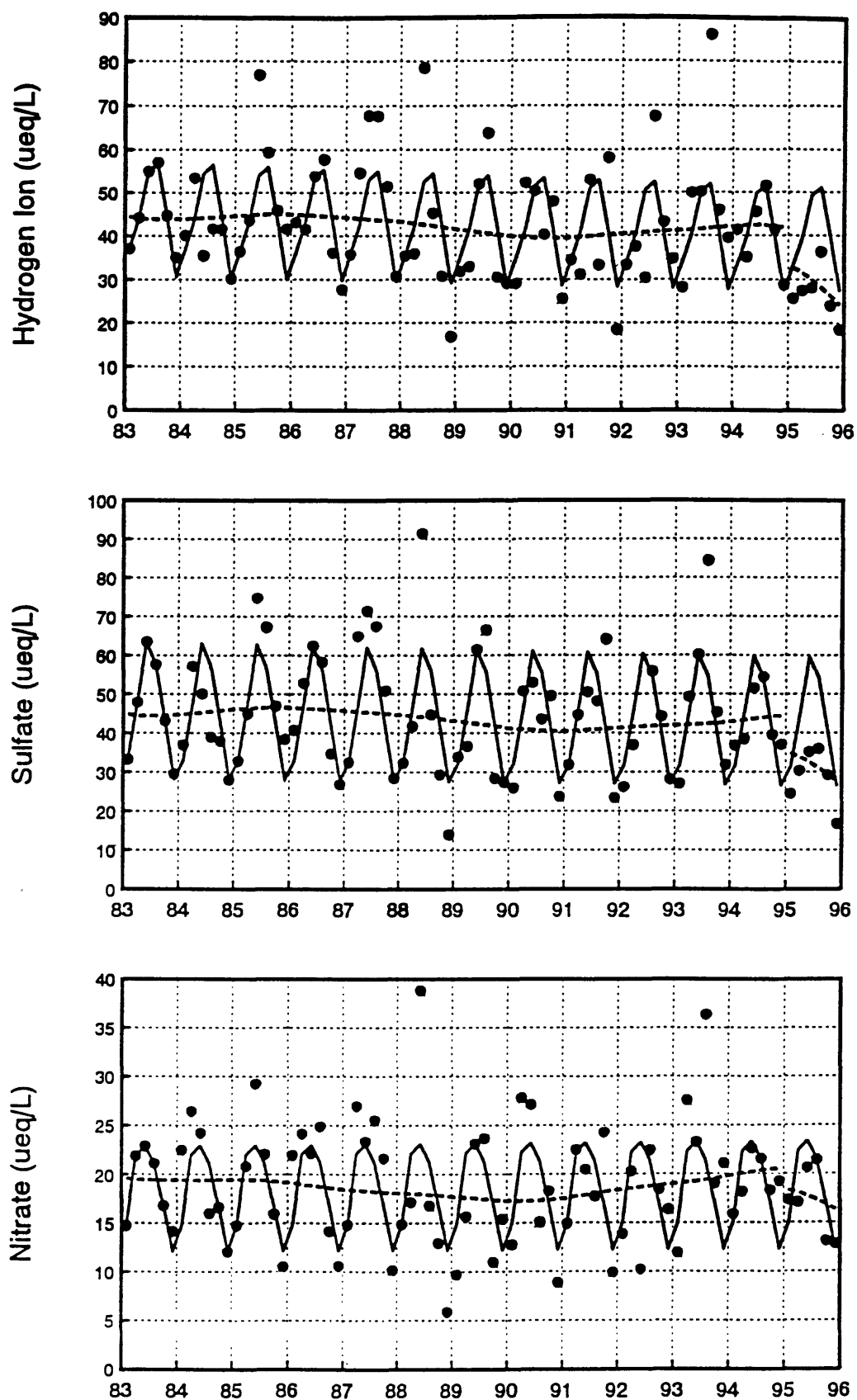


Figure 10. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for H^+ , SO_4^{2-} and NO_3^- at Mackville, KY.

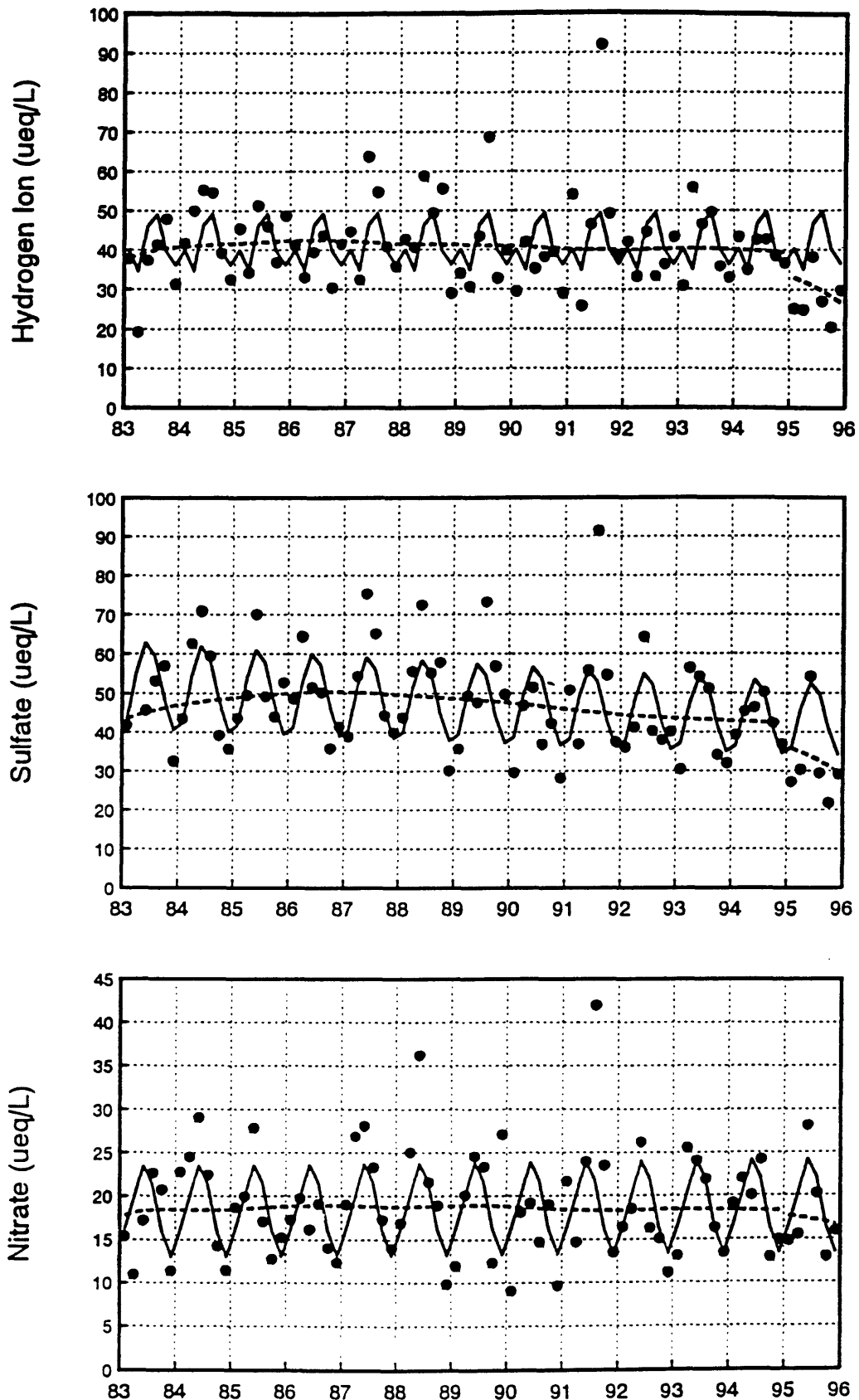


Figure 11. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for H^+ , SO_4^{2-} and NO_3^- at Dixon Springs Agricultural Center, IL.

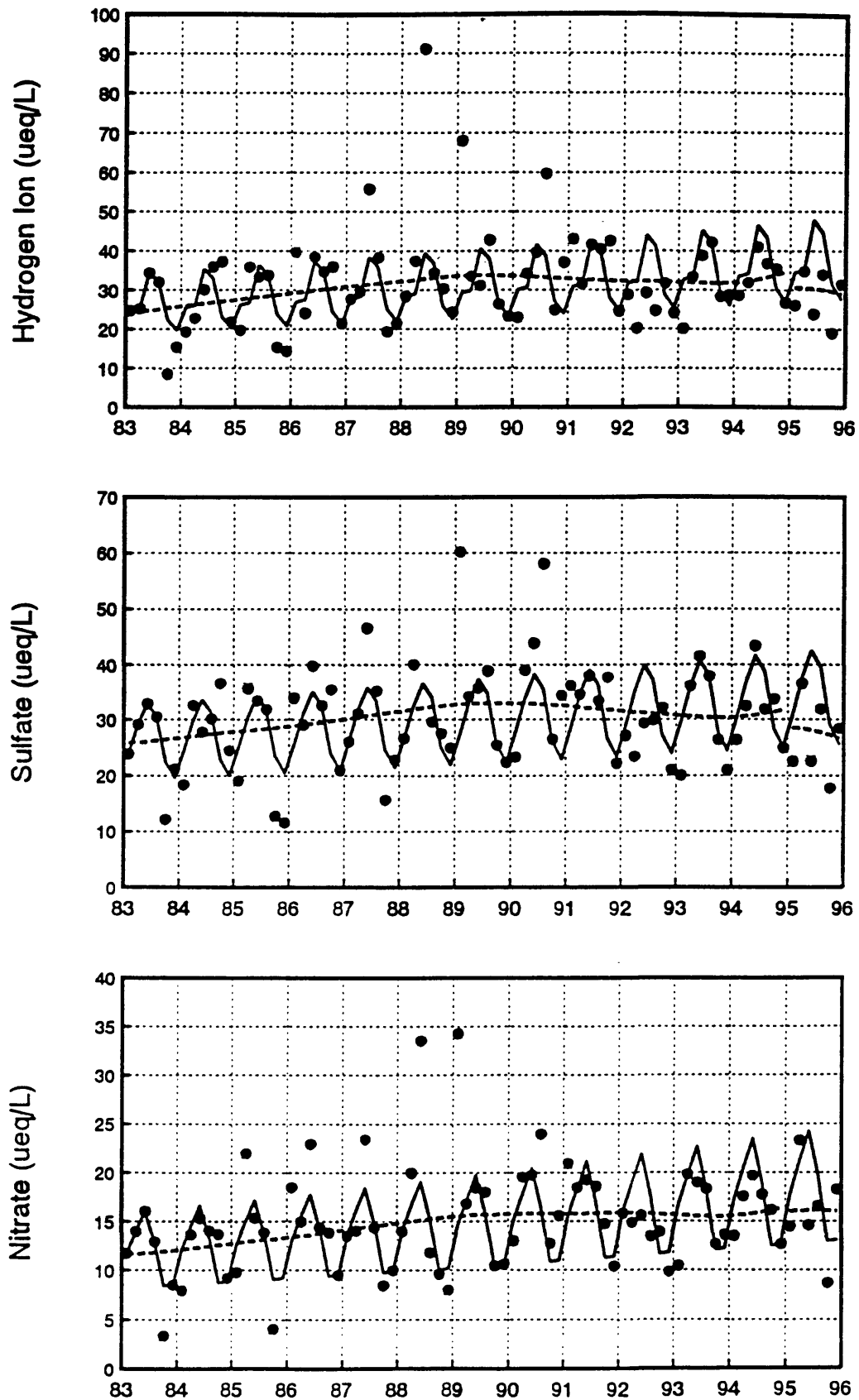


Figure 12. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for H^+ , SO_4^{2-} and NO_3^- at Jordan Creek, NC.

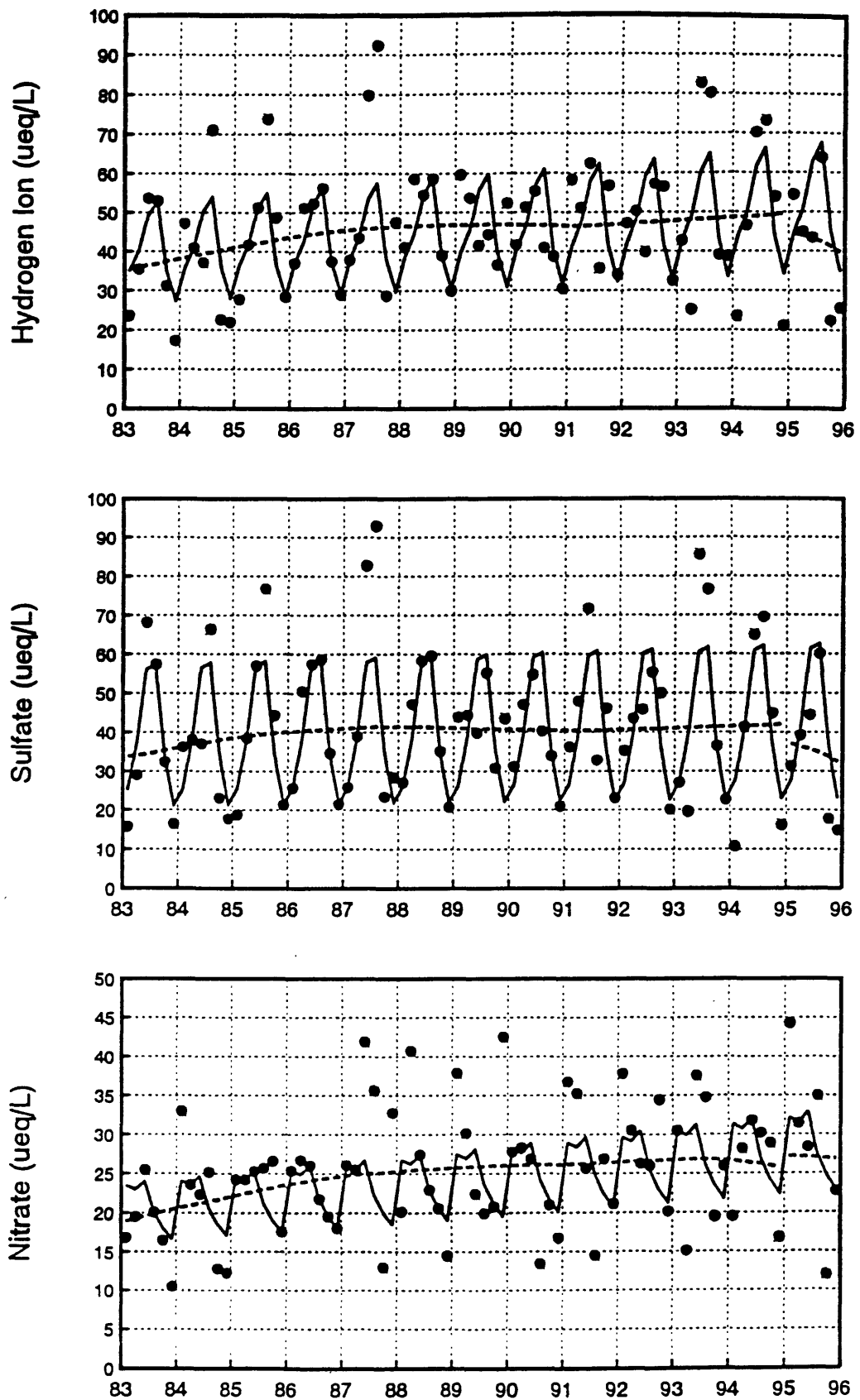


Figure 13. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for H^+ , SO_4^{2-} and NO_3^- at Bennington, VT.

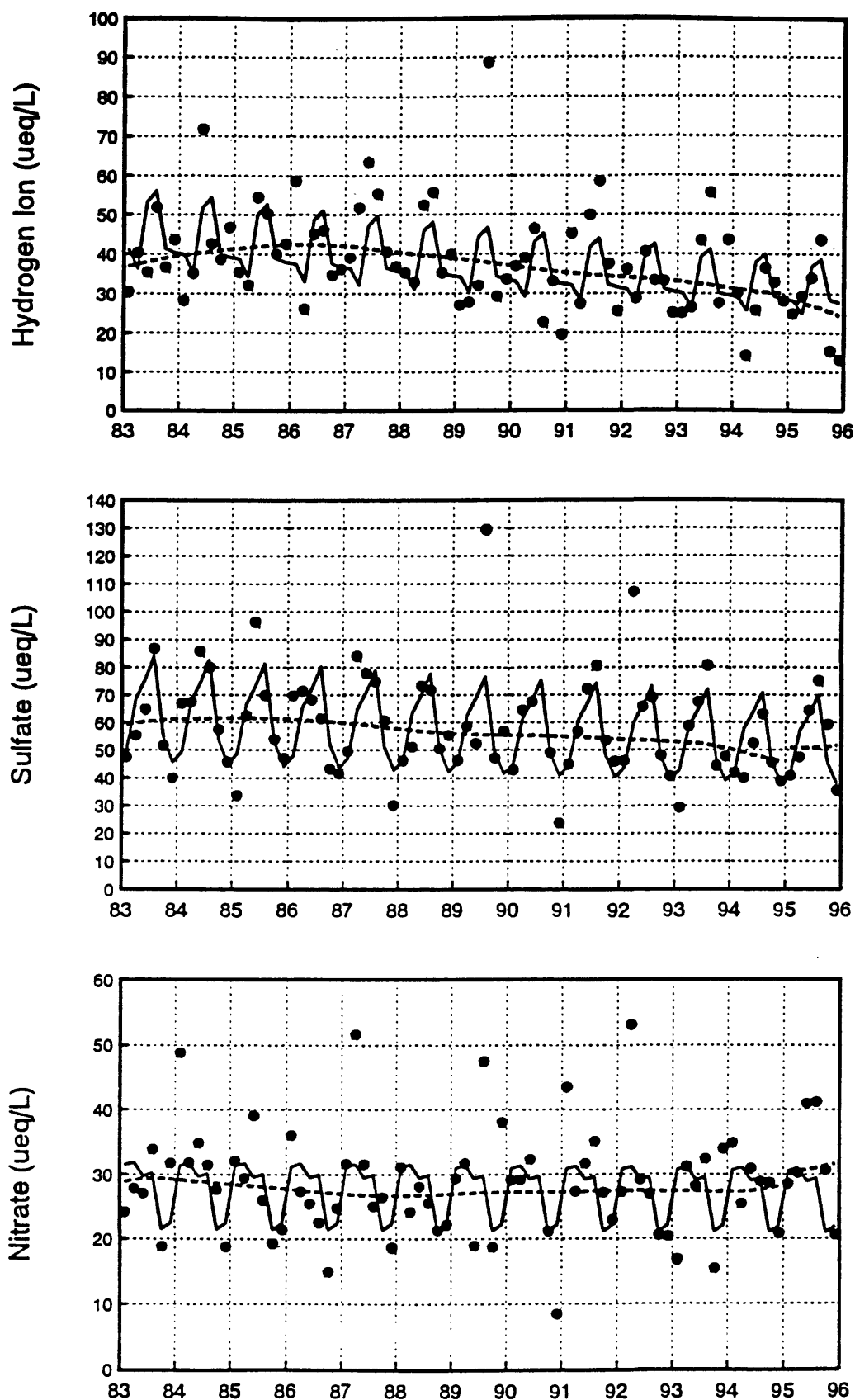


Figure 14. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for H^+ , SO_4^{2-} and NO_3^- at Indiana Dunes Nat'l Lakeshore, IN.

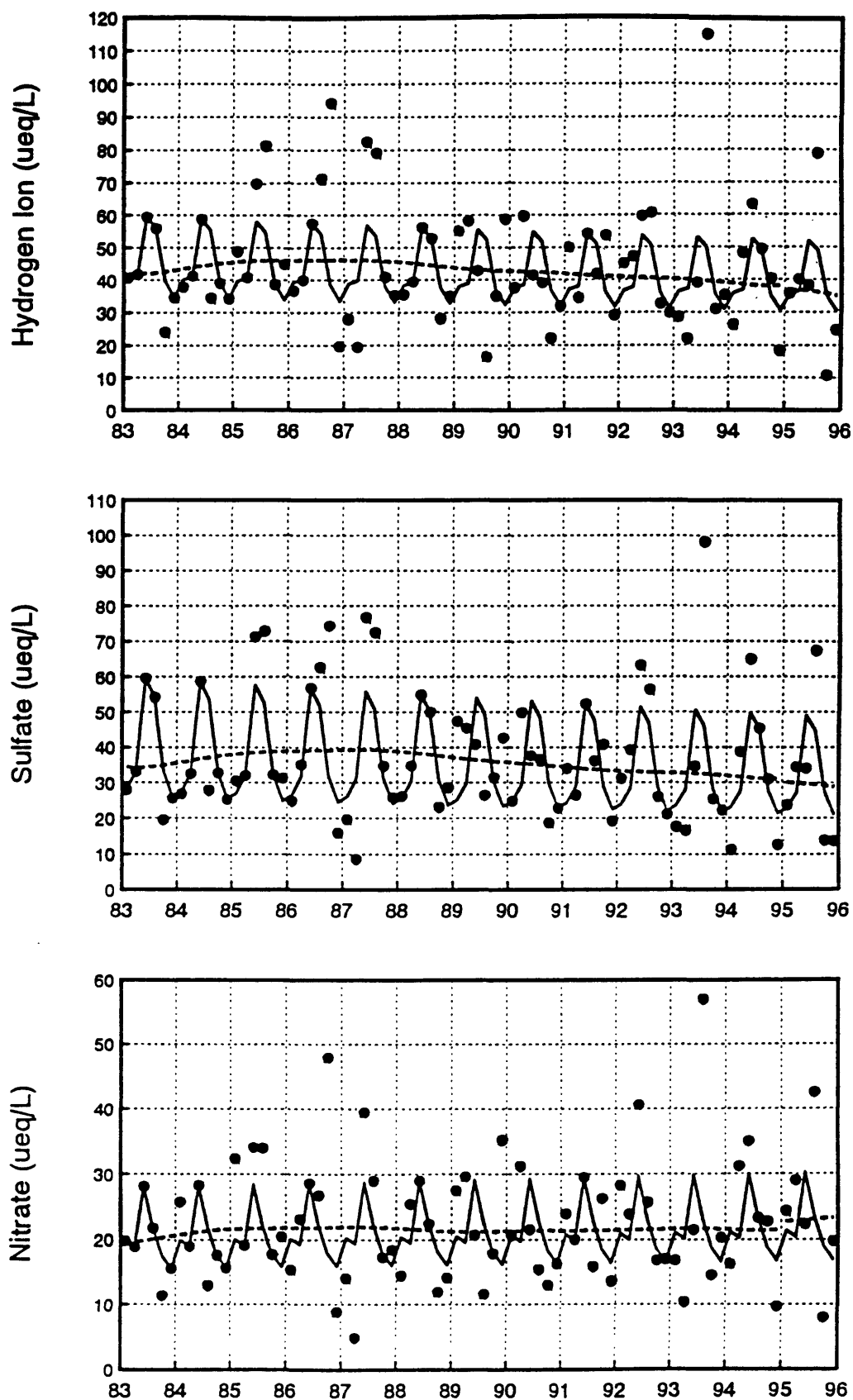


Figure 15. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for H^+ , SO_4^{2-} and NO_3^- at Quabbin Reservoir, MA.

Figure 16

Departures of 1995 Annual Sulfate Ion Concentrations from
Predictions of the 1983-94 Seasonalized Trend Model

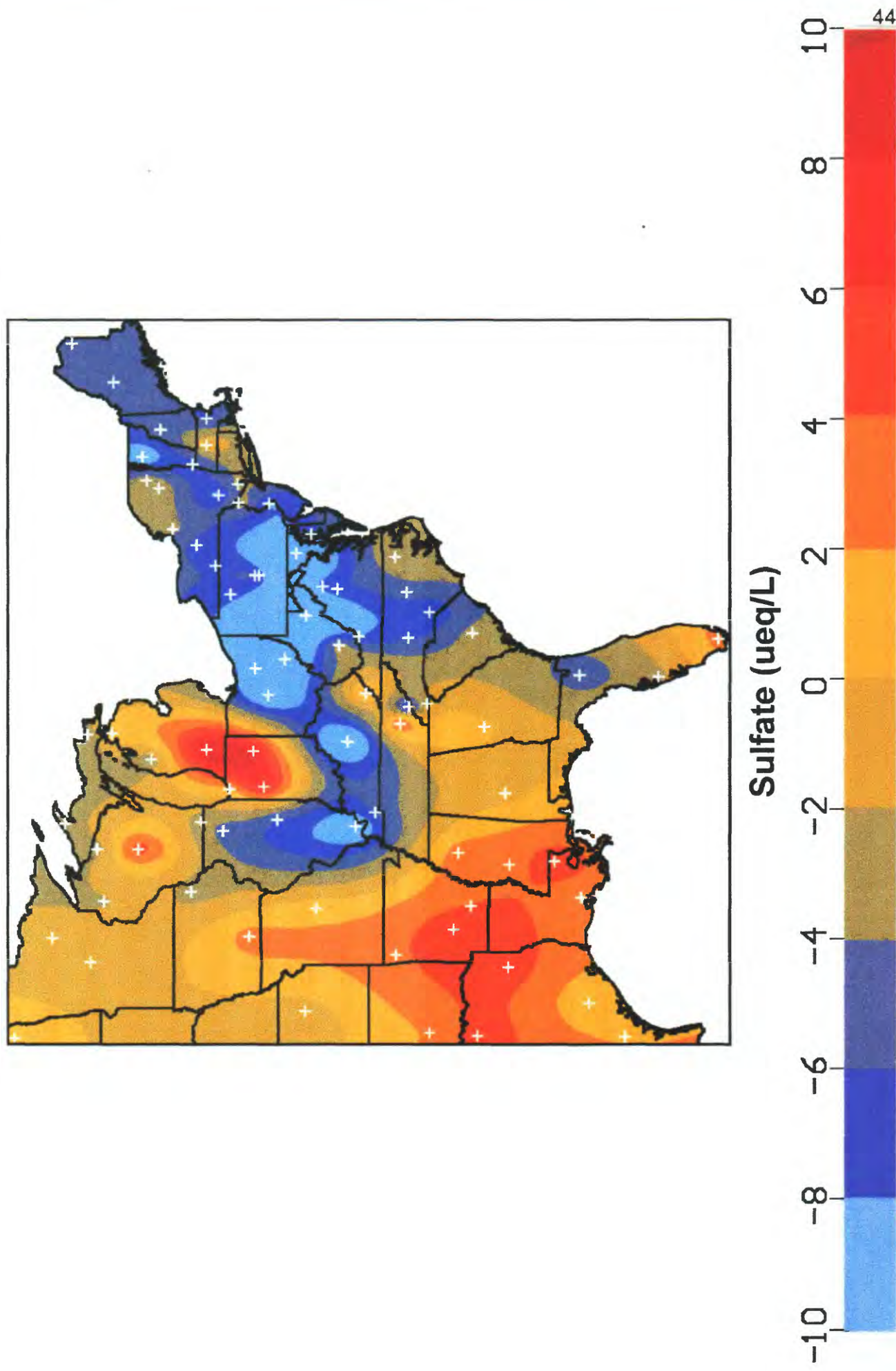


Figure 17

Percent Departures of 1995 Annual Sulfate Ion Concentrations from Predictions of the 1983-94 Seasonalized Trend Model

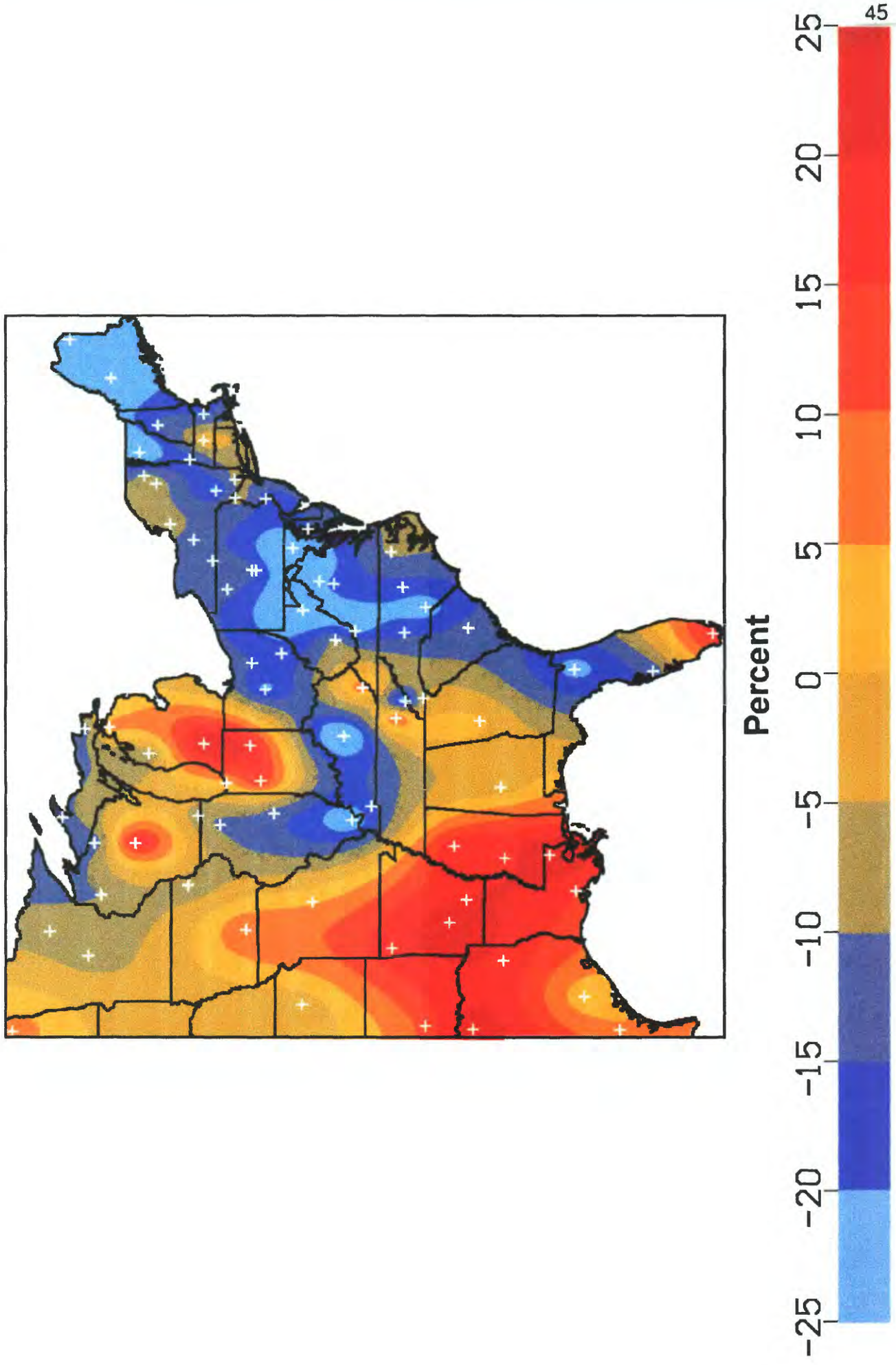


Figure 18

**Departures of 1995 Annual Hydrogen Ion Concentrations from
Predictions of the 1983-94 Seasonalized Trend Model**

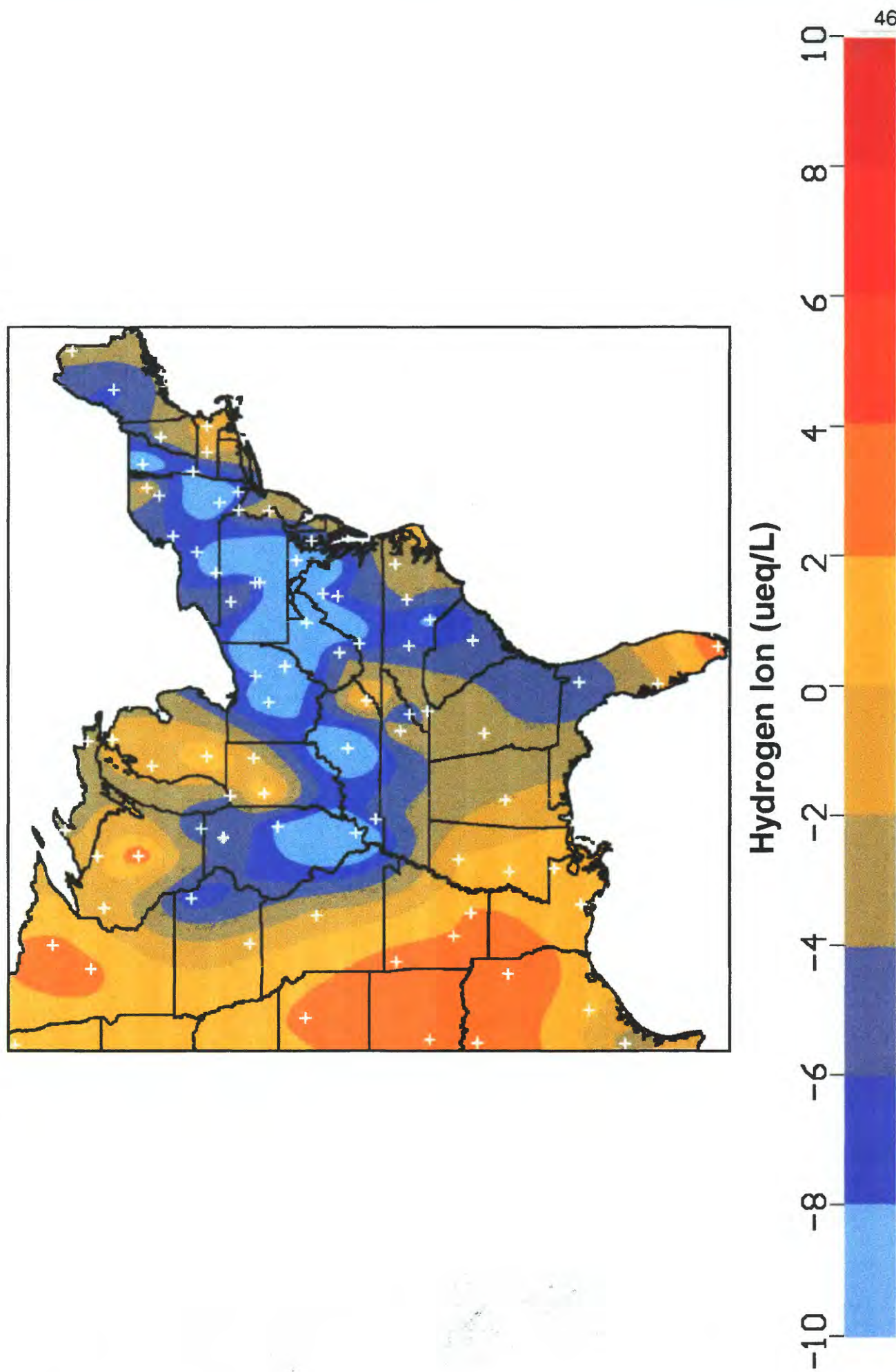


Figure 19

Percent Departures of 1995 Annual Hydrogen Ion Concentrations from Predictions of the 1983-94 Seasonalized Trend Model

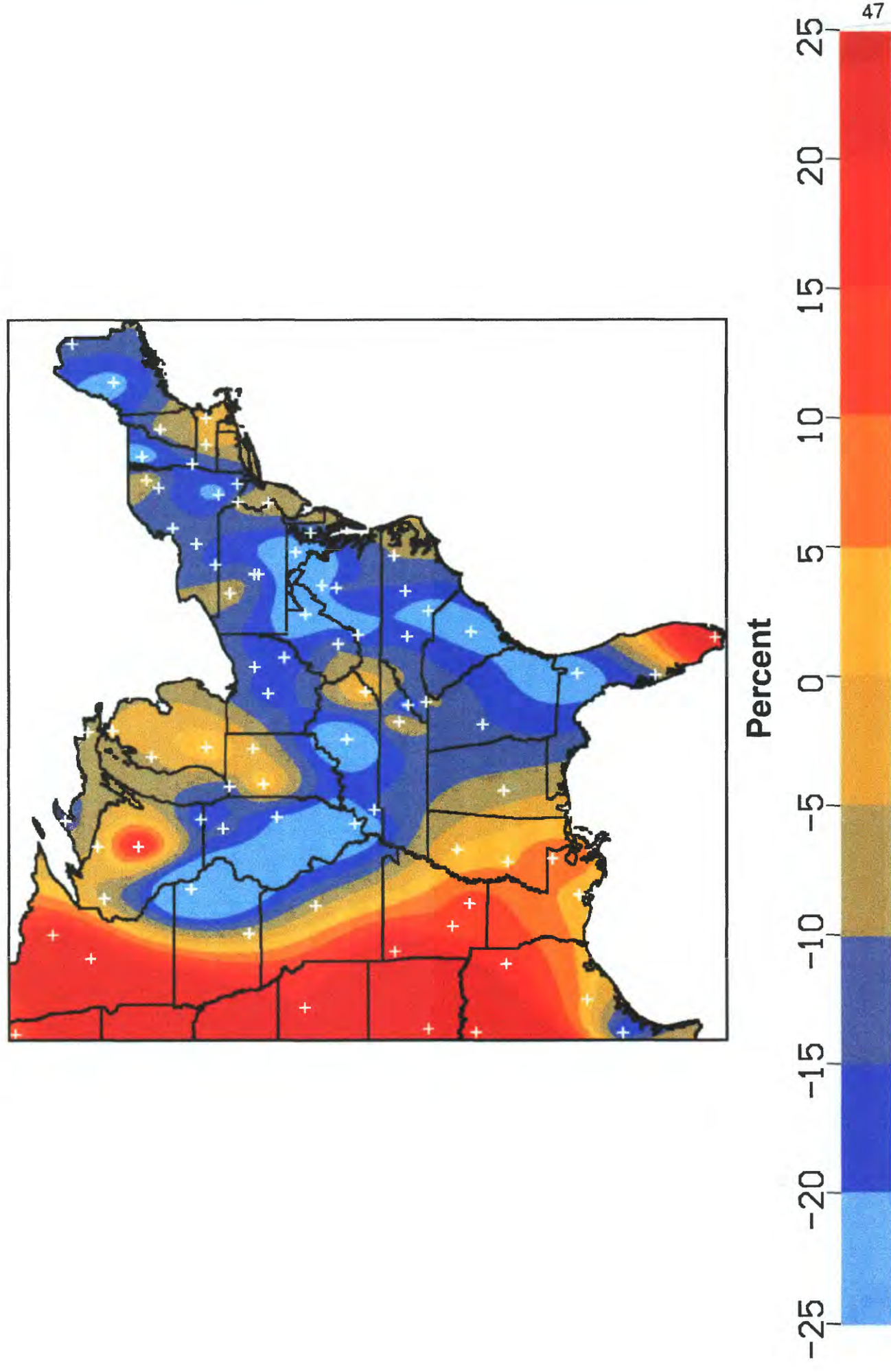


Figure 20

Departures of 1995 Annual Nitrate Ion Concentrations from Predictions of the 1983-94 Seasonalized Trend Model

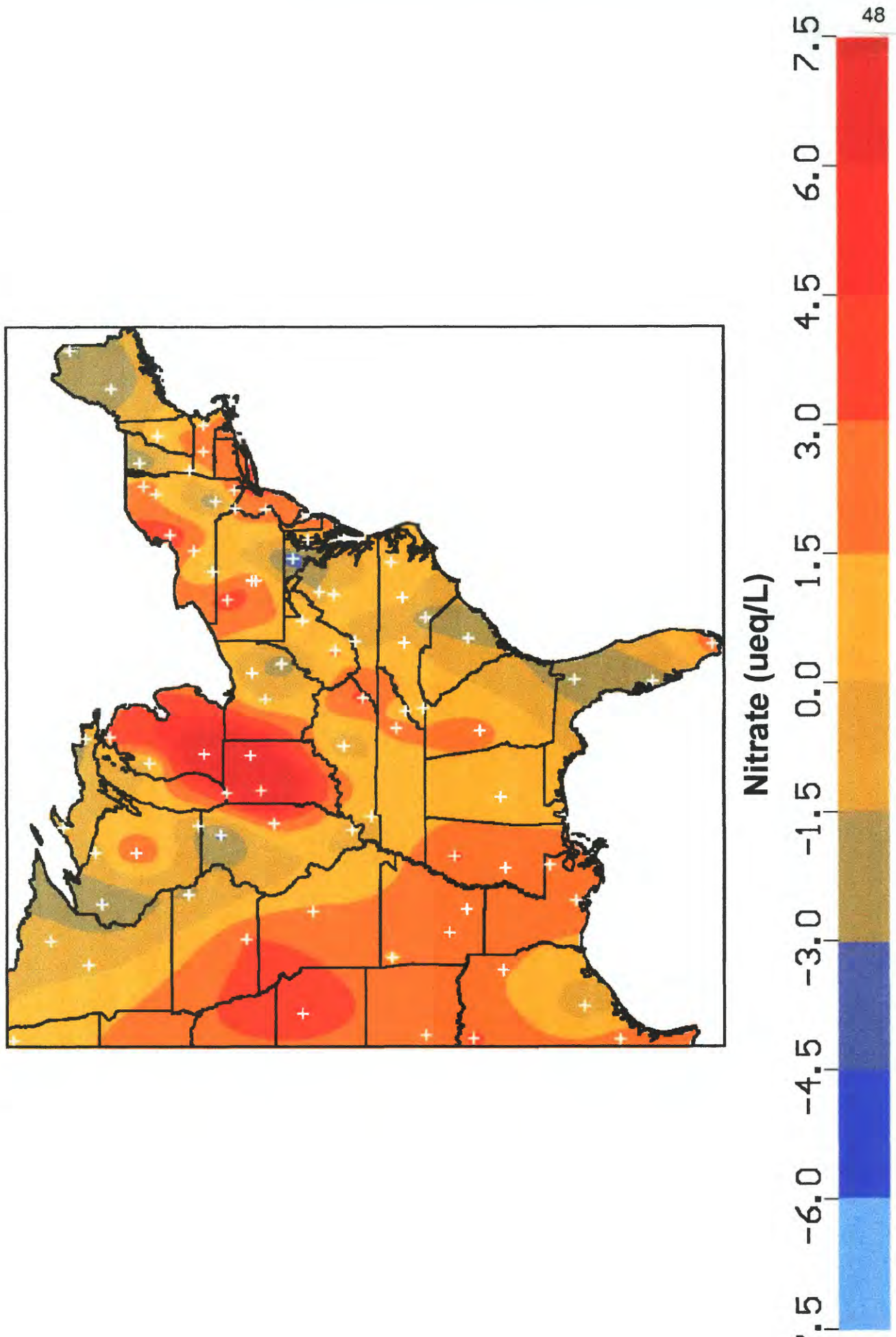


Figure 21

Percent Departures of 1995 Annual Nitrate Ion Concentrations from
Predictions of the 1983-94 Seasonalized Trend Model

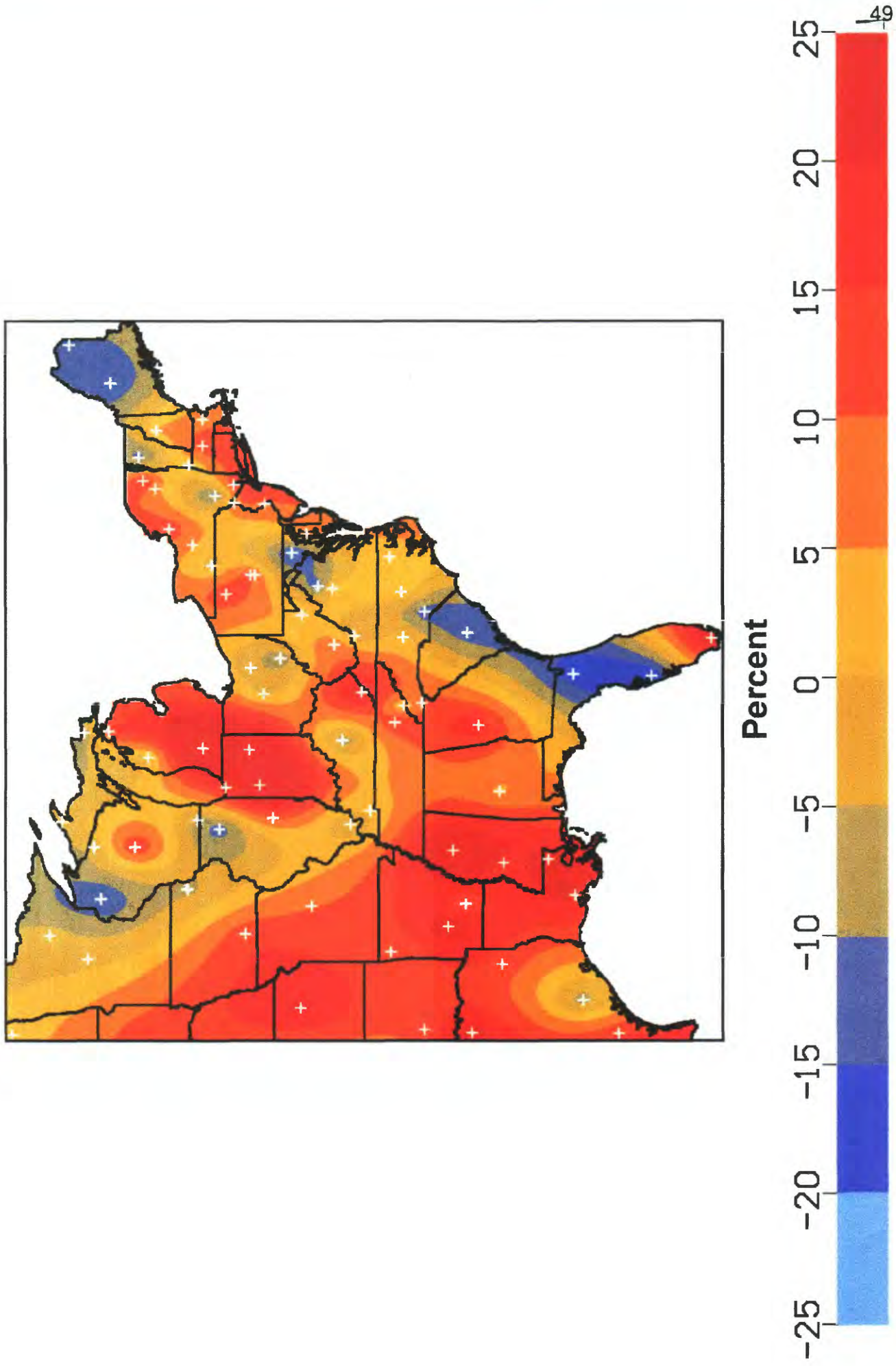


Figure 22

Departures of 1995 Annual Precipitation from the Mean Annual Precipitation during 1983-94

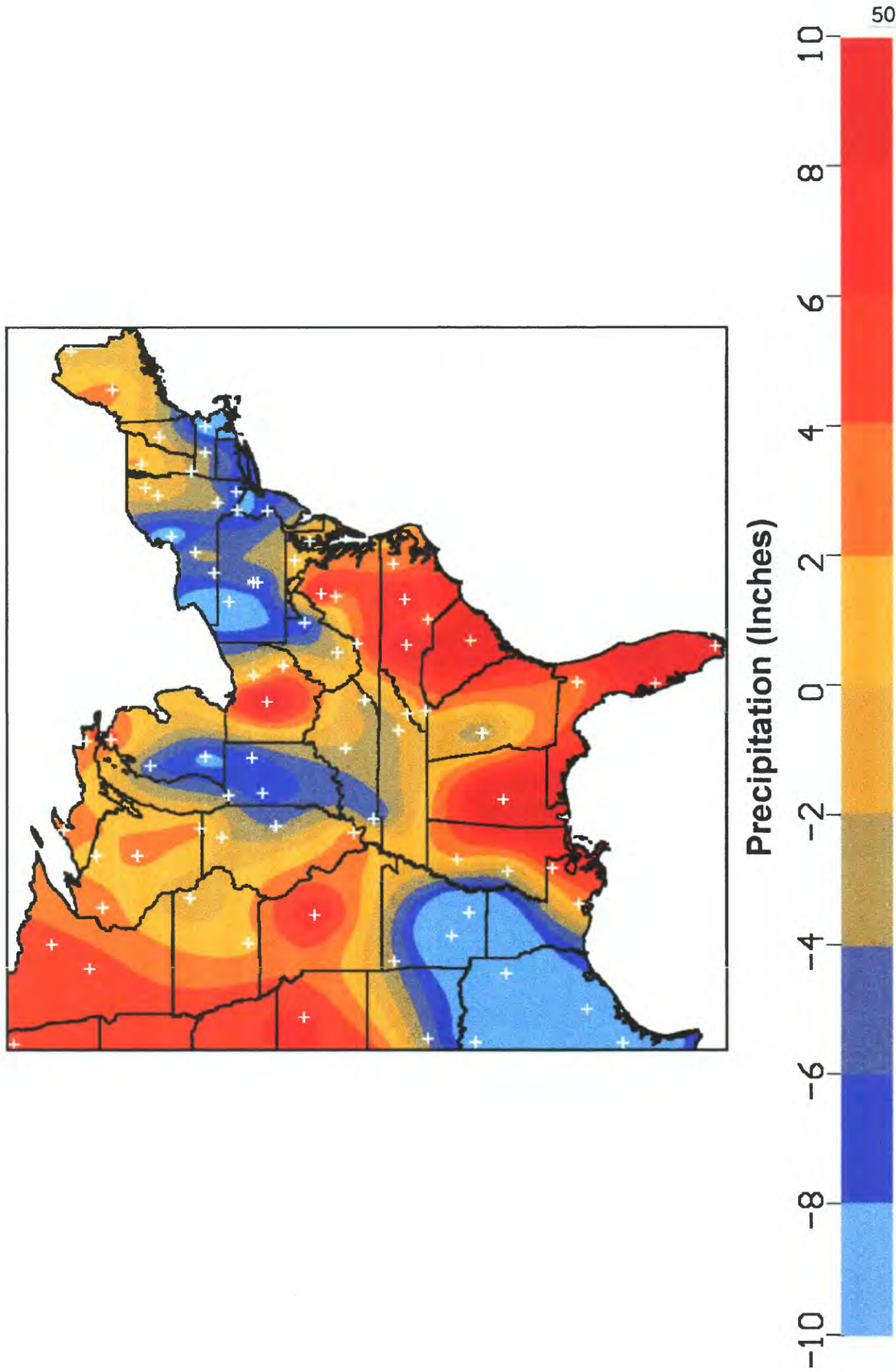
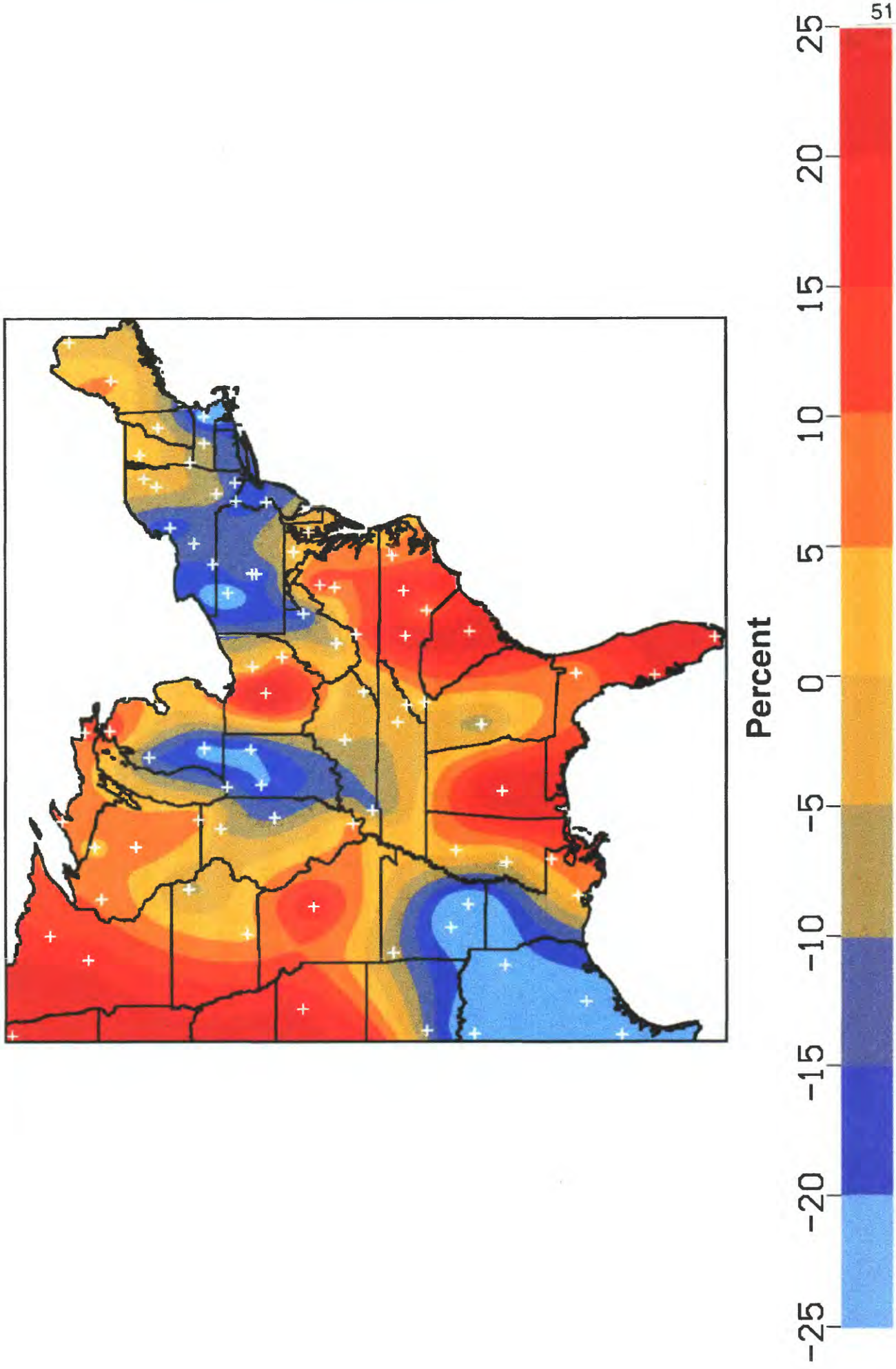


Figure 23
Percent Departures of 1995 Annual Precipitation from the
Mean Annual Precipitation during 1983-94



APPENDIX

Table A.1. Algorithms for adjusting pre-1994 NADP/NTN data for the effects of contamination from the lid o-ring. The "cor" and "unc" subscripts designate the concentrations that are corrected or uncorrected for the o-ring. Volume (Vol) is in mL and pH is in pH units. Volume restriction categories for the algorithms with volume and pH factors are listed. These corrections effectively limit the size of the corrections at very low and very high pH values.

Volume-Only Factors:

$$\text{Ca}_{\text{cor}} = \text{Ca}_{\text{unc}} - (3.70/\text{Vol}) (1 - \exp^{-0.00214\text{Vol}})$$

$$\text{Mg}_{\text{cor}} = \text{Mg}_{\text{unc}} - (2.21/\text{Vol}) (1 - \exp^{-0.00252\text{Vol}})$$

$$\text{NH}_{4\text{cor}} = \text{NH}_{4\text{unc}} - (8.46/\text{Vol}) (1 - \exp^{-0.00287\text{Vol}})$$

$$\text{Cl}_{\text{cor}} = \text{Cl}_{\text{unc}} - (5.04/\text{Vol}) (1 - \exp^{-0.00289\text{Vol}})$$

Volume and pH Factors:

A. For pH > [5.13 + (2000/Vol)], use the minimum of [5.13 + (2000/Vol)] or 6.86

For pH < [5.13 + (2000/Vol)], use the maximum of [5.13 + (2000/Vol)] or 3.80

$$\text{K}_{\text{cor}} = \text{K}_{\text{unc}} - [(61.25 - 23.19\text{pH} + 2.20\text{pH}^2) / \text{Vol}] [1 - \exp^{-0.00552\text{Vol}}]$$

$$\text{NO}_{3\text{cor}} = \text{NO}_{3\text{unc}} - [(146.29 - 50.47\text{pH} + 4.64\text{pH}^2) / \text{Vol}] [1 - \exp^{-0.00593\text{Vol}}]$$

B. For pH > [5.13 + (2000/Vol)], use the minimum of [5.13 + (2000/Vol)] or 6.72

For pH < [5.13 + (2000/Vol)], use the maximum of [5.13 + (2000/Vol)] or 3.80

$$\text{Na}_{\text{cor}} = \text{Na}_{\text{unc}} - [(163.66 - 64.07\text{pH} + 6.46\text{pH}^2) / \text{Vol}] [1 - \exp^{-0.00246\text{Vol}}]$$

C. For pH > (5.13 + 2000/Vol), use the minimum of (5.13 + 2000/Vol) or 6.67

For pH < (5.13 + 2000/Vol), use the maximum of (5.13 + 2000/Vol) or 3.80

$$\text{SO}_{4\text{cor}} = \text{SO}_{4\text{unc}} - [(177.73 - 53.44\text{pH} + 4.62\text{pH}^2) / \text{Vol}] [1 - \exp^{-0.00230\text{Vol}}]$$

Table A.5 (continued).

Region Site	Annual Mean			January-February			March-April			May-June			July-August			September-October			November-December		
	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.
tx03	21.67	20.91	0.76	27.47	21.89	5.58	20.61	34.60	-13.99	43.46	25.38	18.08	13.91	10.08	3.83	13.00	12.73	0.27	11.60	20.76	-9.16
tx10	10.10	12.68	-2.58	11.89	12.47	-0.58	10.14	18.13	-7.99	16.28	20.22	-3.94	9.87	10.53	-0.66	4.83	7.62	-2.79	7.56	7.12	0.44
tx16	20.22	16.44	3.78	17.57	13.72	3.85	18.65	22.14	-3.49	27.80	24.02	3.78	16.87	11.43	5.44	19.89	11.23	8.66	20.51	16.10	4.41
tx21	13.65	8.76	4.89	7.93	8.41	-0.48	19.96	11.16	8.80	16.48	14.06	2.42	14.58	7.48	7.10	10.47	5.83	4.64	12.47	5.61	6.86
tx56	16.97	17.30	-0.33	12.06	17.17	-5.11	21.65	32.35	-10.70	26.00	20.81	5.19	10.08	13.22	-3.14	23.93	8.60	15.33	8.08	11.63	-3.55
wa14	1.72	1.35	0.37	1.39	1.40	-0.01	1.33	1.39	-0.06	2.32	1.41	0.91	2.07	1.36	0.71	2.13	1.25	0.88	1.11	1.30	-0.19
wa21	4.75	4.12	0.63	2.59	2.13	0.46	5.14	5.11	0.03	10.21	5.47	4.74	5.62	5.16	0.46	2.97	4.64	-1.67	1.96	2.24	-0.28
wy02	7.02	6.66	0.36	3.27	2.97	0.30	11.66	9.01	2.65	5.57	6.57	-1.00	11.03	14.01	-2.98	8.29	5.12	3.17	2.31	2.27	0.04
wy08	7.96	9.80	-1.84	3.79	4.69	-0.90	6.22	9.79	-3.57	10.94	14.87	-3.93	12.49	16.98	-4.49	9.59	7.76	1.83	4.71	4.69	0.02
wy99	15.17	12.45	2.72	17.40	7.74	9.66	18.14	19.66	-1.52	15.21	16.69	-1.48	15.73	17.40	-1.67	14.09	8.86	5.23	10.45	4.34	6.11

Table A.7 (continued).

Region Site	Annual Mean			January-February			March-April			May-June			July-August			September-October			November-December		
	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.
tx03	6.67	4.67	2.00	10.17	3.96	6.21	7.83	5.95	1.88	10.44	4.32	6.12	4.65	3.96	0.69	3.70	4.08	-0.38	3.22	5.77	-2.55
tx10	3.51	2.94	0.57	4.94	2.95	1.99	5.13	3.33	1.80	3.39	2.67	0.72	2.98	2.27	0.71	2.51	2.49	0.02	2.13	3.93	-1.80
tx16	2.65	2.06	0.59	2.14	1.59	0.55	3.55	3.20	0.35	2.82	2.17	0.65	3.29	2.07	1.22	1.72	1.65	0.07	2.35	1.65	0.70
tx21	2.19	1.94	0.25	1.75	1.67	0.08	2.57	2.56	0.01	2.07	1.77	0.30	3.68	2.05	1.63	1.45	1.47	-0.02	1.60	2.10	-0.50
tx56	2.07	1.47	0.60	1.49	1.12	0.37	2.68	2.77	-0.09	3.78	1.39	2.39	1.75	1.34	0.41	1.81	0.94	0.87	0.90	1.24	-0.34
wa14	3.73	3.11	0.62	2.97	4.19	-1.22	5.82	3.10	2.72	3.30	3.31	-0.01	2.19	1.25	0.94	3.02	1.87	1.15	5.08	4.95	0.13
wa21	1.61	0.98	0.63	0.78	0.92	-0.14	1.19	1.11	0.08	2.66	0.89	1.77	1.53	0.64	0.89	1.46	0.88	0.58	2.02	1.43	0.59
wy02	1.56	0.89	0.67	1.13	0.50	0.63	1.57	0.87	0.70	1.04	0.79	0.25	3.13	2.07	1.06	1.95	0.72	1.23	0.52	0.36	0.16
wy08	0.97	1.31	-0.34	0.31	0.48	-0.17	0.67	1.06	-0.39	1.52	2.73	-1.21	1.70	1.81	-0.11	0.95	1.39	-0.44	0.67	0.38	0.29
wy99	2.08	1.30	0.78	0.92	0.95	-0.03	1.47	1.47	0.00	1.81	1.73	0.08	3.53	1.67	1.86	2.01	1.18	0.83	2.72	0.80	1.92

Table A.8 (continued).

Region Site	Annual Mean		January-February		March-April		May-June		July-August		September-October		November-December								
	Obs.	Diff.	Obs.	Diff.	Obs.	Diff.	Obs.	Diff.	Obs.	Diff.	Obs.	Diff.	Obs.	Diff.							
tx03	1.57	1.25	0.32	1.43	0.94	0.49	1.58	1.62	-0.04	2.61	1.44	1.17	0.94	1.28	-0.34	2.00	1.17	0.83	0.88	1.07	-0.19
tx10	0.70	0.94	-0.24	0.81	0.83	-0.02	0.93	1.12	-0.19	1.15	1.34	-0.19	0.53	0.87	-0.34	0.41	0.67	-0.26	0.38	0.81	-0.43
tx16	0.80	0.73	0.07	0.66	0.53	0.13	1.06	1.11	-0.05	1.34	1.22	0.12	0.63	0.53	0.10	0.40	0.41	-0.01	0.70	0.61	0.09
tx21	0.74	0.74	0.00	0.59	0.53	0.06	1.32	1.24	0.08	0.93	1.26	-0.33	0.86	0.52	0.34	0.28	0.42	-0.14	0.47	0.47	0.00
tx56	0.71	0.59	0.12	0.39	0.47	-0.08	1.08	1.27	-0.19	1.60	0.60	1.00	0.48	0.48	0.00	0.43	0.27	0.16	0.29	0.45	-0.16
wa14	0.50	0.43	0.07	0.30	0.40	-0.10	0.63	0.38	0.25	0.69	0.63	0.06	0.37	0.26	0.11	0.35	0.33	0.02	0.69	0.58	0.11
wa21	0.64	0.40	0.24	0.95	0.23	0.72	0.46	0.41	0.05	1.26	0.42	0.84	0.42	0.50	-0.08	0.37	0.42	-0.05	0.38	0.43	-0.05
wy02	0.38	0.22	0.16	0.15	0.09	0.06	0.23	0.15	0.08	0.13	0.21	-0.08	1.37	0.59	0.78	0.27	0.18	0.09	0.12	0.10	0.02
wy08	0.54	0.48	0.06	0.11	0.12	-0.01	0.13	0.23	-0.10	0.66	0.89	-0.23	1.50	0.99	0.51	0.55	0.51	0.04	0.26	0.16	0.10
wy99	0.55	0.38	0.17	0.21	0.23	-0.02	0.22	0.36	-0.14	0.39	0.67	-0.28	1.36	0.59	0.77	0.52	0.30	0.22	0.62	0.15	0.47

Table A.9 (continued).

Region Site	Annual Mean		January-February		March-April		May-June		July-August		September-October		November-December								
	Obs.	Est.	Obs.	Est.	Obs.	Est.	Obs.	Est.	Obs.	Est.	Obs.	Est.	Obs.	Est.							
tx03	29.88	18.91	10.97	49.13	16.44	32.69	32.00	22.63	9.37	45.21	18.55	26.66	21.08	13.18	7.90	18.15	17.09	1.06	13.70	25.55	-11.85
tx10	14.46	12.15	2.31	22.38	12.67	9.71	20.96	14.06	6.90	12.93	10.92	2.01	11.09	8.30	2.79	10.40	10.31	0.09	9.00	16.61	-7.61
tx16	8.87	6.65	2.22	8.48	4.91	3.57	10.38	9.42	0.96	8.43	7.63	0.80	12.39	6.69	5.70	5.93	6.23	-0.30	7.60	5.05	2.55
tx21	7.38	6.76	0.62	6.14	6.42	-0.28	7.57	8.82	-1.25	7.69	5.92	1.77	12.81	6.04	6.77	4.06	5.53	-1.47	6.03	7.84	-1.81
tx56	4.62	4.07	0.55	3.47	3.28	0.19	6.65	6.83	-0.18	7.43	4.46	2.97	3.32	3.31	0.01	4.18	3.01	1.17	2.66	3.52	-0.86
wa14	18.05	15.37	2.68	17.35	19.39	-2.04	26.03	13.95	12.08	15.14	15.51	-0.37	10.49	6.57	3.92	15.12	9.56	5.56	24.15	27.25	-3.10
wa21	7.89	4.84	3.05	4.48	4.73	-0.25	4.73	5.37	-0.64	12.93	3.95	8.98	6.25	2.68	3.57	7.71	4.50	3.21	11.21	7.82	3.39
wy02	3.77	1.47	2.30	5.42	0.85	4.57	3.31	1.79	1.52	1.68	1.21	0.47	3.34	2.42	0.92	7.50	1.25	6.25	1.39	1.30	0.09
wy08	1.79	2.45	-0.66	1.20	1.96	-0.76	1.46	2.56	-1.10	2.37	3.76	-1.39	2.85	2.82	0.03	1.73	2.21	-0.48	1.14	1.40	-0.26
wy99	2.99	1.44	1.55	2.93	1.92	1.01	2.17	1.70	0.47	1.79	1.52	0.27	3.94	1.19	2.75	2.15	1.07	1.08	4.97	1.24	3.73

Table A.10 (continued).

Region Site	Annual Mean			January-February			March-April			May-June			July-August			September-October			November-December		
	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.	Obs.	Est.	Diff.
tx03	32.50	20.92	11.58	51.05	17.94	33.11	36.07	23.84	12.23	51.70	20.15	31.55	21.86	17.13	4.73	19.40	18.86	0.54	14.93	27.63	-12.70
tx10	15.67	14.05	1.62	24.34	14.09	10.25	22.77	15.14	7.63	14.74	12.47	2.27	12.32	9.53	2.79	11.21	12.95	-1.74	8.62	20.09	-11.47
tx16	8.38	6.71	1.67	8.76	5.18	3.58	9.46	8.91	0.55	7.07	7.26	-0.19	11.71	7.45	4.26	5.36	6.67	-1.31	7.93	4.79	3.14
tx21	7.75	7.28	0.47	6.44	7.12	-0.68	7.95	8.99	-1.04	7.78	6.59	1.19	14.06	6.55	7.51	3.75	5.83	-2.08	6.53	8.61	-2.08
tx56	4.33	4.57	-0.24	2.80	3.68	-0.88	5.96	7.26	-1.30	7.60	4.98	2.62	3.34	3.80	-0.46	4.15	3.72	0.43	2.15	4.00	-1.85
wa14	20.14	16.84	3.30	17.20	23.51	-6.31	31.17	16.83	14.34	17.83	15.93	1.90	11.32	6.34	4.98	16.30	10.00	6.30	27.01	28.43	-1.42
wa21	8.14	5.28	2.86	5.19	5.49	-0.30	4.97	5.81	-0.84	11.78	4.00	7.78	6.86	2.58	4.28	7.82	5.11	2.71	12.21	8.70	3.51
wy02	1.63	1.32	0.31	1.69	0.98	0.71	1.29	0.99	0.30	1.37	1.07	0.30	2.97	2.91	0.06	1.48	1.05	0.43	0.95	0.91	0.04
wy08	1.95	2.14	-0.19	1.41	1.62	-0.21	1.26	1.81	-0.55	2.27	2.80	-0.53	3.42	2.85	0.57	2.23	2.07	0.16	1.08	1.70	-0.62
wy99	2.32	1.58	0.74	1.82	1.54	0.28	1.43	1.46	-0.03	1.63	1.79	-0.16	3.46	2.12	1.34	1.80	1.39	0.41	3.80	1.19	2.61

KY03 - Mackville

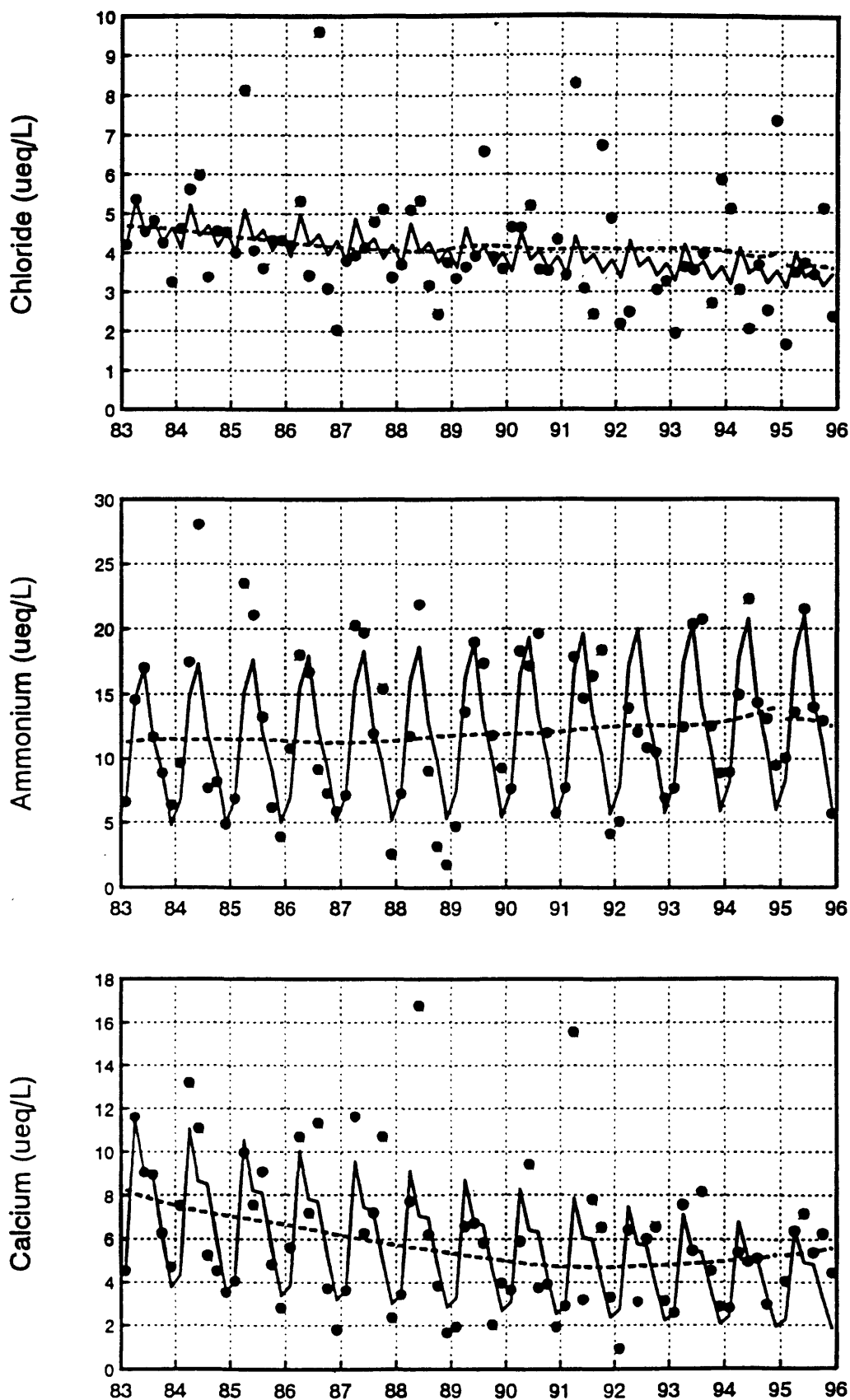


Figure A.1. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for Cl^- , NH_4^+ and Ca^{2+} at Mackville, KY.

KY03 - Mackville

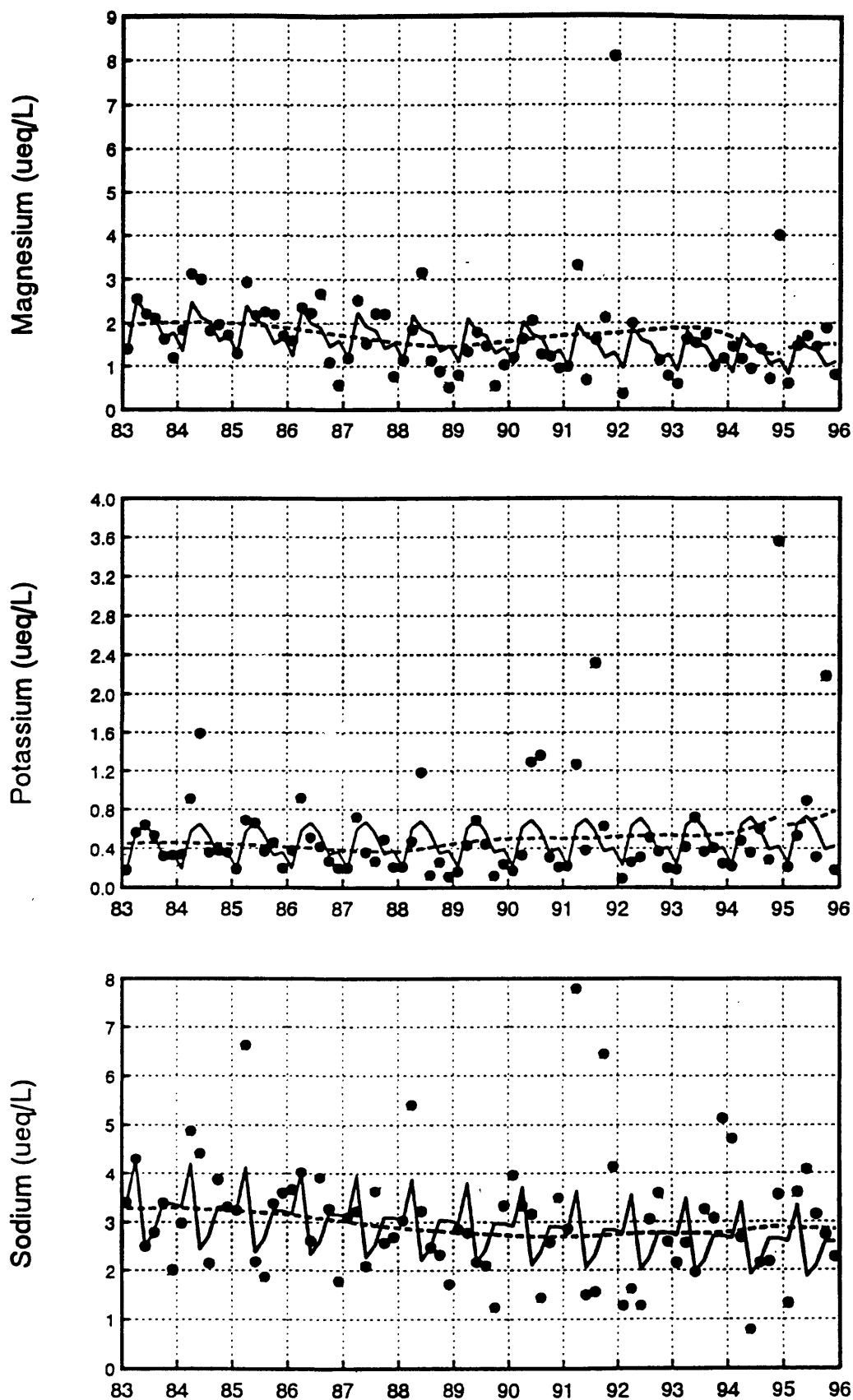


Figure A.2. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for Mg^{2+} , K^+ and Na^+ at Mackville, KY.

IL63 - Dixon Springs Ag. Center

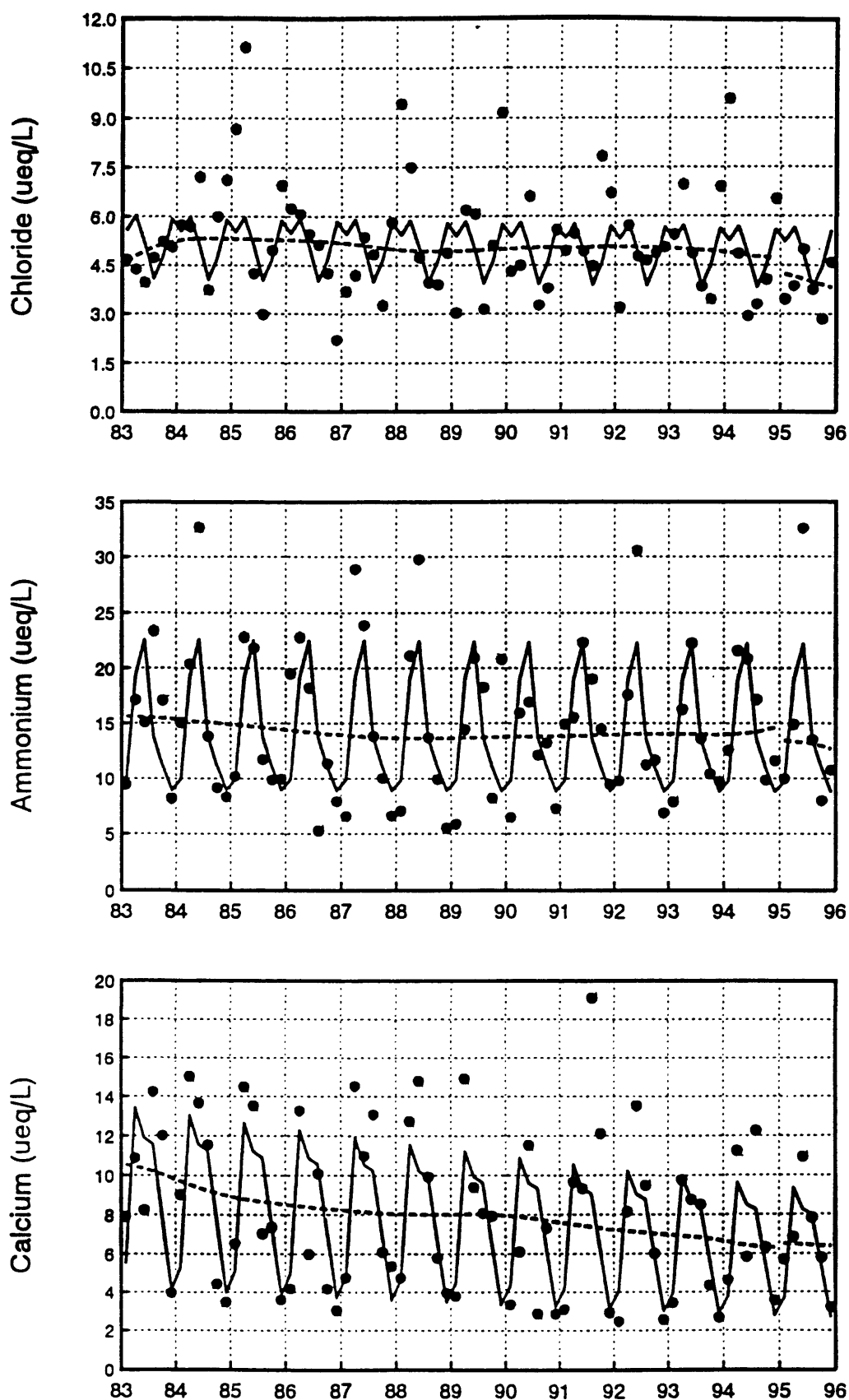


Figure A.3. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for Cl^- , NH_4^+ and Ca^{2+} at Dixon Springs Agricultural Center, IL.

IL63 - Dixon Springs Ag. Center

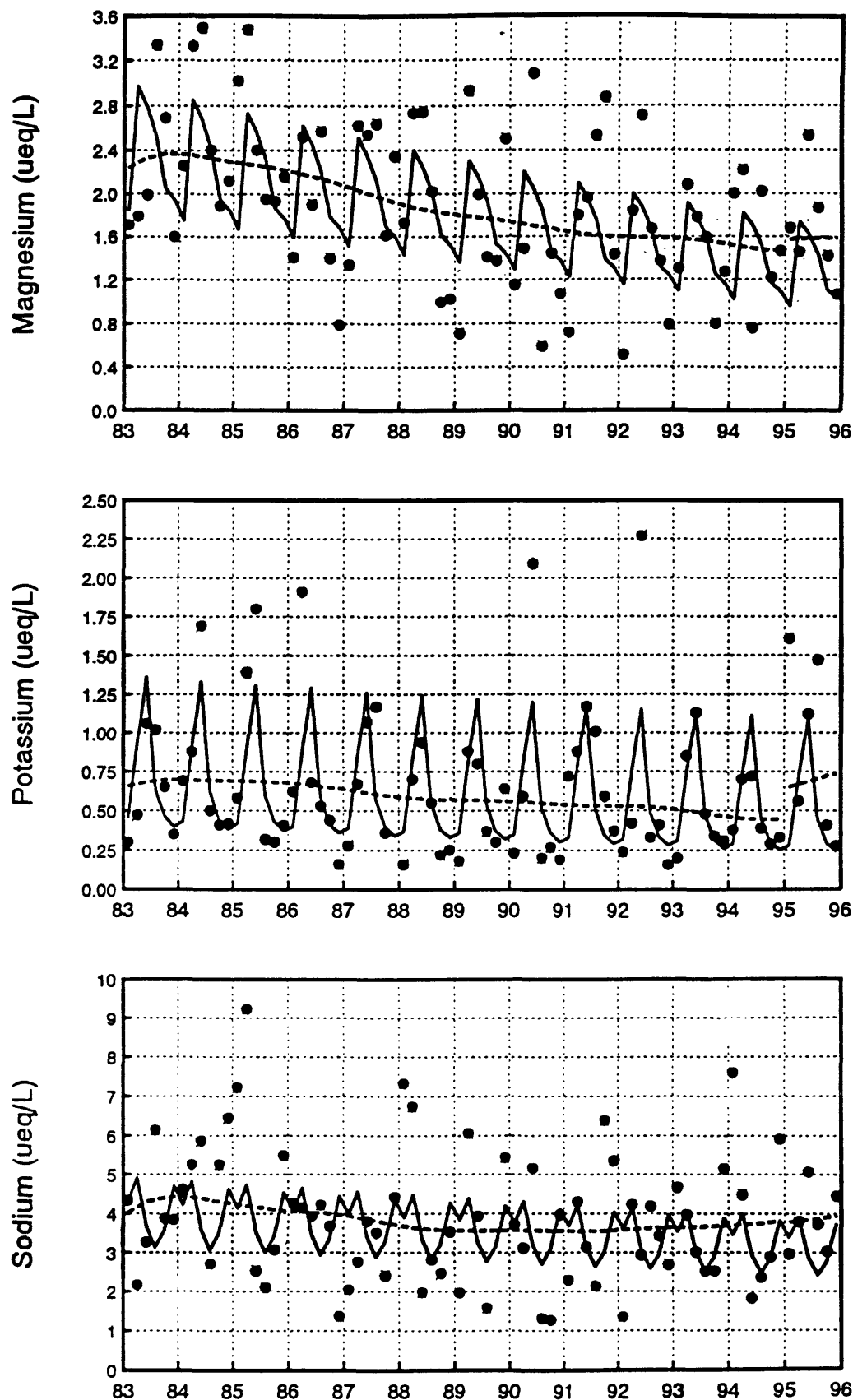


Figure A.4. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for Mg^{2+} , K^{+} and Na^{+} at Dixon Springs Agricultural Center, IL.

NC36 - Jordan Creek

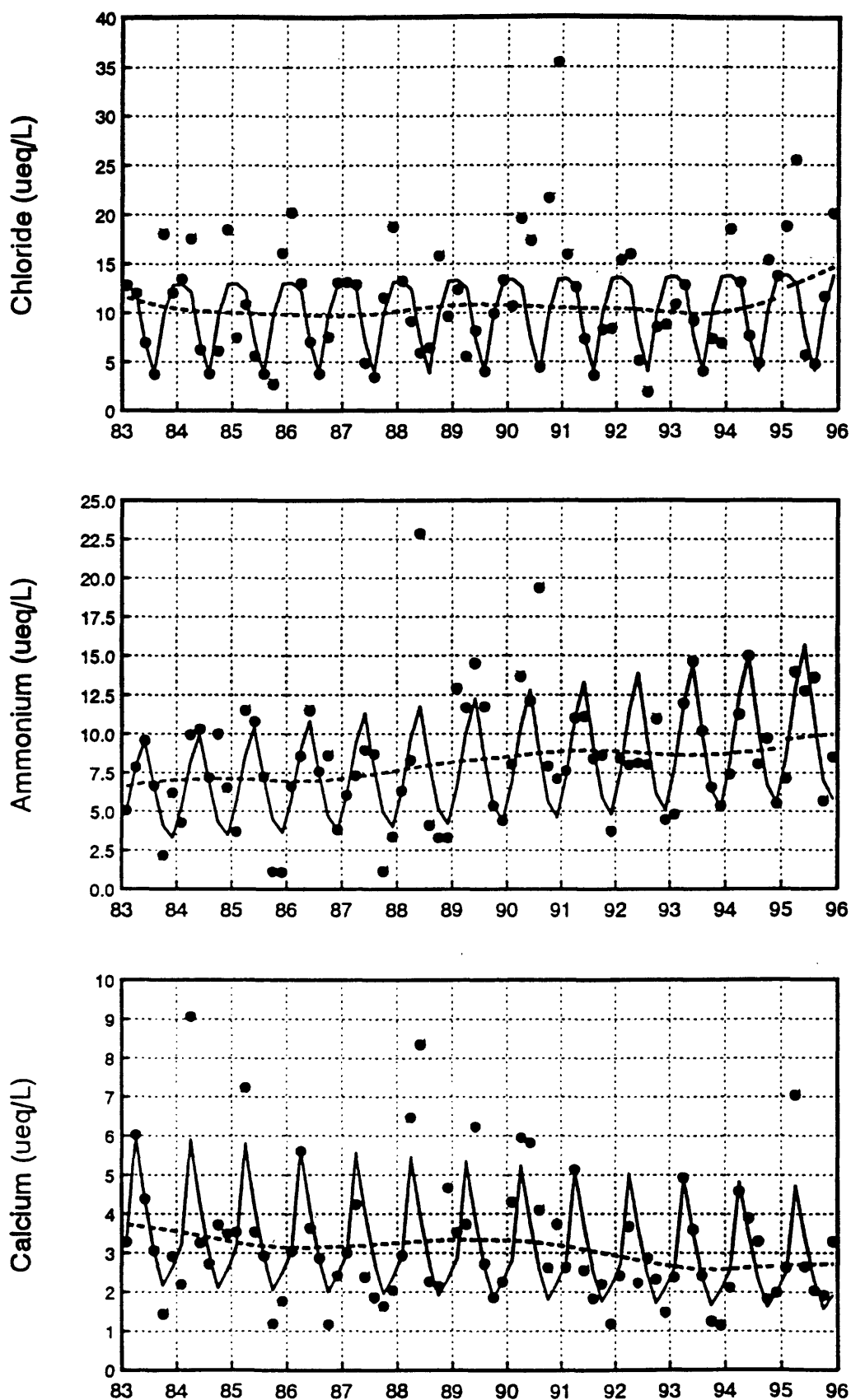


Figure A.5. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for Cl^- , NH_4^+ and Ca^{2+} at Jordan Creek, NC.

NC36 - Jordan Creek

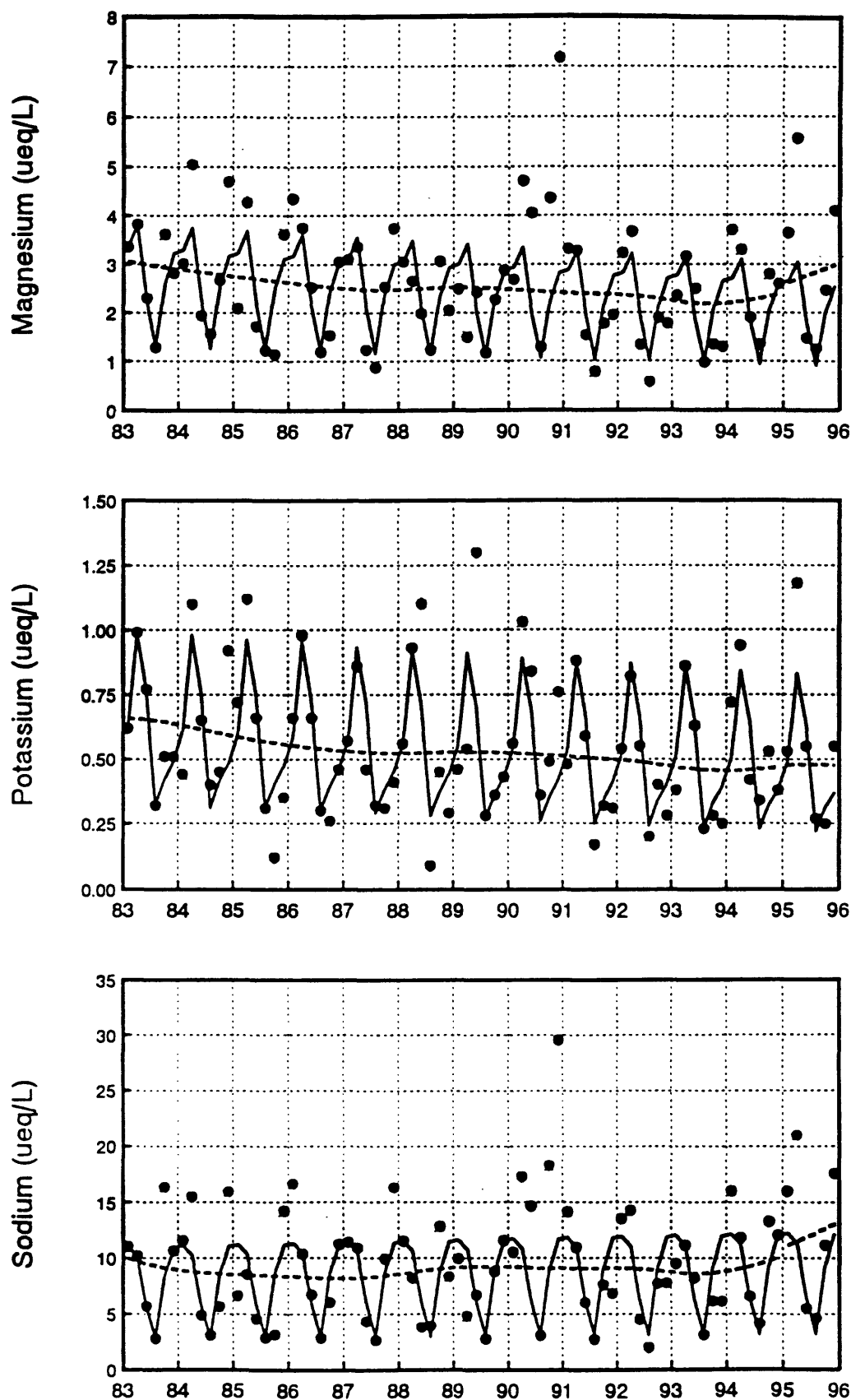


Figure A.6. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for Mg^{2+} , K^+ and Na^+ at Jordan Creek, NC.

VT01 - Bennington

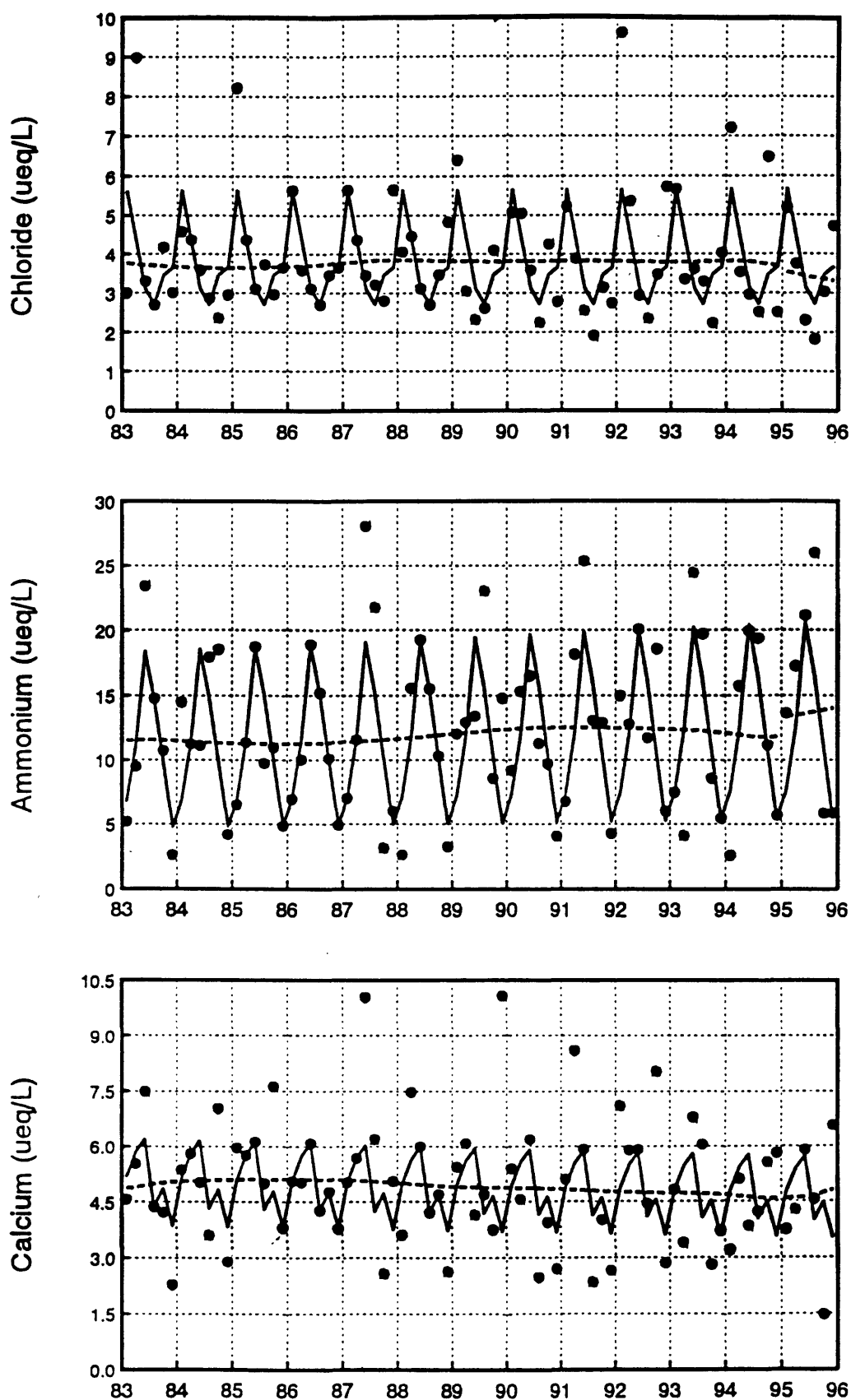


Figure A.7. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for Cl^- , NH_4^+ and Ca^{2+} at Bennington, VT.

VT01 - Bennington

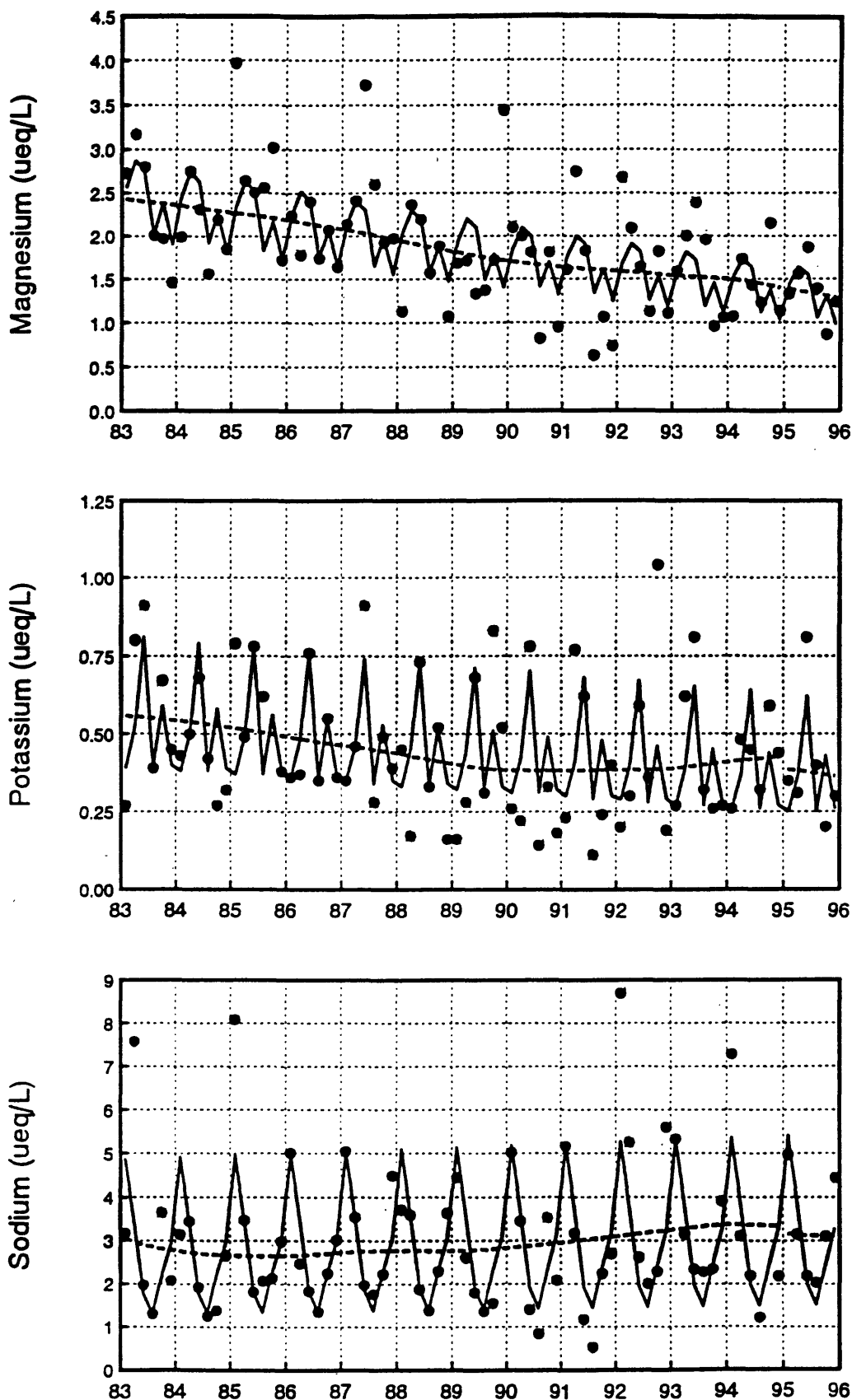


Figure A.8. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for Mg^{2+} , K^+ and Na^+ at Bennington, VT.

IN34 - Indiana Dunes Nat'l Lakeshore

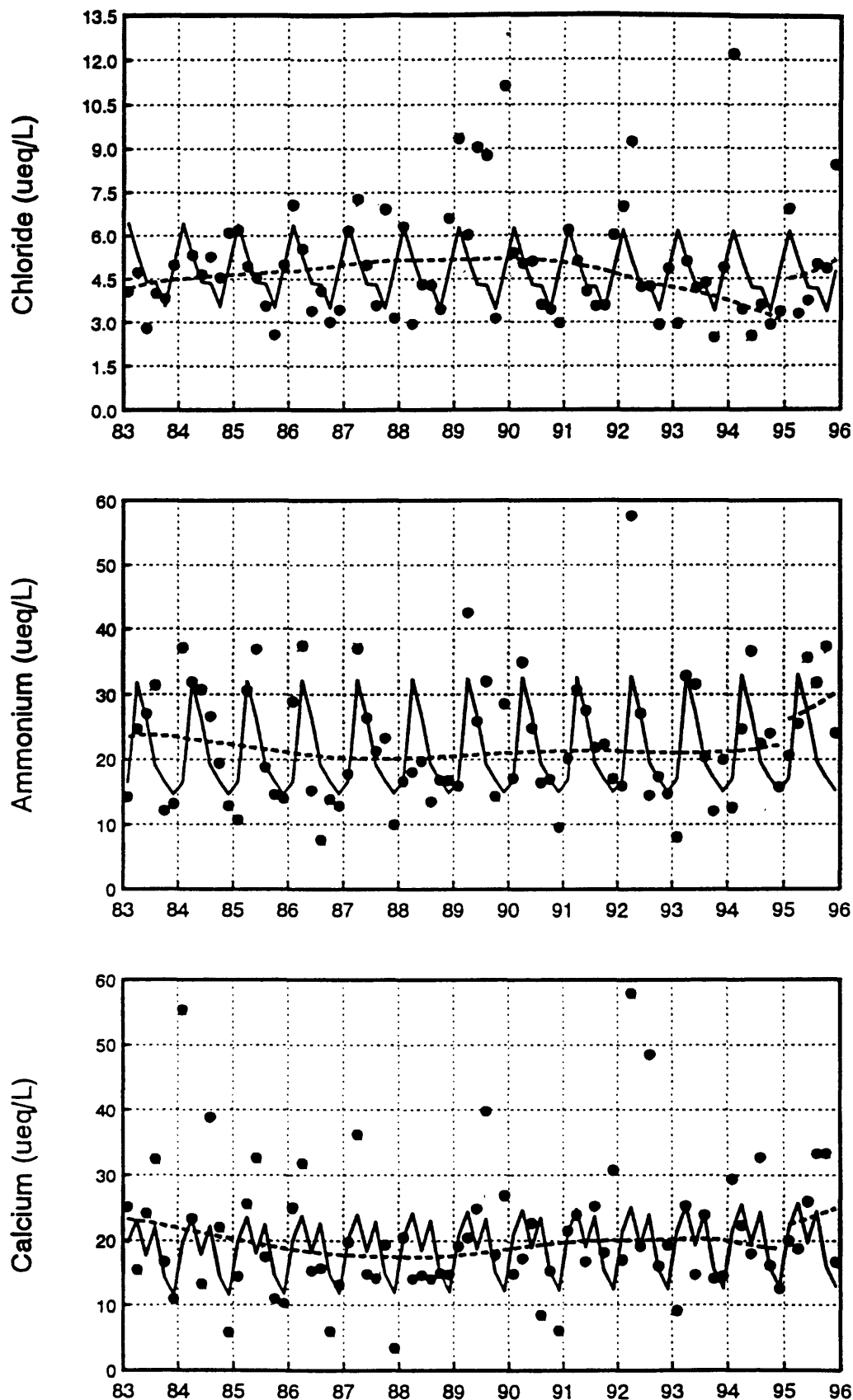


Figure A.9. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for Cl^- , NH_4^+ and Ca^{2+} at Indiana Dunes Nat'l Lakeshore, IN.

IN34 - Indiana Dunes Nat'l Lakeshore

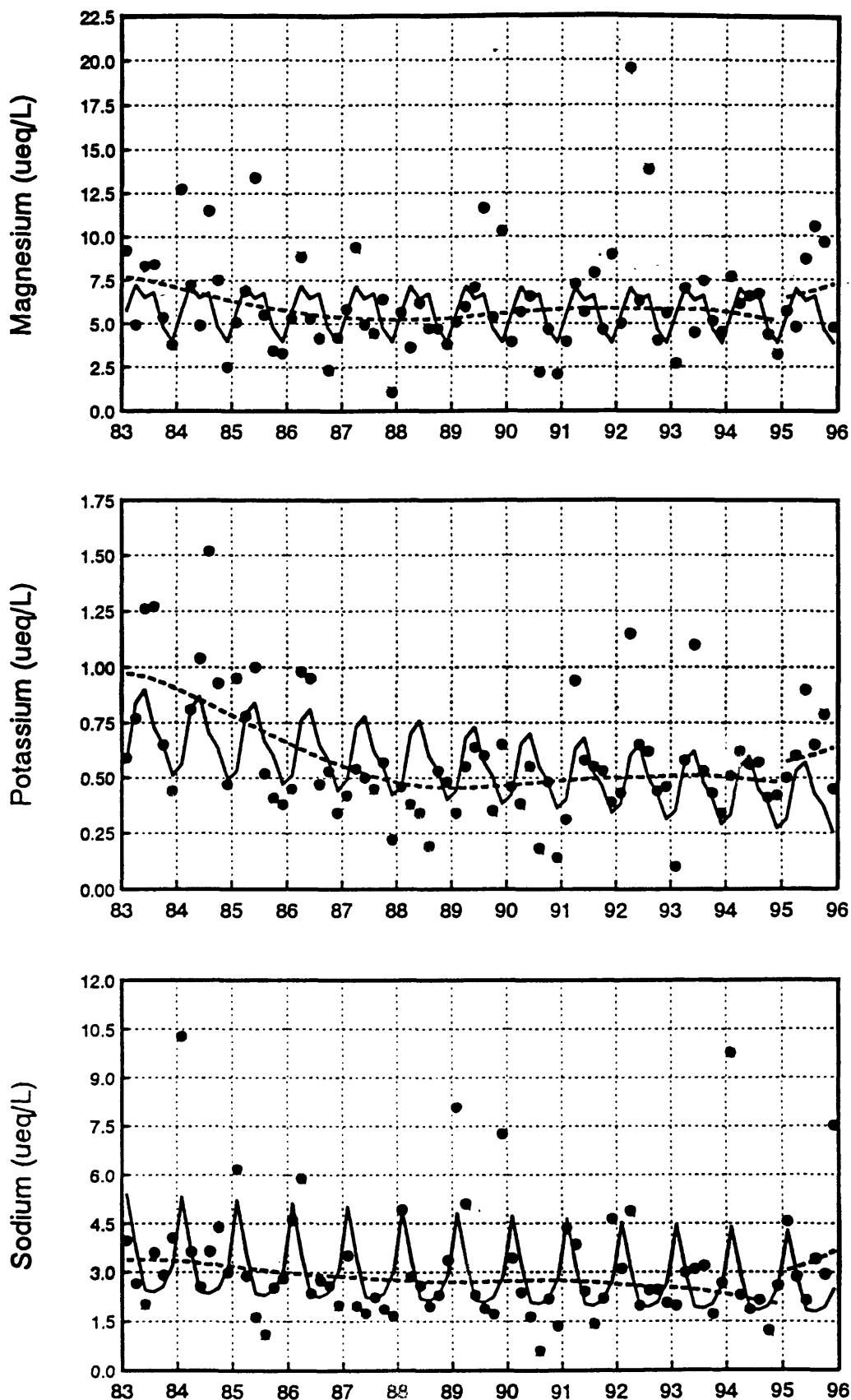


Figure A.10. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for Mg^{2+} , K^{+} and Na^{+} at Indiana Dunes Nat'l Lakeshore, IN.

MA08 - Quabbin Reservoir

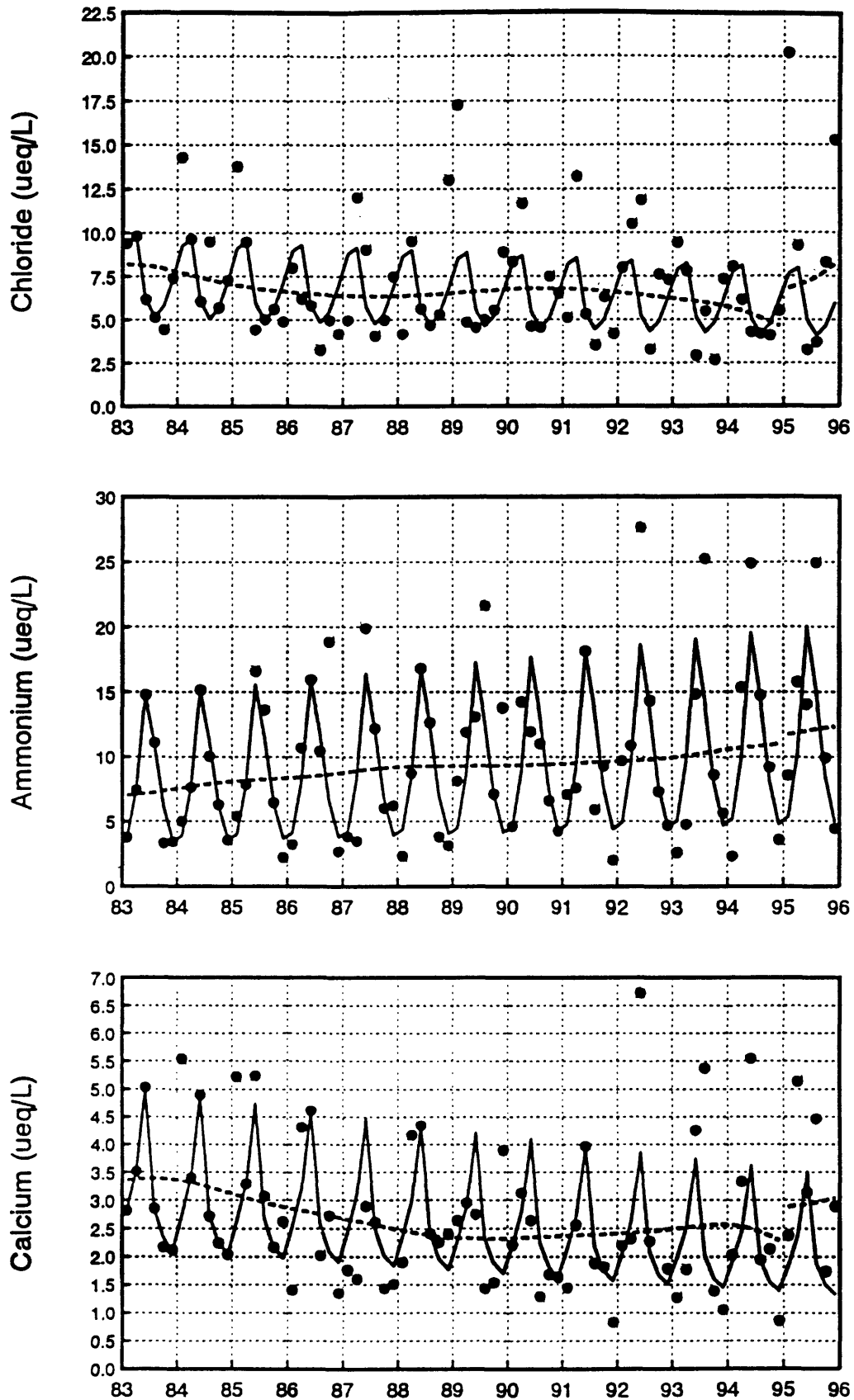


Figure A.11. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for Cl^- , NH_4^+ and Ca^{2+} at Quabbin Reservoir, MA.

MA08 - Quabbin Reservoir

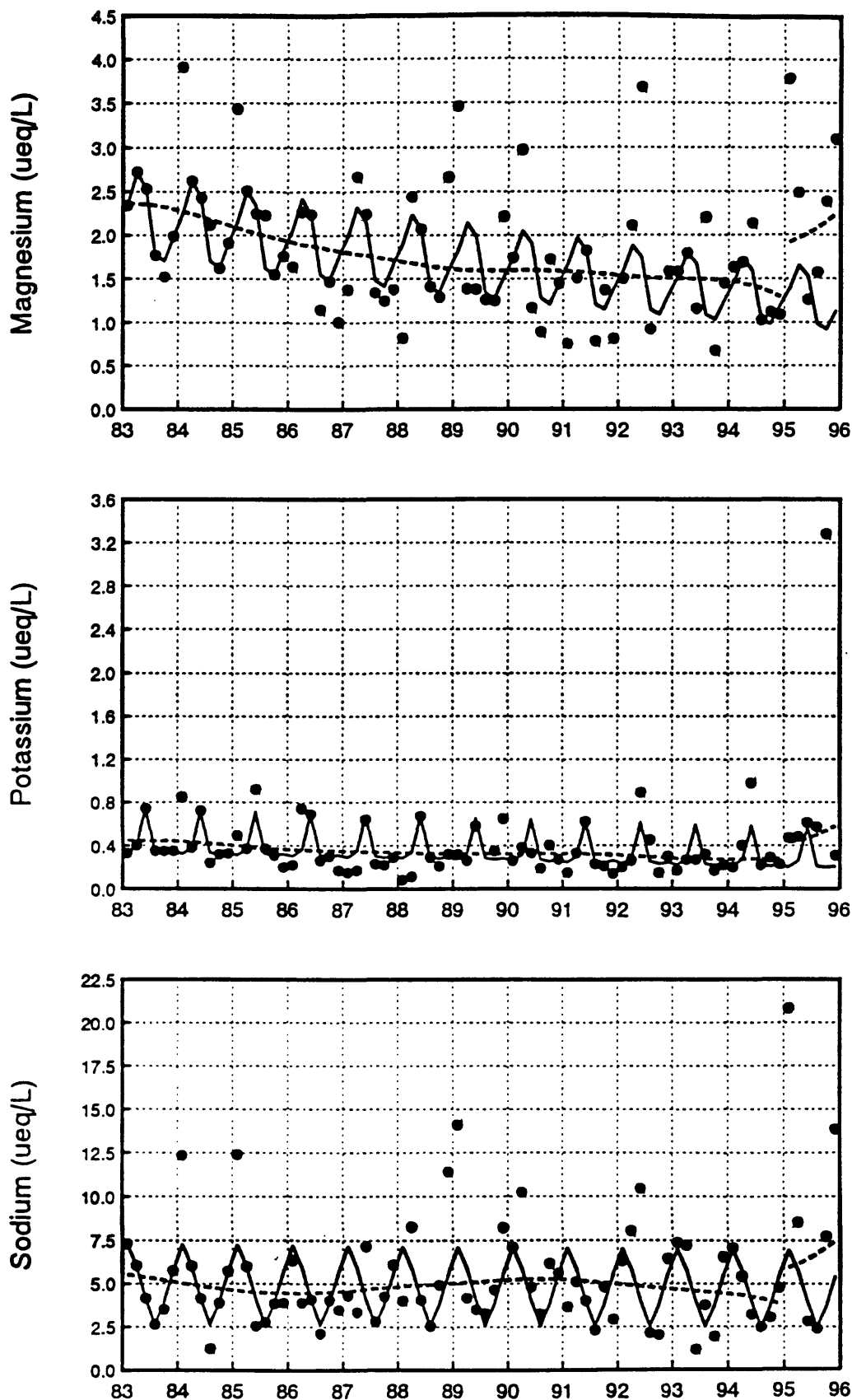


Figure A.12. Linear least-squares trend models (solid line) of observed bi-monthly mean concentrations (solid circles) with LOWESS regression (dashed line) curves for Mg^{2+} , K^{+} and Na^{+} at Quabbin Reservoir, MA.