

APPENDIX A

Trends in Precipitation Chemistry at West Point, NY

1. INTRODUCTION

Weekly composite samples of precipitation have been collected, as part of the National Acid Deposition Program, at West Point, NY beginning in June, 1979 at a site designated as NY 51 . This site is near the west shore of the Hudson River about 80 km north of NYC, and within a few km of Black Rock Forest in the Hudson Highlands. Collectors are open to the atmosphere only during precipitation episodes, and otherwise remain covered. Flux data derived from chemical analysis of these samples are often referred to as representing "wet-only" deposition.

A new site (NY 99), approximately one km from NY 51, was selected in September 1983, based on a set of criteria established for the approximately 200 NADP stations, and collection at the first location was terminated at the end of September 1984, providing an overlap at the two sites of 13 months. Data from both sites are compared here, and combined into a single time-series of monthly values, using data from the initial collection site (NY 51) through the end of August 1993, and the second site (NY 99) beginning in September 1993 to generate a continuous set of monthly precipitation chemistry values for the period 6/79 through 2/96.

These data can provide information on temporal variations in amounts of dissolved ions in precipitation at a location within the densely populated NE USA, near the northern fringe of the New York City metropolitan region. They also permit estimates of wet deposition of a range of ions to the Hudson Highlands, an area predominantly covered by second-growth deciduous forest that has received acidic precipitation for many decades.

2. METHODS AND DATA QUALITY

The data discussed here were obtained from the NADP world wide web site as monthly amount-weighted values in mass units, and then converted to equivalents units. Although there are a number of individual monthly ion concentration values that appear to have analytical errors, all of the monthly data on the web site were used for initial examination. Monthly concentrations of various ions as a function of concentrations of other ions were assessed for the entire series of 200 months, and as a function of time.

Comparison of monthly concentrations for the overlap period of September 1983 through September 1994 at NY 99 and NY 51 provides some indication of the combined effects of local site collection efficiency differences and analytical quality. Scatter plots of monthly concentrations at NY 99 vs NY 51 for chloride, sulfate, nitrate, sodium, potassium, magnesium and calcium ions suggest that uncertainties are generally within 5 to 10% for most ion concentrations, but that individual months may have substantially larger cumulative sampling and analytical errors (Figs 1A-1F).

Chloride (Fig 1A) and sodium (Fig 1D) concentrations were quite similar at both sites for all months except January 1984, when NY 99 averaged higher in both ions, suggesting a systematic site collection difference rather than laboratory analytical error. Correlation coefficients for both sulfate (Fig 1B) and magnesium (Fig 1E) at the two sites were slightly lower than for sodium and chloride, but still above $r = 0.9$. Nitrate monthly values (Fig 1C) were quite similar at the two sites except for January 1984, where NY 99 was appreciable higher, as for sodium and chloride. Calcium monthly concentrations at the two sites were less consistent, with November 1983 (higher at NY 51) and March 1984 (higher at NY 99) differing substantially. Potassium concentrations were much greater at NY 99 for January and June 1984 (not shown) and ammonia concentrations much greater at NY 99 for September 1994 (not shown).

Hydrogen ion concentrations at the two sites were similar for all 13 months, with a correlation coefficient (r) = 0.87 (Fig 2A). Large month to month changes in hydrogen ion (Fig 2B) and sulfate (Fig 2C) concentrations in precipitation were observed simultaneously at both sites during this 13 month period, with no consistent differences in these two ions that could be readily attributed to local collection site characteristics.

There were significant differences in monthly amount-weighted values at the two sites for about 10% of concentrations for some ion pairs, which may reflect cumulative sample collection contamination and laboratory analytical errors rather than local site collection efficiencies. The general agreement of values at the two sites (Figs 1A-1E, 2A-2C) appear sufficient to treat the data sets as a single combined series beginning in June 1979.

3. MARINE AEROSOL CONTRIBUTION TO WEST POINT PRECIPITATION

The West Point sample collection sites experience highest frequency of winds from the NW and SW (continental interior), but are less than 100 km from Long Island Sound and the Atlantic Ocean off NY and NJ, and thus readily accessible to marine air during some precipitation episodes,

especially during intense low pressure coastal storms with easterly winds. The ions for which dominant marine aerosol contributions are most likely in West Point precipitation are chloride, sodium and magnesium. Any of these three would be plausible candidates to consider in developing a first-order approach for estimating of marine aerosol contributions in a given precipitation sample [Keene et al, 1986]. Scatter plots of chloride vs sodium (Fig 2D), magnesium vs chloride (Fig 2E) and magnesium vs sodium (Fig 2F) all show a tendency for covariation of these three ions at higher concentrations, which is consistent with important marine contributions to all three ions. However, magnesium also was high in an appreciable number of months when both chloride and sodium were relatively low, suggesting an important contribution of continental dust as well as marine aerosols for magnesium in West Point precipitation. There were a limited number of months for which either chloride or sodium deviated from the general pattern of covariation, but far fewer than for magnesium relative to either of the highest abundance sea salt ions.

A scatter plot of magnesium to sodium ratios vs sodium concentrations (Fig 3A) shows a large number of months with high ratios at low sodium concentrations, and nearly all months had ratios well above that for sea salt (0.227) [Wilson, 1975]. A similar pattern is evident for a scatter plot of chloride to sodium ratios vs sodium concentrations (Fig 3B), with high ratios at low sodium concentrations. Although there were a number of values with ratios below that for sea water (1.16), a large fraction of the months had precipitation chloride to sodium ratios well excess of the sea water ratio.

If chloride were assumed to be derived exclusively from marine aerosols, then the concentration of chloride for each monthly precipitation composite can be multiplied by the ratio of any other ion (eg. sodium) to chloride in sea water to derive an estimate of the marine contribution to sodium. The resultant marine sodium contribution can then be subtracted from the measured sodium concentration and the difference reported as "excess" sodium. In the interior of continents, there is usually appreciable excess sodium (ie. non marine) in precipitation, using the above assumptions [Junge and Werby, 1958; Berner and Berner, 1996]. The source of the extra sodium in continental interior precipitation is thought to be primarily from atmospheric dust, derived especially from soils in semi-arid regions. The monthly values of excess sodium in West Point precipitation have appreciable scatter near the beginning of the record, especially during the first two years, with most of the largest departures having positive excess values (Fig 3C), with a maximum sodium excess in May 1980 of about 33 uEq/L. A linear

least squares fit to the temporal trend indicates a small negative slope as a function of time, suggesting a cumulative decrease in excess sodium of about 5 uEq/l over a 16 year period.

The range of excess sodium values was then truncated at ± 12 uEq/L (Fig 3D) to facilitate examination of the temporal pattern of departures from the marine ratio exclusive of the four monthly values (11/79, 5/80, 6/80, 3/81) with greatest excess sodium departures (positive or negative). There appear to be several distinct patterns of sodium excess at West Point since 1979. After the first two years with several months having large positive excess sodium values, there was a period of several years with no systematic deviation from the marine ratio, followed by about 12 years with consistently negative excess sodium values. This latter shift in about 1983 approximately coincides with the shift of sample collection site from NY 51 to NY 99.

The consistent pattern of negative sodium excess values beginning in about 1983 suggests that sodium probably provides a better indicator of marine aerosol contribution to precipitation at West Point than does chloride. Using sodium as the reference ion for sea salt (sea salt ratio of chloride to sodium = 1.16), excess chloride values at West Point have been predominately positive since 1983. Excess magnesium values (with sodium as the sea salt reference ion) have been nearly all positive, except for the first year of operation of site NY 51 (Fig 4A). There appears to have been a slight decrease in mean excess magnesium (about 1.6 uEq/L) over the 16 year period. All of the excess calcium values have been positive (sea salt ratio of calcium to sodium = 0.0439), including the first few years of operation, but appear to have declined by an average of about 3.6 uEq/L since 1979 (Fig 4B). Excess potassium concentrations have generally been quite small and positive (sea salt ratio of potassium to sodium = 0.0218), but there have been a few months with large positive departures during recent years (Fig 4C).

Based on the above discussion, the choice of sodium as the preferred reference ion for marine aerosol contributions to precipitation chemistry at West Point appears to be quite clear, and is consistent with that choice for coastal and marine precipitation chemistry in a number of studies at other locations. In subsequent discussions here involving estimates of excess ion concentrations, sodium is used as the indicator of marine contribution.

4. SOURCES OF ACIDITY IN WEST POINT PRECIPITATION

Hydrogen ion concentrations in monthly precipitation at West Point have high correlations in scatter plots with excess sulfate (Fig 5A, $r =$

0.93) and nitrate (Fig 5B, $r = 0.87$), as would be expected for precipitation in the NE USA where hydrogen ion is usually the most abundant cation [Likens et al. 1984]. Nitrate is also strongly correlated with sulfate (Fig 5C, $r = 0.83$), with an appreciable number of monthly values of nitrate to sulfate well above the ratio of 0.48 from the linear least squares fit of nitrate to sulfate for all of the data. Considering all values beginning in June 1979 as a single one pool, nitrate concentrations have been about half of sulfate (equivalents units). Hydrogen ion concentrations have averaged about 67% of the sum of sulfate and nitrate (Fig 5D), indicating that about 33% of the cationic charge to balance these anions derived from strong acids is provided by base cations rather than H^+ .

A scatter plot of ammonia vs nitrate indicates strong positive correlation of these two ions (Fig 5E, $r = 0.78$), almost as high as for nitrate vs sulfate. Since the ratio of ammonia to nitrate in precipitation is about 0.4, a significant portion of the positive charge balance in addition to hydrogen ion appears to be provided by ammonia.

Chloride and sulfate are not correlated (Fig 5F), as would be expected given their very different dominant sources (marine vs pollution emissions). A plot of sulfate vs chloride (or sodium) appears to provide a first order way to resolve three general source categories for West Point precipitation: (1) marine (high Cl, low SO_4), (2) polluted continental (low Cl, high SO_4), (3) "clean" continental (low Cl, low SO_4).

5. TEMPORAL TRENDS IN ION CONCENTRATIONS AT WEST POINT

Temporal trends based on linear least square fits of monthly concentrations against time since 1979 for hydrogen ion (Fig 6A), sulfate (Fig 6B) and nitrate (Fig 6C) suggest decreases in mean concentrations of 15 $\mu\text{Eq/L}$, 19 $\mu\text{Eq/L}$ and 4.4 $\mu\text{Eq/L}$, respectively. This indicates a decrease in mean hydrogen ion concentration of about 20% over this 16 year period, caused primarily by decreases in acid sulfate components in the atmosphere due to pollution emission controls. The change in mean hydrogen ion concentration in West Point precipitation from 65.5 $\mu\text{Eq/L}$ to 50.7 $\mu\text{Eq/L}$ represents an increase in pH of about 0.11 units (4.18 to 4.29) since 1979.

The decrease in nitrate has been much smaller (if significantly different from zero) than for sulfate. The increase in relative importance of nitrate compared to excess sulfate as a source of acidity can be seen in a plot of nitrate to sulfate ratios against time (Fig 7A). The mean value of nitrate to excess sulfate appears to have increased from about 0.5 to about 0.7 since 1979. Over the same period excess chloride has increased from -1.1 to +5.8 (Fig 7B). If all departures of excess chloride from the

sea water ratio of greater ± 12 uEq/L are excluded (Fig 7C), there appears to be little trend with time of excess chloride since about 1983 when sample collection at NY 99 began. The mean value of excess chloride over the past 12 years has been on the order of 4 uEq/L (Fig 7C), about 5% of the sum of excess sulfate plus nitrate (Fig 8A).

Concentrations of ammonia appear to have increased by about 2 uEq/L (about 20%) over the 16 years from 1979 (Fig 8B), resulting in a substantial increase in the ratio of ammonia to nitrate (Fig 8C). The concentration of fixed nitrogen in precipitation at West Point currently averages about one-third ammonia, and two-thirds nitrate.

6. POTENTIAL CAUSES OF EXCESS CHLORIDE IN WEST POINT PRECIPITATION

Chloride concentrations in West Point precipitation probably primarily reflect contributions from marine aerosols and appear to have experienced little systematic temporal trend since 1979 (Fig 9A), although there have been large excursions in concentration from one month to the next. One plausible source of excess chloride in precipitation could be reactions of cloud and rain drops with hydrochloric acid vapor. The HCl vapor could be generated by reactions of marine aerosols with strong acids derived by pollution emissions (sulfur dioxide and nitrogen oxides). If this were occurring primarily in regional-scale plumes of acidic gas emissions, there would potentially be a positive correlation in magnitudes of excess chloride with excess sulfate plus nitrate in precipitation. A scatter plot of excess chloride vs the sum of excess sulfate plus nitrate (Fig 9B) provides evidence of a limited number of monthly values which may reflect analytical errors in one or more of the ions used to generate Figs 9B (Na, Cl, SO₄, NO₃). A large fraction of the excess chloride concentrations, however, are < 10 uEq/L. If excess chloride values are restricted to ± 12 uEq/L to exclude the few samples with large departures in excess chloride (positive or negative), there does not appear to be any obvious correlation with excess sulfate plus nitrate (Fig 9C). This suggests that if excess Cl in precipitation at West Point is primarily the result of HCl generated by sulfuric and nitric acid reactions with marine aerosols, the concentration of this gas may be far more uniform in the regional atmosphere than sulfate and nitrate aerosols.

7. CONCLUSIONS

- 1) Monthly amount-weighted concentrations of most ions in precipitation at West Point from two separate collection sites separated by about 1 km (NY 51, NY 99) are sufficiently consistent during 13 months of overlapping

samples (September 1983 - September 1984) to justify construction of a single combined series of data beginning in June 1979.

- 2) Sodium ion is preferred over chloride or magnesium as indicative of marine aerosol contributions to precipitation at West Point.
- 3) Sulfate and hydrogen ion have both declined appreciable (30% and 20%, respectively) at this location since 1979, with a mean pH increase from 4.18 to 4.29.
- 4) Nitrate and sulfate concentrations are strongly correlated, with ratios of nitrate to sulfate (in equivalents units) now averaging about 0.7.
- 5) Ammonia and nitrate concentrations are strongly correlated throughout the period since 1979, with ammonia now accounting for about one third of total fixed nitrogen in West Point precipitation.
- 6) Nitrate concentrations have decreased slightly (14%); while ammonia concentrations have increased by about 20% since 1979.
- 7) Excess chloride concentrations have been positive at West Point since 1983, averaging about 4 $\mu\text{Eq/L}$, with no consistent temporal trend or covariation with excess sulfate plus nitrate.
- 8) Average excess chloride since 1983 has been about one-third of average total chloride concentrations in precipitation at West Point.

8. REFERENCES

Berner, E.K. and R.A. Berner, Global Environment: Water, Air and Geochemical Cycles, Prentice Hall, Upper Saddle River, NY, 376 pp, 1996.

Junge, C.E. and R.T. Werby, The concentrations of chloride, sodium, potassium, calcium and sulfate in rainwater over the United States, J. Meteorol. 15, 421, 1958.

Keene, W.C., A.A.P. Pszenny, J.N. Galloway and M.E. Hawley, Sea-salt corrections and interpretation of constituent ratios in marine precipitation, J. Geophys. Res. 91, 6647-6658, 1986.

Likens, G.E., F.H. Bormann, R.S. Pierce, J.S. Eaton and R.E. Munn, Long-term

trends in precipitation chemistry at Hubbard Brook, New Hampshire, Atmos. Environ. 18, 2641-2647, 1984.

Wilson, T.R.S., Salinity and the major elements of sea water, in Chemical Oceanography, Vol. 1, 2nd ed, edited by J.P. Riley and G. Skirrow, pp. 365-413, Academic, Orlando, FL, 1975.

FIGURE CAPTIONS (Appendix)

1. Scatter plots of monthly amount-weighted precipitation concentrations (micro equivalents per L) for two NADP collections sites (NY 51, NY 99) located approximately one km apart at West Point, NY. Values represent precipitation from Sep '93 - Sep '84: A) Cl, B) SO₄, C) NO₃, D) Na, E) Mg, F) Ca.

2. A) Scatter plot of monthly hydrogen ion concentrations in precipitation for NADP NY 99 vs NY 51. B) Monthly H⁺ concentration at two West Point NADP sites as a function of time for overlap period of 13 months. C) Monthly SO₄ concentration at two West Point NADP sites as a function of time for overlap period of 13 months. D) Linear least-squares fit of monthly Cl vs Na since Jun '79. E) Linear least-squares fit of monthly Mg vs Cl since Jun '79. D) Linear least-squares fit of monthly Mg vs Na since Jun '79.

3) A) Monthly West Point precipitation Mg/Na vs Na since Jun '79. B) Monthly West Point precipitation Cl/Na vs Na since Jun '79. C) Monthly excess Na (assuming Cl exclusively from marine aerosols) vs time since Jun '79; linear least squares fit to all data points. D) Monthly excess Na vs time since Jun '79, excluding four months of data for which deviation from sea salt ratio was > ±12 uEq/L.

4) A) Monthly excess Mg (assuming Na exclusively from marine aerosols) vs time since Jun '79; solid line indicates linear least squares fit to all data points. B) Monthly excess Ca (assuming Na exclusively from marine aerosols) vs time since Jun '79; line indicates linear least squares fit to all data points. C) Monthly excess K (assuming Na exclusively from marine aerosols) vs time since Jun '79.

5) Scatter plots of monthly West Point precipitation since Jun '79: A) H⁺ vs excess SO₄, B) H⁺ vs NO₃, C) NO₃ vs SO₄, D) H⁺ vs [SO₄ + NO₃], E) NY4 vs NO₃, F) SO₄ vs Cl.

6) A) Linear least squares fit of H^+ vs time at West Point since Jun '79.
B) Linear least squares fit of SO_4 vs time at West Point since Jun '79. C)
Linear least squares fit of NO_3 vs time at West Point since Jun '79.

7) A) Linear least squares fit of ratio of NO_3 to excess SO_4 vs time at
West Point since Jun '79. B) Linear least squares fit of excess Cl vs time
for all months at West Point since Jun '79. C) Excess Cl vs time at West
Point since Jun '79, excluding four months of data for which deviation
from sea salt ratio was $>\pm 12 \mu Eq/L$.

8) A) Linear least squares fit of excess $SO_4 + NO_3$ vs time at West Point
since Jun '79. B) Linear least squares fit of NH_4 vs time at West Point
since Jun '79. C) Linear least squares fit of ratio of NH_4 to NO_3 vs time
at West Point since Jun '79.

9) A) Linear least squares fit of Cl vs time at West Point since Jun '79.
B) Excess Cl vs time at West Point since Jun '79. C) Excess Cl vs time at
West Point since Jun '79, excluding three months of data for which excess
 $Cl > \pm 12 \mu Eq/L$.

Fig. 1

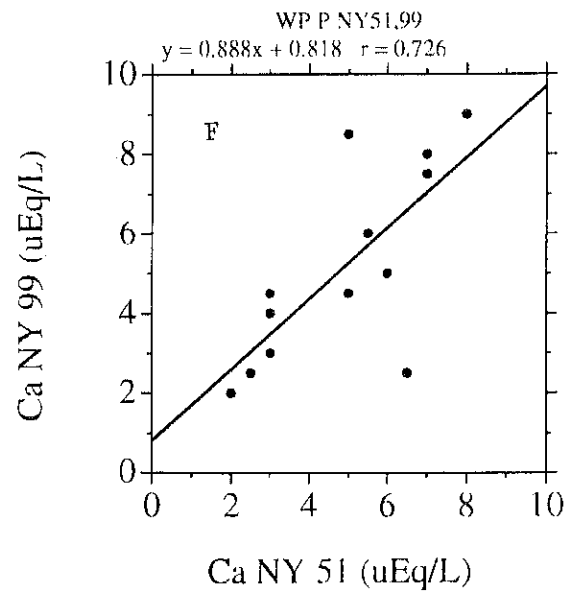
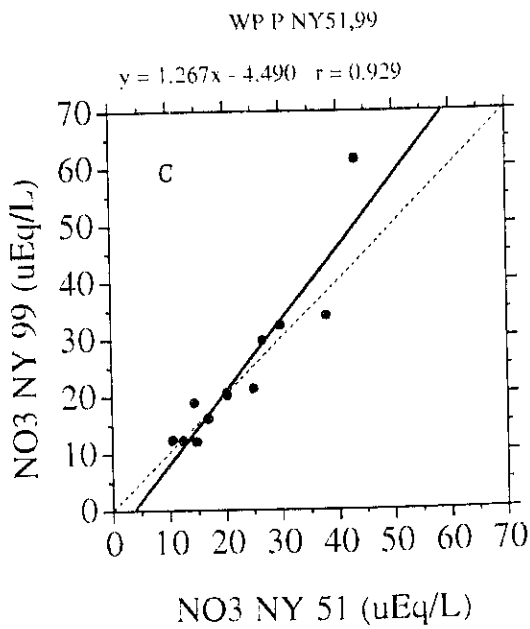
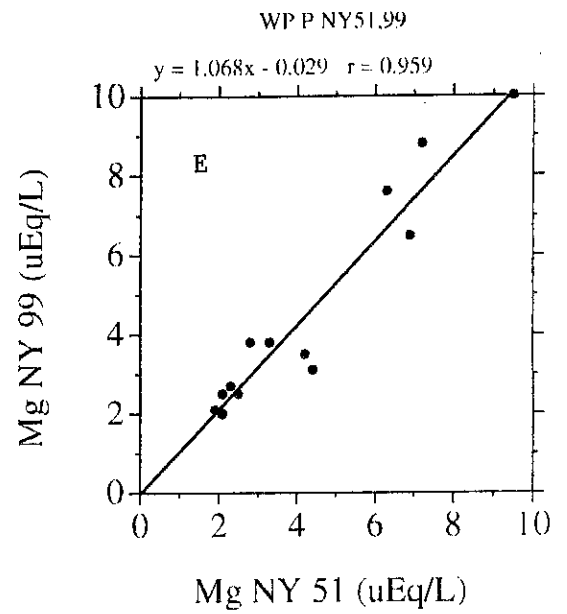
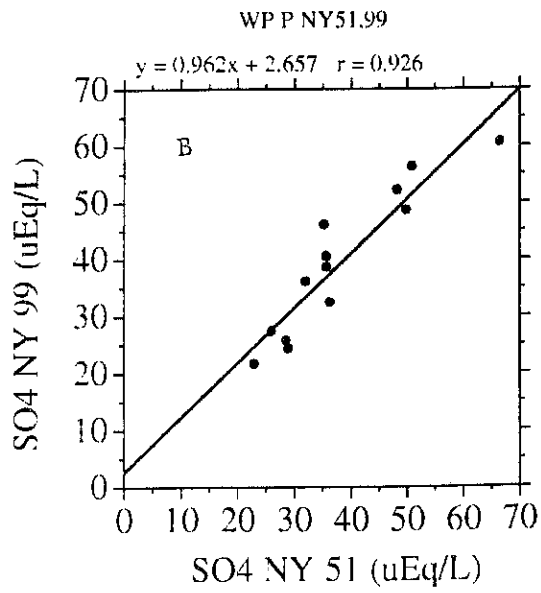
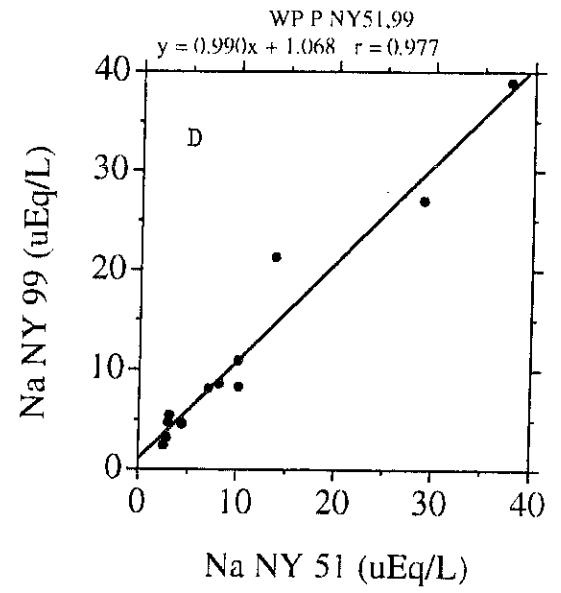
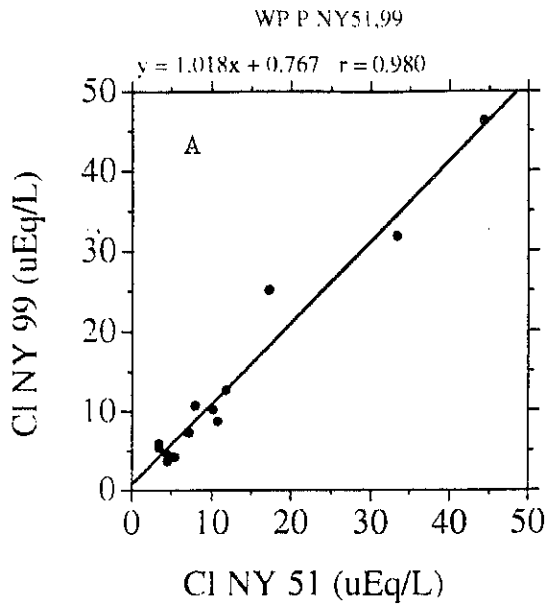
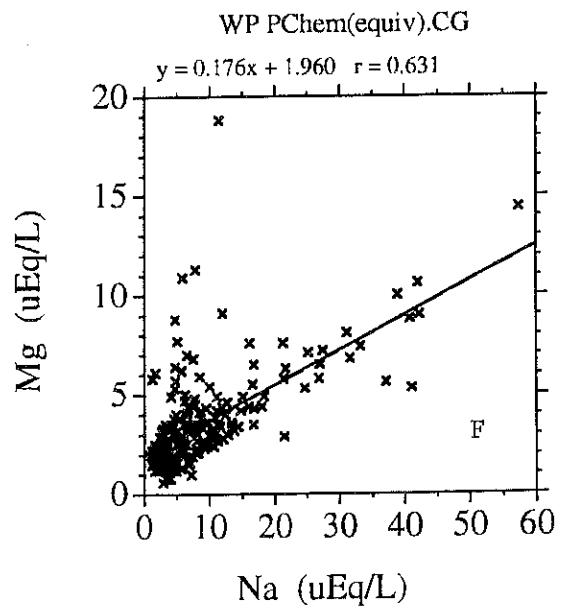
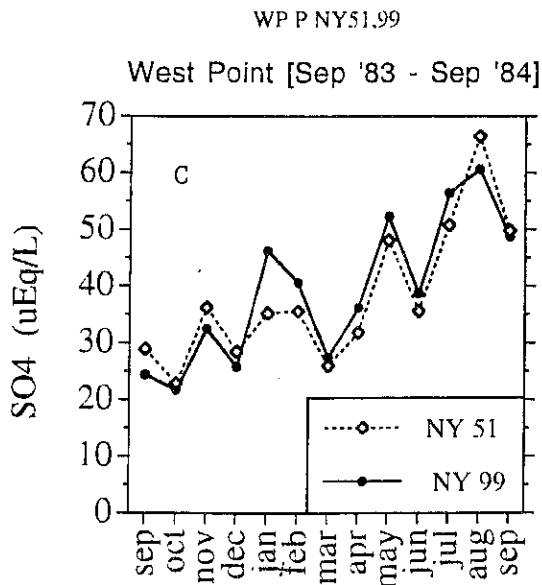
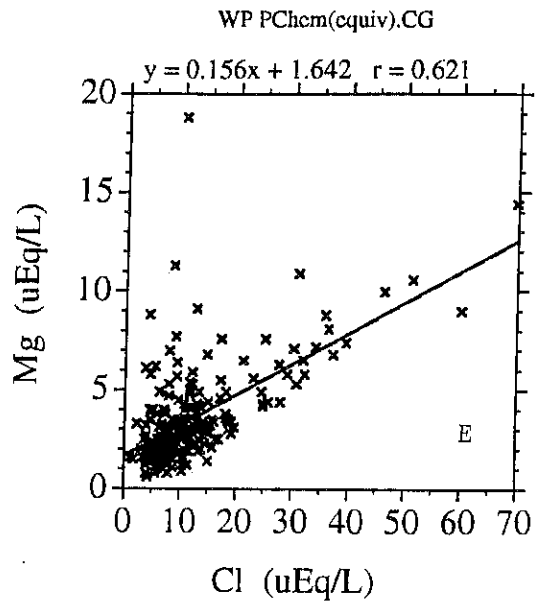
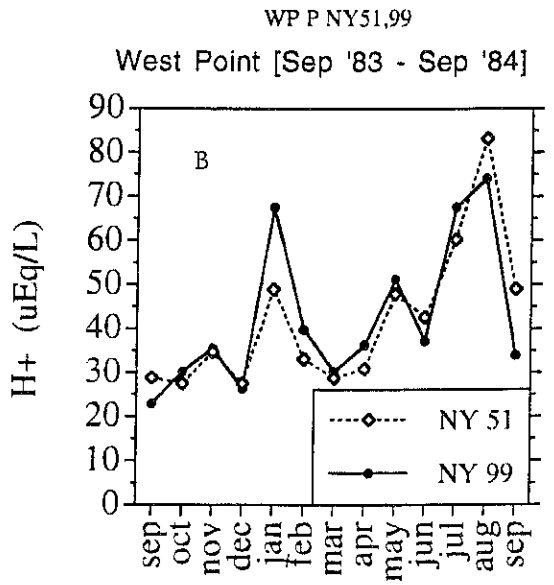
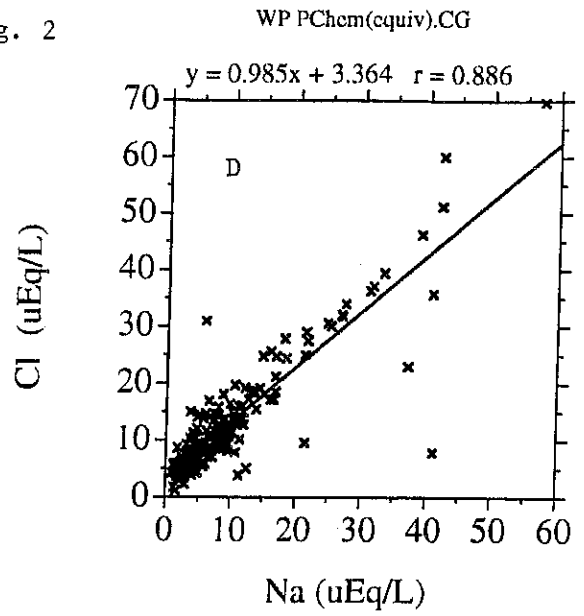
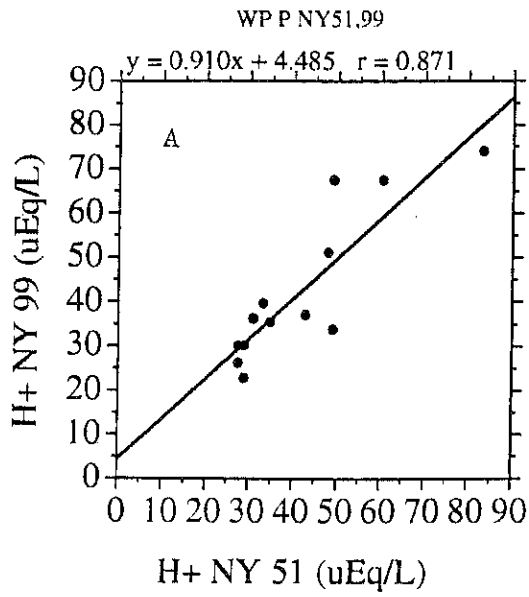


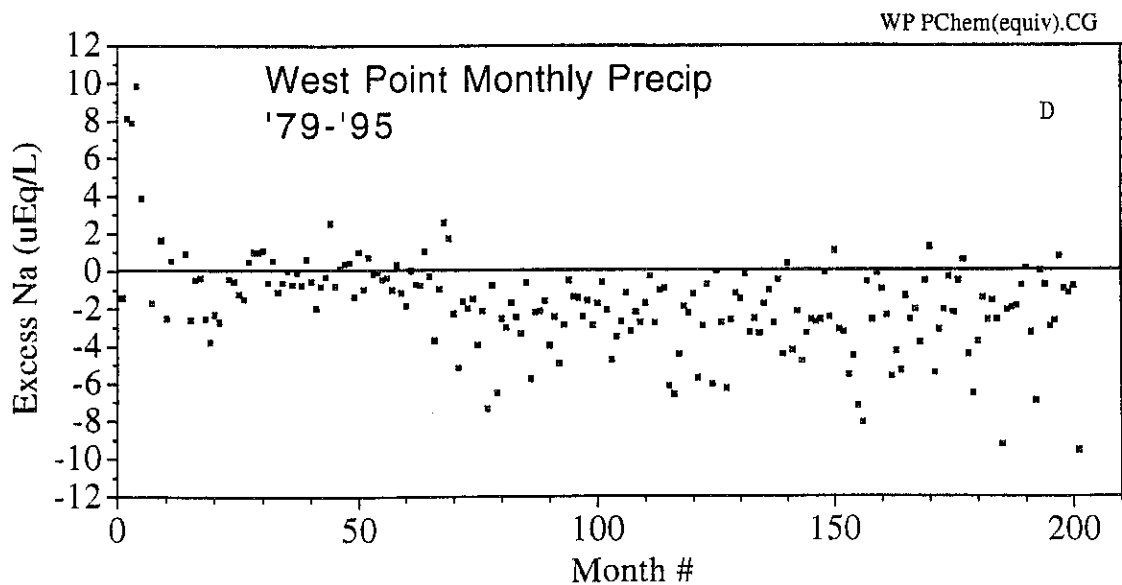
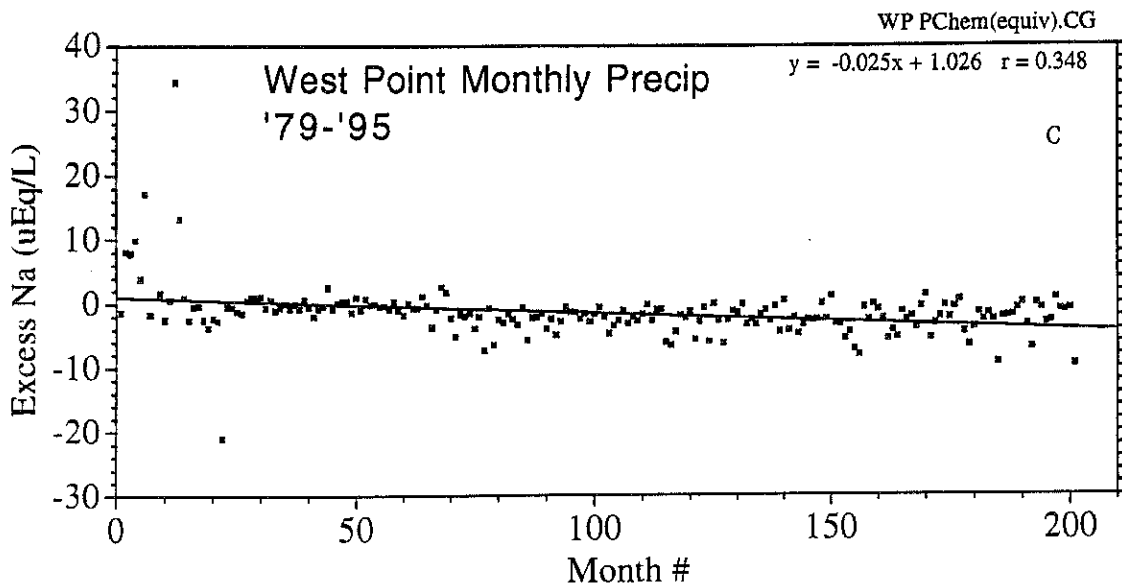
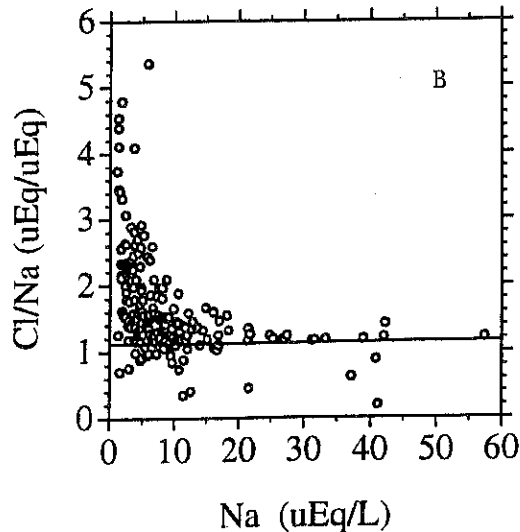
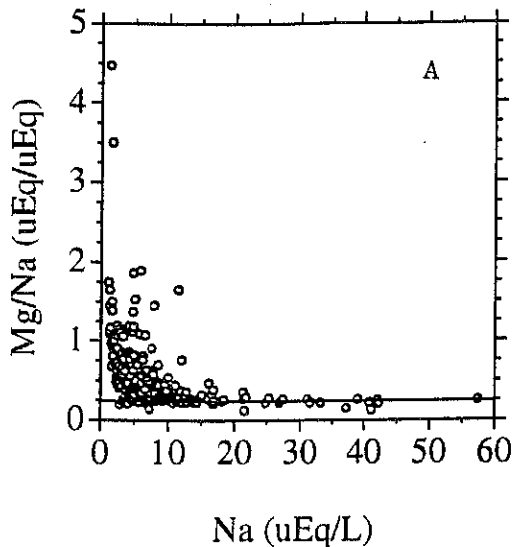
Fig. 2



WP PChem(equiv).CG

Fig. 3

WP PChem(equiv).CG



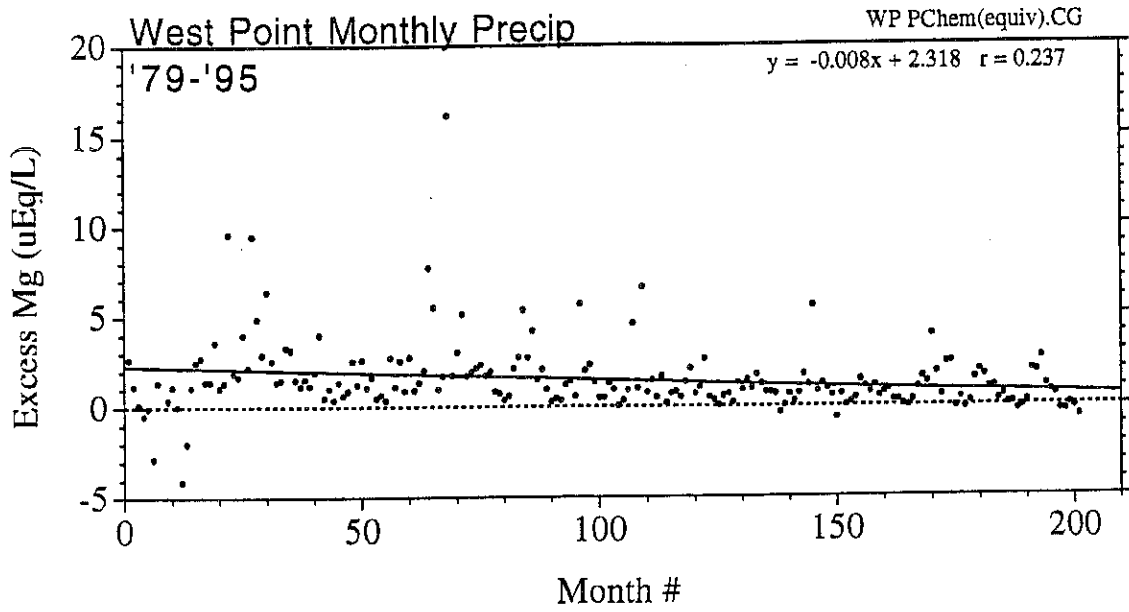
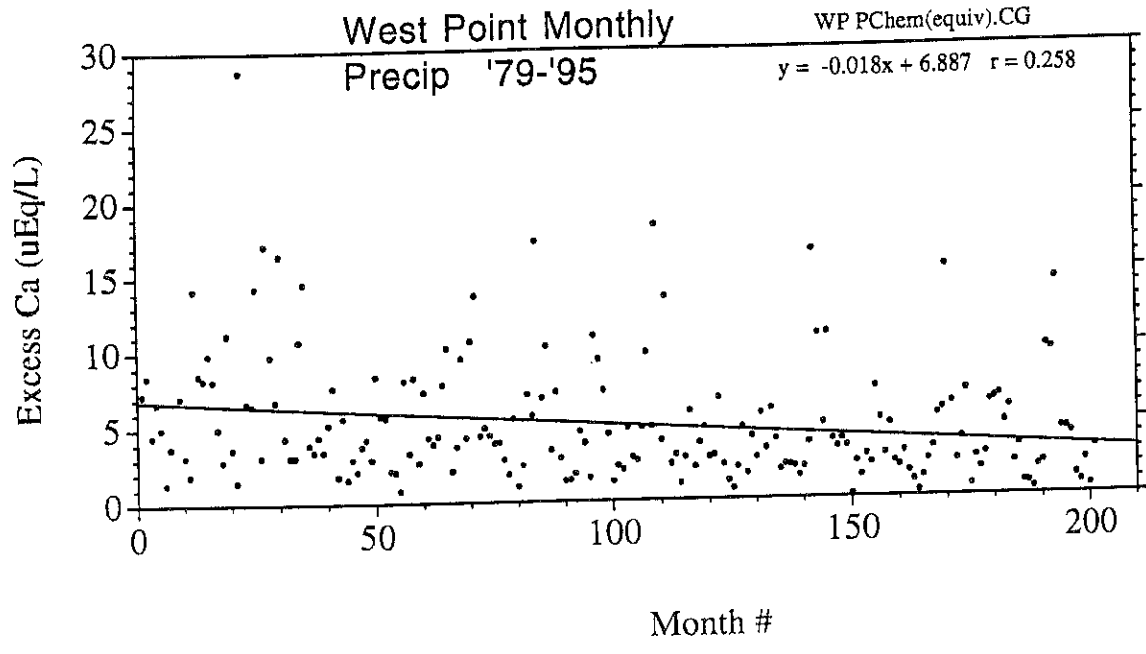
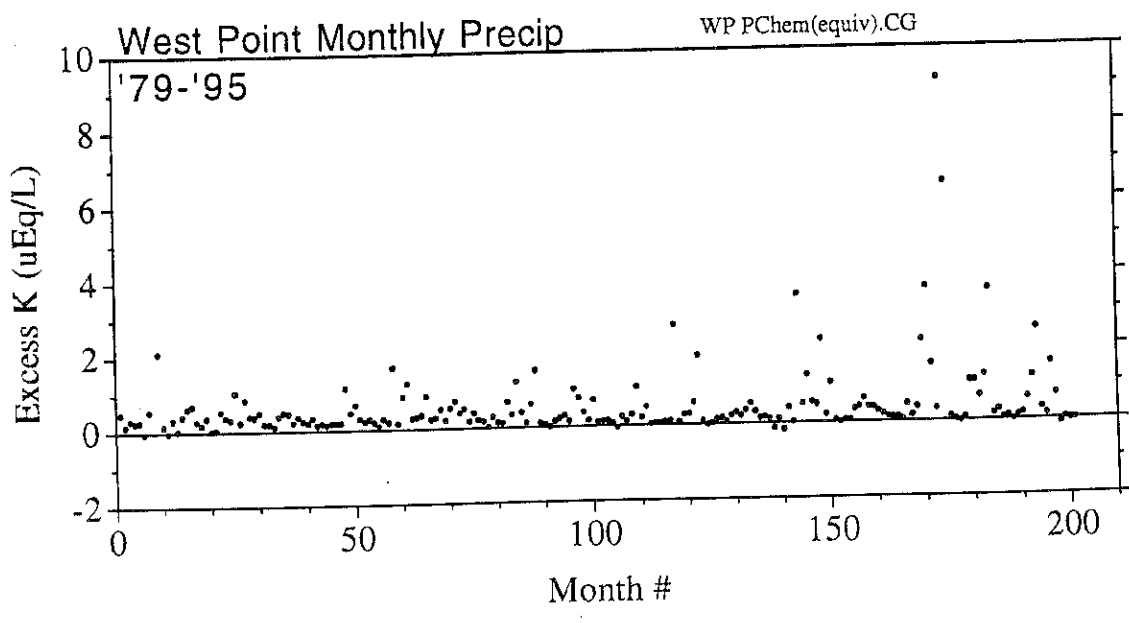


Fig. 4

A



B



C

West Point Monthly
Precip '79-'95

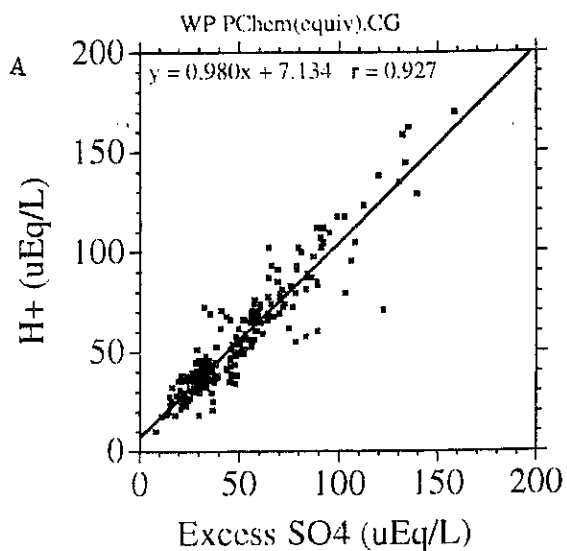
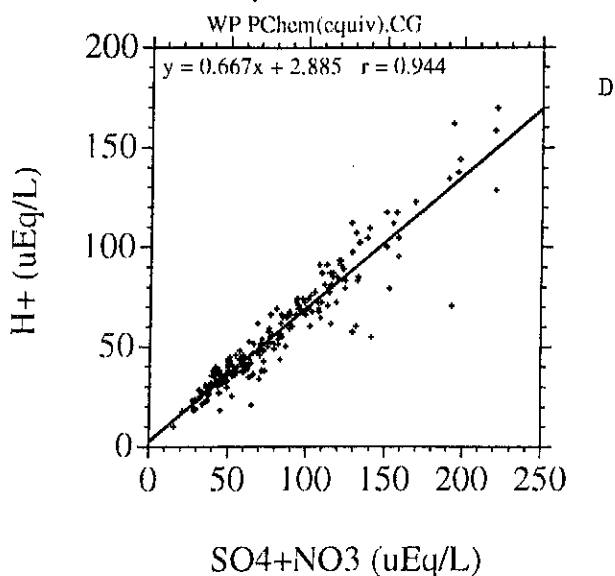
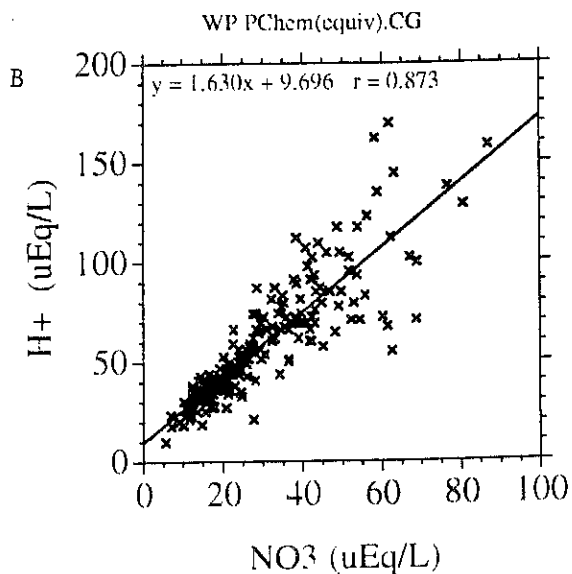


Fig. 5

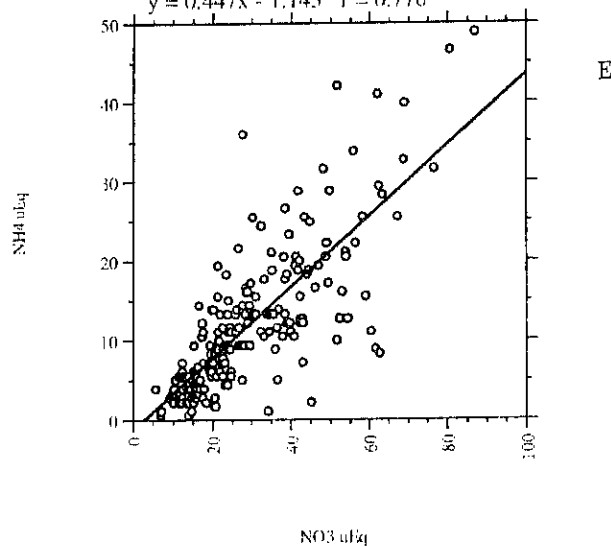
West Point Monthly
Precip '79-'95



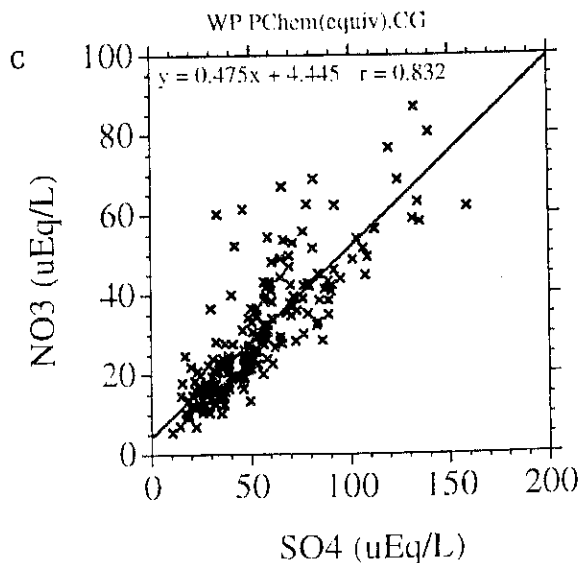
West Point Monthly
Precip '79-'95



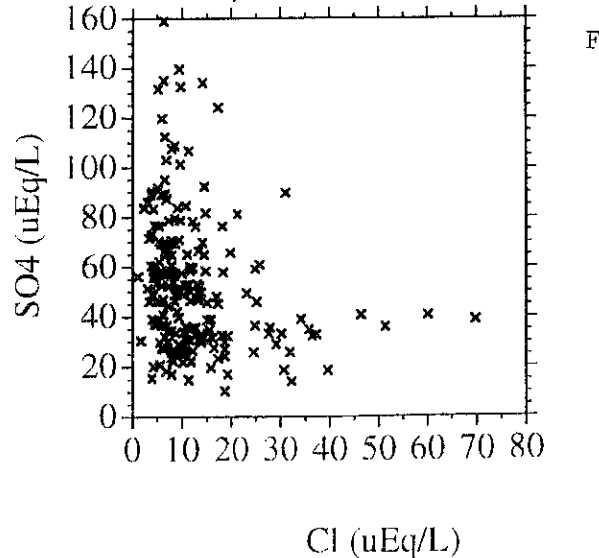
WP PChem(equiv).CG



West Point Monthly
Precip '79-'95



West Point Monthly
Precip



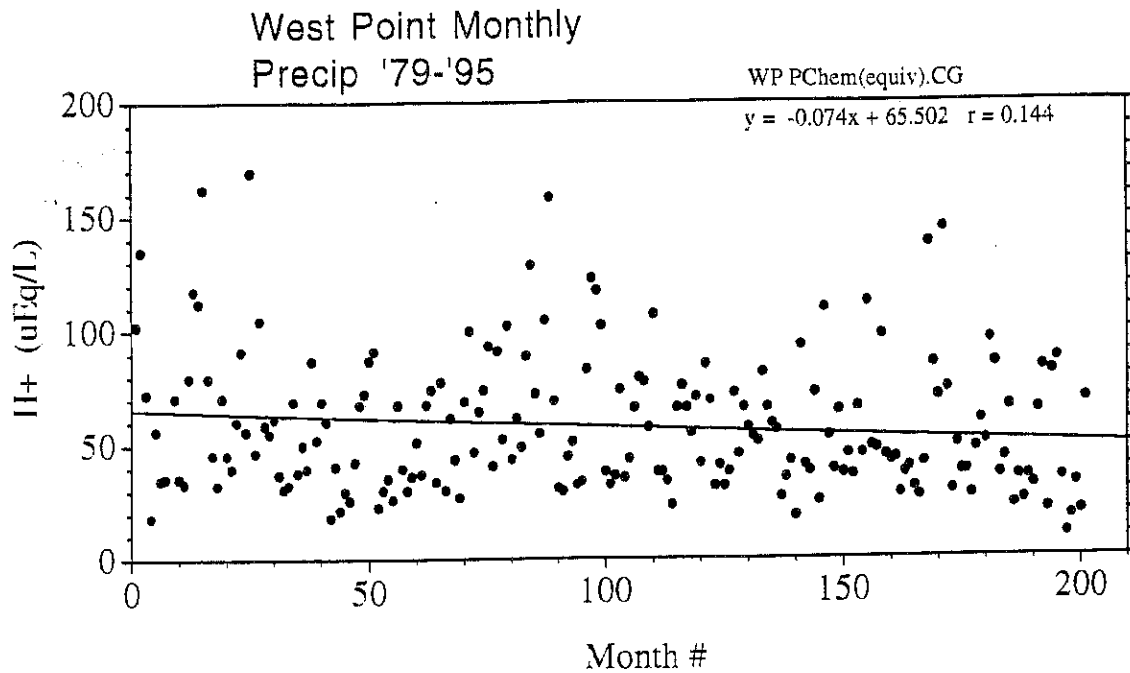
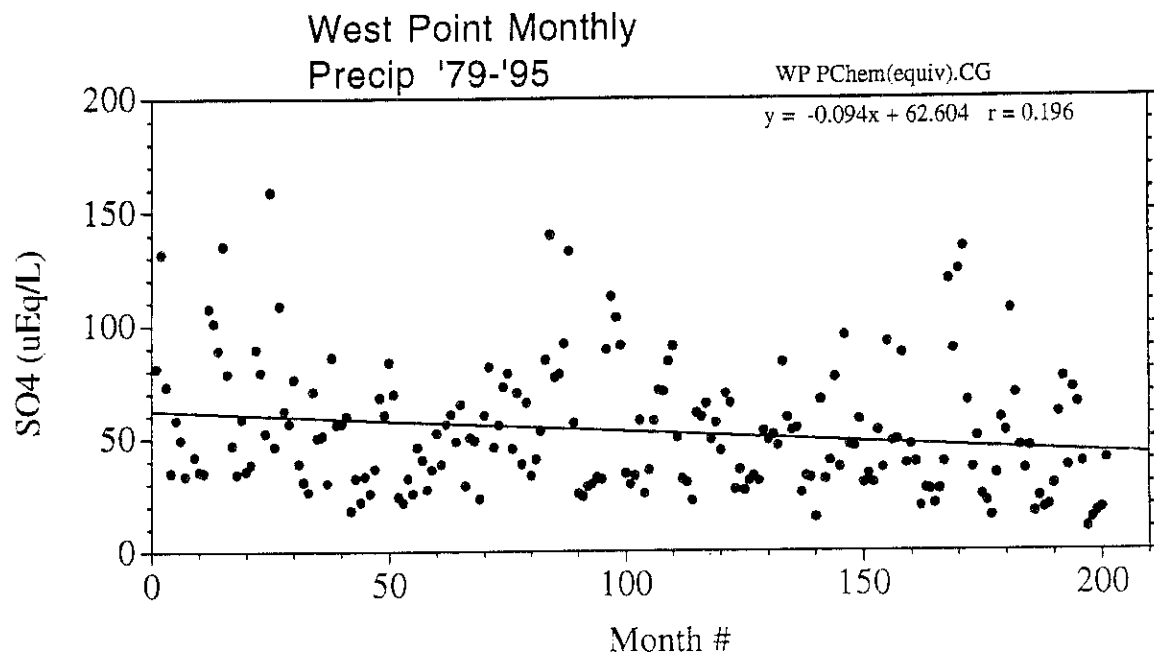
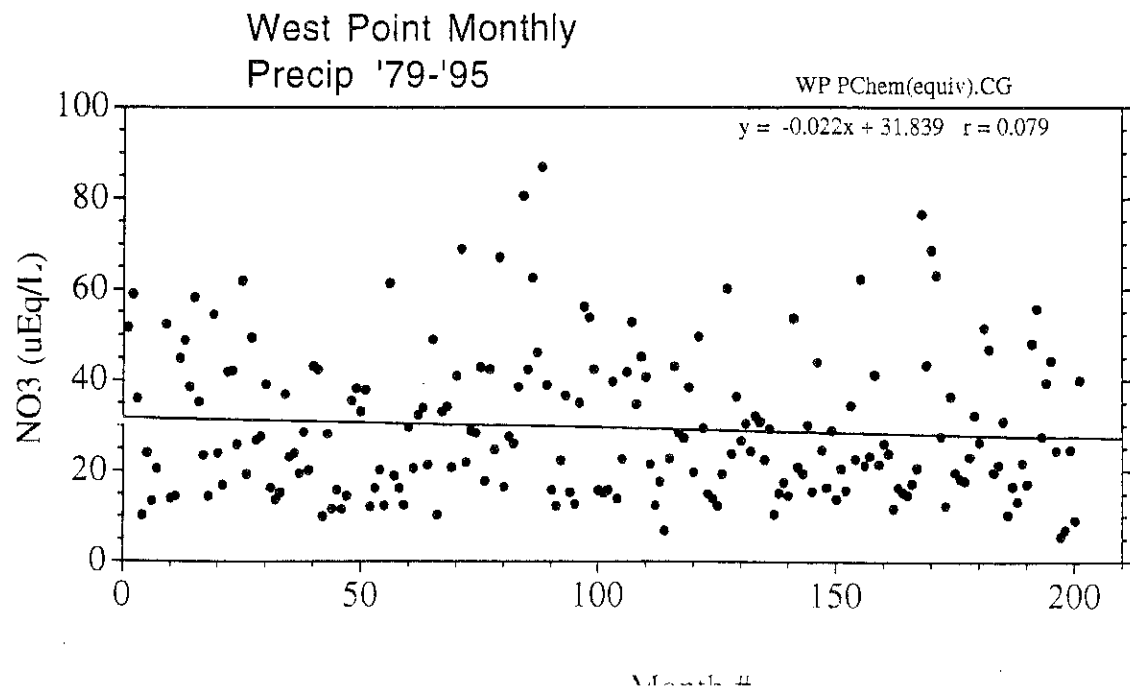


Fig. 6

A



B



C

West Point Monthly
Precip '79-'95

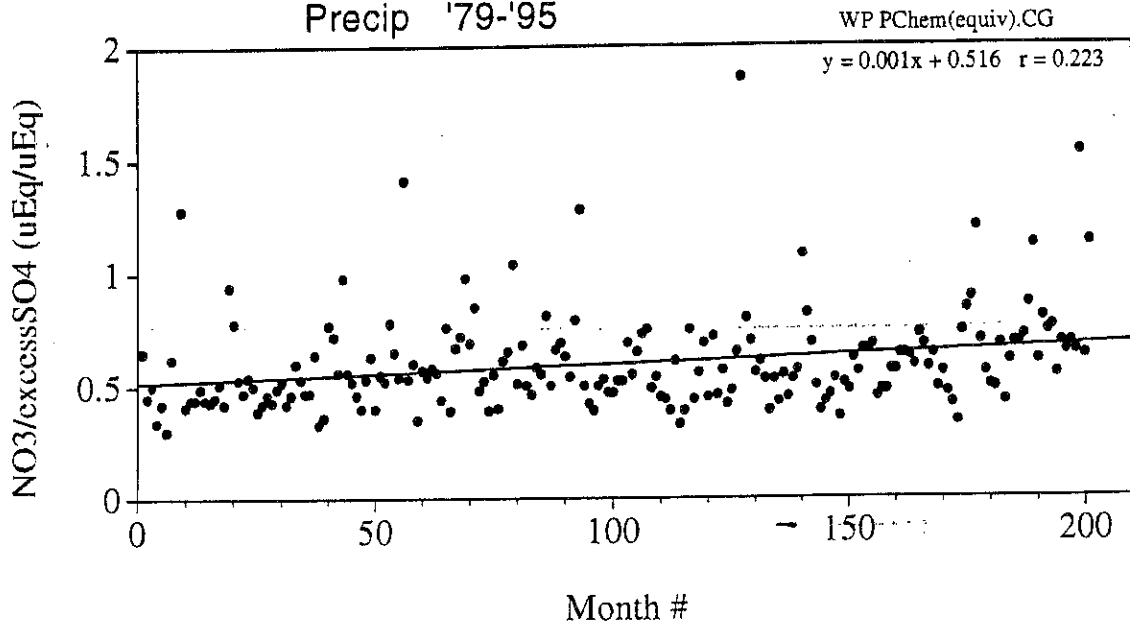
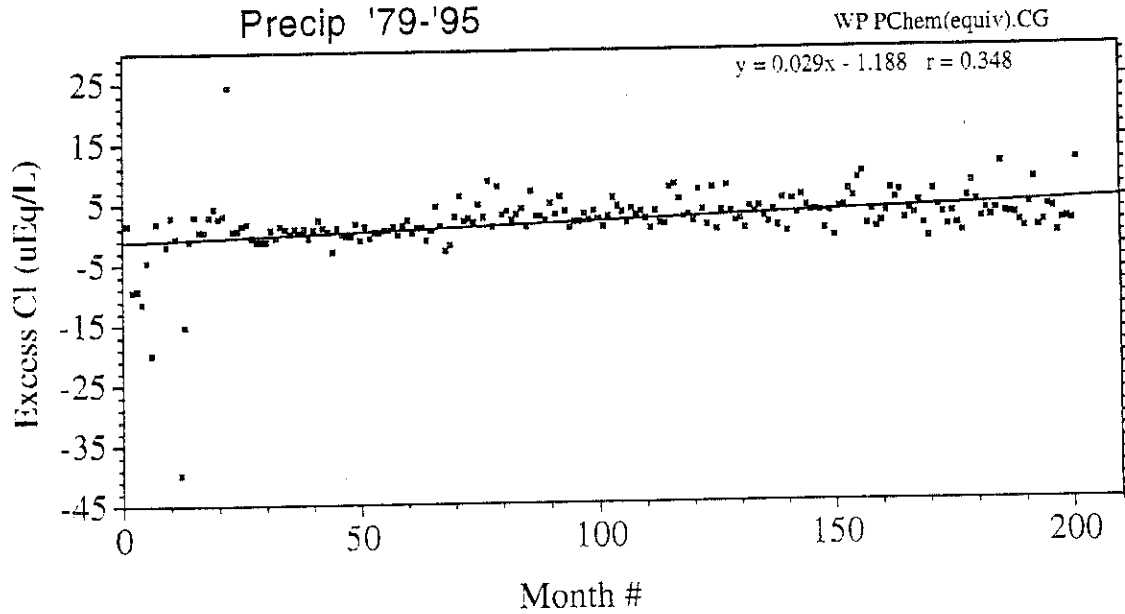


Fig. 7

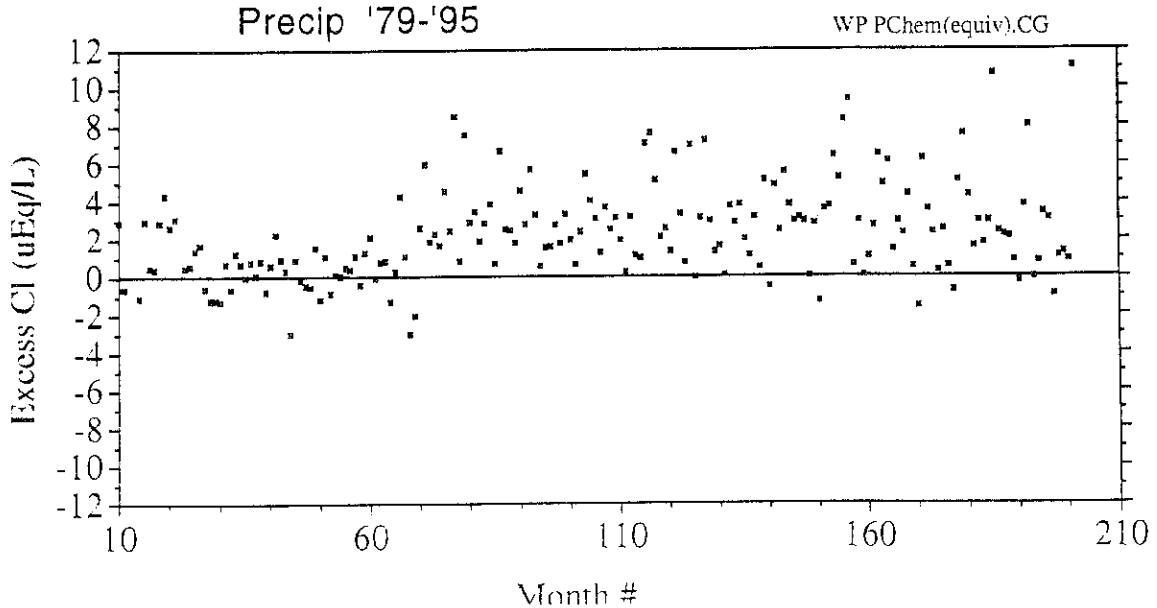
A

West Point Monthly
Precip '79-'95



B

West Point Monthly
Precip '79-'95



C

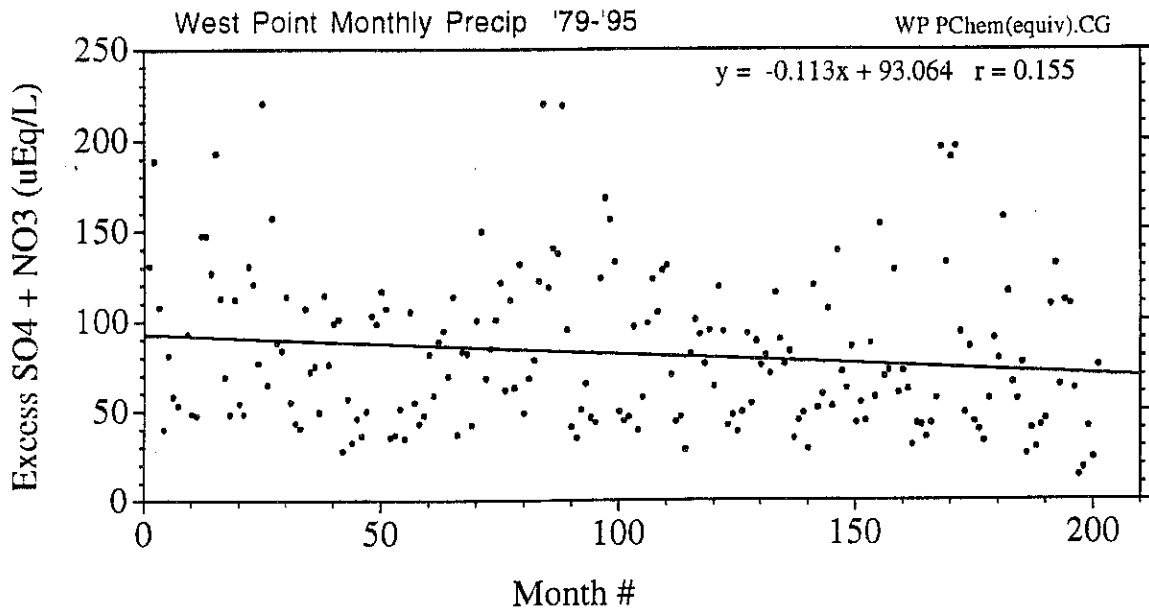
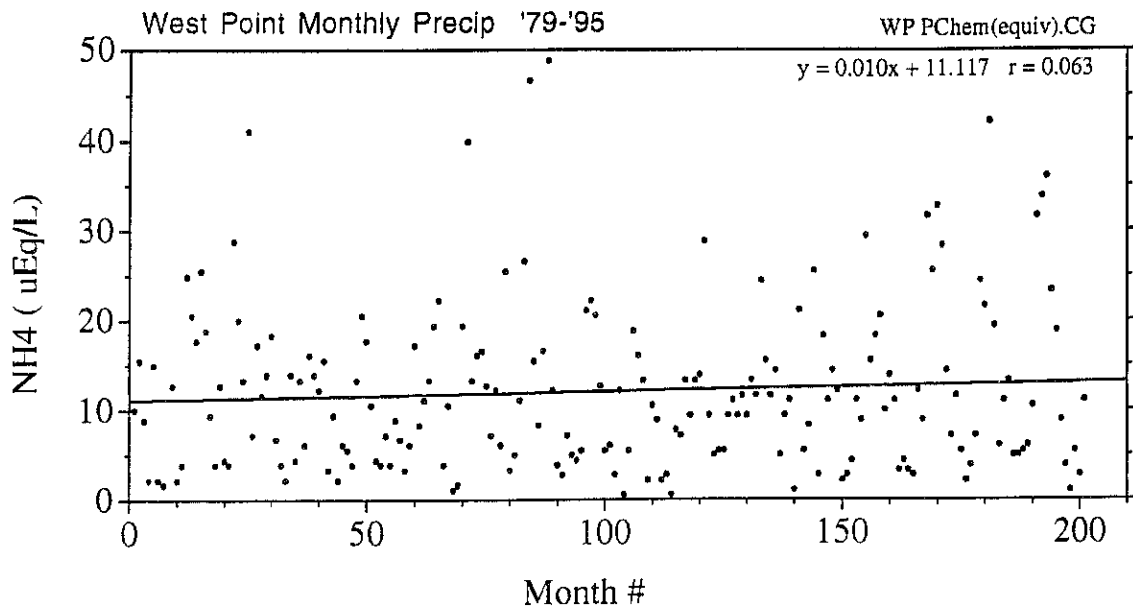
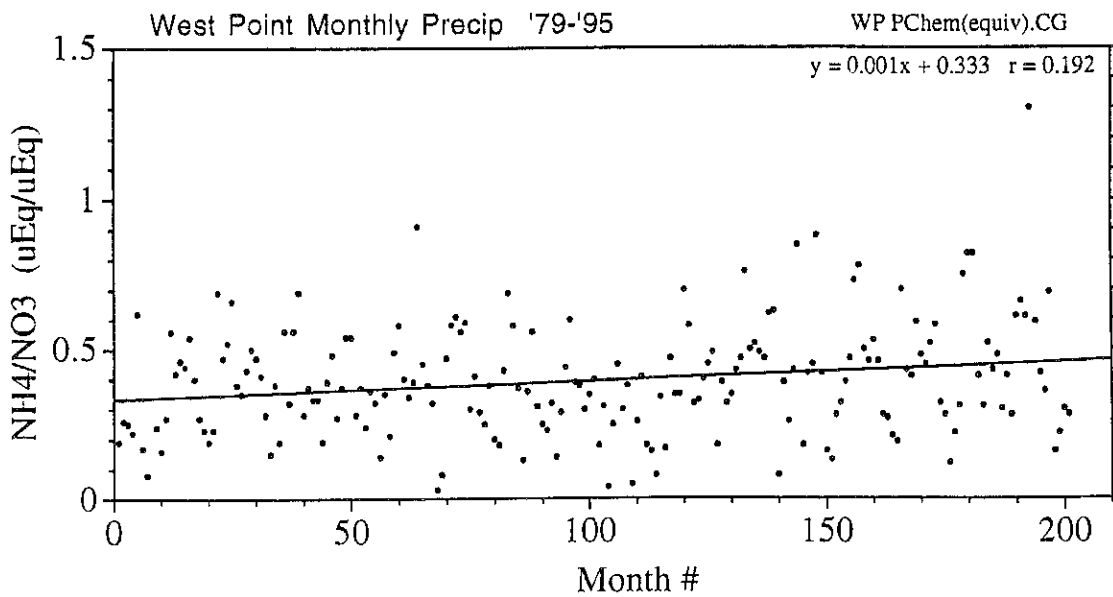


Fig. 8

A



B



C

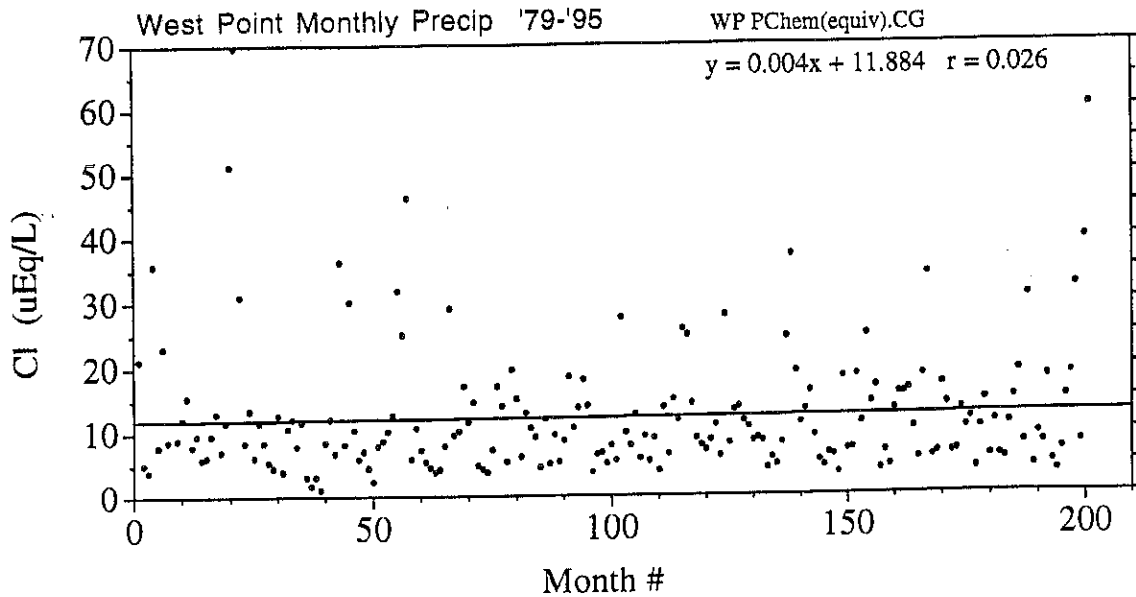
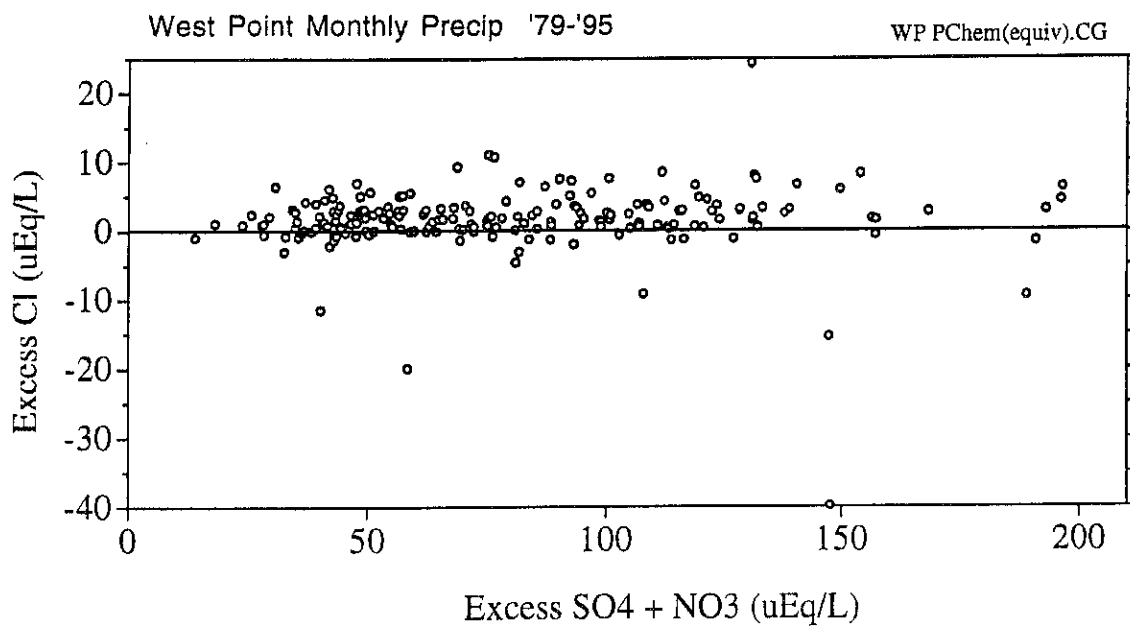
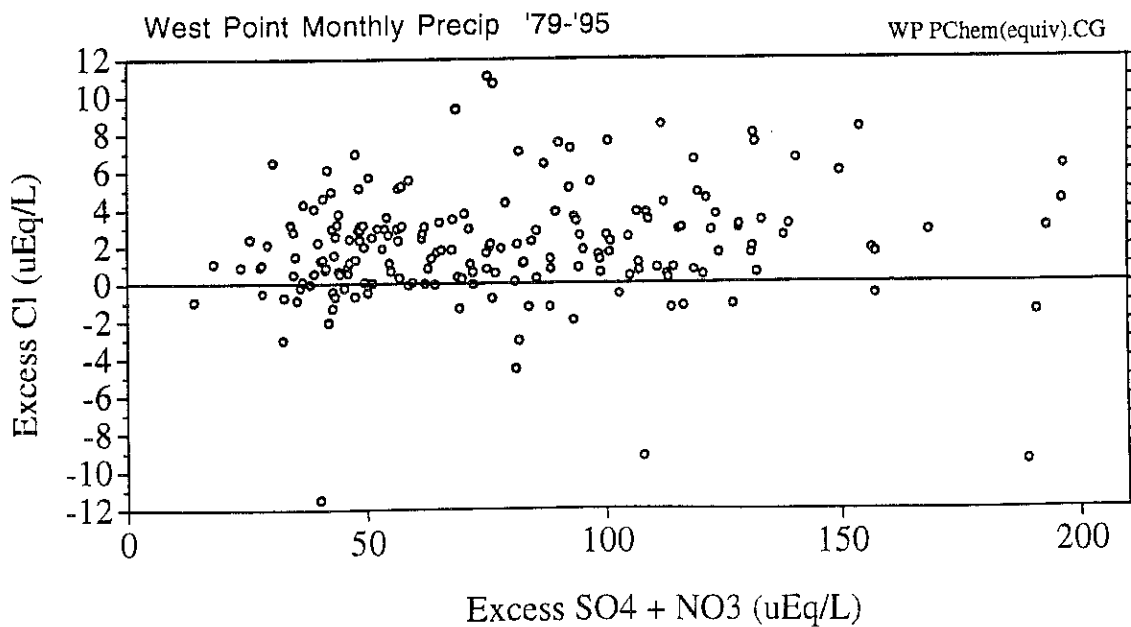


Fig. 9

A



B



C