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A study conducted to assess the potential importance of atmospheric nitrate deposition for a north Florida estuary. Funds were provided by the Florida Department of Environmental Regulation, Office of Coastal Management, made available through the National Oceanic and Atmospheric Administration under the Coastal Zone Management Act of 1972, as amended.

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The report is in three parts, in the form of papers for publication:

Paper 1. Atmospheric Deposition of Nitrate and Its Transport to the Apalachicola Bay Estuary in Florida, by John W. Winchester and Ji-Meng Fu

Paper presented at the Florida Acidic Deposition Conference, Tampa, October 22, 1990. Submitted for publication in proceedings of the conference, edited by Curtis Watkins, and in the journal *Water, Air, and Soil Pollution*. Portions were also described in an invited seminar talk by John W. Winchester at the University of Maryland, November 20, 1990.

Paper 2. Acid Deposition Relationships in Florida and Southeastern U.S.A., by Jin-You Liang and John W. Winchester

Paper 3. Comparison of Acid Deposition and Surface Transport in Three Watersheds of North Florida, by Ji-Meng Fu and John W. Winchester

Executive Summary

I

A comparison of fluxes of ten dissolved constituents of rain water and river water has been carried out for the watershed of the Apalachicola River in order to estimate the magnitude of nitrate contribution from the atmosphere to surface water that may flow to the Apalachicola Bay estuary. The comparison is based on statistical analysis of both atmospheric and river water monitoring data: weekly rain water chemical data from the National Acid Deposition Program (NADP) for five sites within the watershed area, from 1978-84 until late 1989, and less frequent river water chemical data from the U.S. Geological Survey for one site at Chattahoochee, Florida, from 1965 until late 1989.

As descriptive statistics, the means and standard errors of the fluxes from the atmosphere and in the river flow were determined. As a measure of correlations between different ionic concentrations in the rain and river water data sets, factor analysis was used to account for data variance by a sum of principal components according to a linear mixing model. By comparing the compositions and magnitudes of these components, judgments could be made concerning the importance of atmospheric deposition as a source of nitrate in the watershed as well as of chemical transformations and possible loss of nitrate during its residence in the watershed and transport to the estuary.

Although surface sources of nitrogen and extent of loss to the atmosphere by denitrification have not yet been quantitatively determined, atmospheric deposition to the watershed appears to be sufficient to account for essentially all the dissolved nitrate and ammonium and total organic nitrogen flow in the river. However, after deposition most of the nitrate may be transformed to other chemical forms during the flow, except possibly under high flow conditions mainly in winter. But either nitrate or the other forms could, with high efficiency, reach the estuary and be available for its marine biological processes.

II

The general uniformity of yearly average nitrate and sulfate deposition fluxes from acid air pollution over southeastern U.S.A. obscures possibly important differences on a smaller geographic scale and on seasonal or shorter time scales. A statistical analysis of weekly NADP wet chemical data from 18 sites over most of an eight state region has been carried out. Groupings of sites are identified that indicate uniformity over a state-wide scale, but not larger, in correlations based on short term variability in acid air pollution deposition fluxes. Thus, groups of sites within this geographic scale could serve as predictors of deposition on a shorter time scale than is possible based on long term averages of deposition data. For deposition to the watershed of the Apalachicola River, both meteorological conditions and transport from pollution sources appear to control deposition fluxes of nitrate and sulfate acid air pollutants.

III

Comparison of sulfate, different forms of nitrogen, and other chemical compositions between atmospheric deposition and surface transport has been made for the Apalachicola, Sopchoppy, and Ochlockonee Rivers in north Florida by mass balance and multivariate statistical methods. The results show that the chemical compositions of all rivers, in general, can be represented as a mixture of three groups of dissolved constituents. One, containing nitrogen and sulfate, resembles the composition of rain water; another, containing calcium, resembles ground water; and a third, containing chloride and sodium, resembles sea salt. Total mass flow of nitrogen in all three rivers agrees well with the average atmospheric deposition to their watersheds, suggesting that the atmosphere is the major source of nitrogen to their watersheds. However, for Cl^- , Na^+ , Mg^{2+} , Ca^{2+} , K^+ , PO_4^{3-} , the calculated atmospheric contribution is much less than their river fluxes, implying that surface processes, including urban, agricultural, and industrial releases and weathering of soil, are dominant. The three rivers differ considerably in types of watersheds. The finding that atmospheric nitrogen deposition fluxes agree well with transport of nitrogen by river flow and that river nitrate is largely correlated with non-seasalt sulfate implies that on the average the watersheds are in a quasi steady state and that additional surface sources or sinks are relatively small. Moreover, the high relative river flow of organic nitrogen, which is not present in rain water, suggests that it may be a watershed transformation product of atmospheric inorganic nitrogen.

**Atmospheric Deposition of Nitrate and Its Transport
to the Apalachicola Bay Estuary in Florida**

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Abstract

A comparison of fluxes of ten dissolved constituents of rain water and river water has been carried out for the watershed of the Apalachicola River in order to estimate the magnitude of nitrate contribution from the atmosphere to surface water that may flow to the Apalachicola Bay estuary. The comparison is based on statistical analysis of both atmospheric and river water monitoring data: weekly rain water chemical data from the National Acid Deposition Program (NADP) for five sites within the watershed area, from 1978-84 until late 1989, and less frequent river water chemical data from the U.S. Geological Survey for one site at Chattahoochee, Florida, from 1965 until late 1989.

As descriptive statistics, the means and standard errors of the fluxes from the atmosphere and in the river flow were determined. As a measure of correlations between different ionic concentrations in the rain and river water data sets, factor analysis was used to account for data variance by a sum of principal components according to a linear mixing model. By comparing the compositions and magnitudes of these components, judgments could be made concerning the importance of atmospheric deposition as a source of nitrate in the watershed as well as of chemical transformations and possible loss of nitrate during its residence in the watershed and transport to the estuary.

Although surface sources of nitrogen and extent of loss to the atmosphere by denitrification have not yet been quantitatively determined, atmospheric deposition to the watershed appears to be sufficient to account for essentially all the dissolved nitrate and ammonium and total organic nitrogen flow in the river. However, after deposition most of the nitrate may be transformed to other chemical forms during the flow, except possibly under high flow conditions mainly in winter. But either nitrate or the other forms could, with high efficiency, reach the estuary and be available for its marine biological processes.

1. Introduction

We have selected the estuarine system of Apalachicola Bay in north Florida and its watershed for a case study to address the question raised by the Environmental Defense Fund [Fisher et al., 1988]: Can nitrate input to an estuary, to a significant degree, be due to atmospheric deposition, wet or dry, of acid air pollution? The EDF report has been considered seriously by the U.S. Environmental Protection Agency, and studies have been undertaken along the Atlantic coast to assess this possibility. Some of the findings have been summarized for NAPAP [Waddell, 1989] in its SOS/T Report No. 10. On page A-31 it is stated:

Ecosystem N cycles are exceptionally complex and dynamic. Simple input-output relationships, therefore, may be grossly misleading. It is also exceptionally difficult to determine all potential N losses (especially gaseous

ones) from the most important natural ecosystems. Information on specific impacts of elevated deposition inputs of N is just beginning to accumulate. Ecosystem fates and effects of such inputs, as well as the demarcation between beneficial and harmful impacts, will vary substantially across ecosystems and sites, and over time. Conclusions from studies are highly dependent on experimental conditions. Also, most studies have focused on short-term acute effects rather than longer-term chronic impacts and have not included spatial heterogeneity in the experimental design.

This cursory review of some calculations of N mass balances has reinforced the EDF hypothesis that atmospherically derived N is likely a major contributor to surface water quality in estuaries and near-coastal waters. EPA (1989) reports that at least 13% of total N loading to the Bay is atmospheric deposition. Though details of the EDF study can be criticized, the main conclusion is valid. However, results from the Chesapeake Bay may not necessarily represent other areas. Except for wet deposition over the land, the other estimated contributions of N are difficult to assess and are highly uncertain.

Information suggests that a watershed has a rather high capacity to retain or denitrify N entering it. Furthermore, the variability in the ratio of stream basin yield to total deposition suggests that this capacity is highly variable among watersheds and/or that the relative importance of N sources differs greatly between watersheds.

In our study emphasis has been placed on evaluating existing data for an initial assessment and estimation of atmospheric deposition of nitrate to the Flint, Chattahoochee, and Apalachicola River watersheds and transformation or loss of nitrate in the watershed that may have occurred during transport toward the estuary. An important objective of this assessment is to identify major uncertainties that may be reduced by a measurement program. The design of a meaningful field or laboratory measurement program should be based if possible on an examination of available atmospheric and surface water monitoring data. Fortunately, a considerable amount of such data has been obtained for our evaluation. This includes weekly rain water chemical data from the National Acid Deposition Program (NADP) for five sites that have operated for 5-11 years within or near the watershed area, from 1978-1984 until late 1989. It also includes a more lengthy record of less frequent river water chemical data from the U.S. Geological Survey for one site at Chattahoochee, Florida, from 1965 until late 1989, that represent flow from the Flint and Chattahoochee Rivers, that drain 90% of the watershed, into the Apalachicola River that empties into Apalachicola Bay. These data sets, each consisting of 140-400 or more samples that have been analyzed for ten or more chemical concentrations, are large enough for statistical analysis and precise comparisons that may reveal important deposition and watershed processes and lead to a provisional answer to the question posed by the EDF.

2. Comparisons based on descriptive statistics

a. Geographic uniformity of nitrate wet deposition fluxes to the surface

Table 1 summarizes NADP nitrate concentrations in rainwater at 30 monitoring stations in 8 southeastern states in weekly samples collected over 5 to 11 years up to 1989. From the reported millimeters of precipitation each week we have calculated the average wet deposition flux of nitrate over the years of record in $\text{kg ha}^{-1} \text{ yr}^{-1}$. These average fluxes range

over a factor of 3 from 4.23 in south Florida to 11.56 in western North Carolina (see map accompanying Table 1). Four sites that lie within or near the Apalachicola River watershed (Alabama b, Georgia c and a, and Florida f) have a much narrower range, from 5.90 to 7.49, and differences between these long term averages are not statistically significant at the 95% confidence level (twice the standard error for each site). It should be noted that the number of samples analyzed at each site ranges from 142 to 371; any fewer samples would lead to a less precise result. Week-to-week variability in concentrations and deposition fluxes of nitrate and other ions is very great at any site, so that long-term monitoring with many samples collected is necessary to calculate a meaningful average deposition rate.

It should be remembered that dry deposition may contribute an additional flux of nitrate to the surface, according to estimates made by FCG, the Florida Electric Power Coordinating Group [1987, p. 10-4] who state:

Estimates of total deposition were made by adding wet deposition observed from the monitoring network to dry depositions calculated using ambient air data and assumed deposition velocities. . . . Due to uncertainties in deposition velocities, dry deposition of sulfur is known with much less certainty than wet deposition. . . . About one-half to two-thirds of total nitrogen deposition occurs as dry deposition. Similar to results for sulfur, the majority of nitrogen dry deposition appears to occur in the form of acid precursors (i.e., NO_2).

Therefore, the total atmospheric nitrate flux to the surface may be at least double that due to wet deposition alone, in spite of uncertainties in dry deposition estimates by our national and state programs. Nevertheless, estimates of nitrate deposition from the atmosphere to the Apalachicola River watershed or estuary using these existing data can be useful. Any improvement by additional atmospheric measurements would require an effort greater than that made by NADP or FCG. The need for such improvement is probably less urgent than the need to resolve greater uncertainties concerning the transformation, retention, or loss of nitrate in the watershed during its transport toward the estuary.

b. Comparison of atmospheric deposition fluxes with river flow of dissolved ions

Table 2 presents a comparison of the fluxes of 10 dissolved species in Apalachicola River water as it flows past the Chattahoochee monitoring site with the wet deposition fluxes calculated for the watershed area from data taken at 5 NADP sites situated in the vicinity of the watershed and at its northern extremity. The fluxes suggest two general groups: The first six ions - Cl^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and PO_4^{3-} - have atmospheric wet deposition fluxes much less than the measured river water flows, and even double the rain water fluxes as an estimate of total wet+dry deposition are also less. Thus, atmospheric deposition is not enough to account for the river flows, and additional surface sources must also be present.

The next three species measured in river water - SO_4^{2-} , NO_3^- , and NH_4^+ , - show a different relationship with atmospheric fluxes. For these the atmospheric inputs are at least equal to or are greater than river water flows, suggesting that the atmosphere may be their principal source. Org N (a mixture of organic nitrogen compounds in unfiltered water samples) is also included, and its river flow exceeds that of NO_3^- and NH_4^+ combined. It should be noted that Org N is not routinely monitored in atmospheric samples, since it not a pollutant from carbonaceous fuel combustion and should occur at much lower concentrations than, for example, nitrate. It should be kept in mind that organic nitrogen could be a chemical conversion product of a precursor, e.g. nitrate, after deposition to the watershed, so that its river flux could ultimately to be in part the result of an atmospheric source.

The possibility of a substantial atmospheric source for these four species may better be judged after by comparing fluxes on a molar rather than weight basis as shown in Table 3. Addition of dry deposition would lead to a total deposition at least double the atmospheric wet-only fluxes listed, and the last column lists twice the 5-site wet deposition averages for comparison with river fluxes. For sulfate the average, median, and geometric mean are all close to, or slightly greater than, the river sulfate flux. This close agreement suggests that additional watershed sources or sinks may be relatively small, so that sulfate could be due mainly to atmospheric deposition with little interaction with the watershed during surface transport. If indeed surface sources, e.g. by weathering, or sinks, e.g. by ion exchange, are relatively small, then sulfate may be a conservative tracer of atmospheric input from acid deposition to the watershed.

The river flow of NO_3^- is considerably less than (roughly 1/3 of) twice the atmospheric wet deposition, suggesting that, if the atmosphere is the principal source of NO_3^- , roughly 2/3 has been transformed, lost, or retained by the watershed. For NH_4^+ the discrepancy is much greater, indicating that over 90% of NH_4^+ is transformed, lost, or retained. For Org N we lack chemical concentrations measured in rain water, but these are believed (cf. the above cited statement by FCG [1987, p. 10-4]) to be much less than for nitrate. In contrast, on a molar basis the river fluxes of Org N are larger than those of nitrate and ammonium ion combined, and the total river flux of these three forms of dissolved nitrogen are 60-75% of the average, median, or geometric mean of twice the wet deposition from the atmosphere.

The material balance is not complete, however, until other surface sources of nitrogen compounds and losses back to the atmosphere are estimated. Not only agricultural, industrial, and urban sources, but the evolution of N_2O and N_2 should be considered. It should be noted that a likely range of N_2O from managed agricultural systems is 0.2 to 6 kg $\text{N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$ [Goodroad et al., 1984], a range that translates into $(0.07-2.1) \times 10^9$ moles $\text{N}_2\text{O-N}$ per year for the 5.0×10^6 ha of the watershed draining the Flint-Chattahoochee-Apalachicola River system. This range is the same general order of magnitude as the nitrogen transport data of Table 3, suggesting that N_2O loss to the atmosphere could be an important part of the nitrogen budget of the watershed.

Atmospheric deposition of nitrate appears to be more than enough to account for dissolved nitrogen in the river, but transformation of nitrate to other forms, e.g. Org N, as well as some retention by the watershed or loss by return to the atmosphere through denitrification must occur during watershed or river transport. If surface sources are small enough relative to atmospheric, the transport efficiency of nitrogen-containing nutrients to the estuary after atmospheric deposition of nitrate could be quite high, although the chemical link between nitrate and organic nitrogen compounds in the river must still be demonstrated explicitly.

The last line of Table 2 is included to compare river water flow with rainfall to the watershed measured at 5 NADP sites. The river flow is for one year studied by Matraw and Elder [1984], whereas the rainfall is calculated for the measured rate at each NADP site multiplied by the total watershed area. For two of the sites rainfall was measured for the year of river measurements, whereas for the other three sites the average rainfall is given for the indicated time interval. It appears that average river flow is 2 to 3-fold lower than the estimated rainfall input, indicating a substantial loss of water by evaporation or transpiration. However, soluble ions such as SO_4^{2-} should not be similarly lost, nor should NO_3^- without additional chemical reaction in the watershed.

3. Comparisons based on absolute principal component analysis

a. Absolute principal component analysis

In the foregoing approach based on material balance, long term average atmospheric and river monitoring data were compared. As an alternative, we now examine short term variability by multivariate statistical analysis of measured chemical concentrations. In absolute principal component analysis the correlations between the concentrations in the large number of samples within each data set are the basis for identifying groupings of elements that represent components. These may include, for example, acid rain or sea salt, and be present in different proportions in the different samples. The analysis attempts to account for the observed chemical concentration data as the sum of a small number of these components, assuming each has a fixed composition and the samples differ only in the mixing ratios of the components. The procedure followed here is carried out using a desktop microcomputer and commercial software; it is well known and has been described, for example, by Li and Winchester [1990]. Similar procedures have been used in two recent studies of acid deposition data [Hooper and Peters, 1989; Eder, 1989], but no such study of surface water data is known to us at present.

b. Principal components present in acid rain

Table 4 presents two examples of the factor analysis of NADP rain water concentration data sets from sites, indicated in Table 1, in Florida and North Carolina that are near the watershed. This analysis indicates that, on average, 93% and 79%, respectively, of the variance can be explained as mainly due to the mixing in different proportions of three or two components that may have different origins. The proportions may be caused by exposure of the air mass to different source areas to differing degrees before rain deposits its constituents to the surface. Both the factor loadings (correlation coefficients between measured ion concentrations and factor scores) and the factor compositions (concentrations of ions assigned to each factor) are shown in Table 4. A high loading indicates that most of an ion is assigned to a factor, whereas the actual concentration of an ion in a factor, though perhaps small, can be compared to other ions and provide clues about the physical interpretation and origin of an atmospheric component.

At Quincy, Florida, most variance (factor 1) is explained by a factor with high loadings of Cl^- , Na^+ , Mg^{2+} , and Ca^{2+} ; the ion concentrations calculated for factor 1 show a composition close to that of seasalt, except for a 50% enrichment of SO_4^{2-} . But most SO_4^{2-} together with NO_3^- are present in factor 2 in a proportion close to that expected for acid rain, with NH_4^+ only 8.5% of that needed to neutralize sulfuric and nitric acids, indicating a strongly acidic component, and even Ca^{2+} together with NH_4^+ balance only 19% of the equivalents of SO_4^{2-} and NO_3^- . In addition, factor 3 also contains SO_4^{2-} and NO_3^- together with NH_4^+ sufficient to neutralize 63% (68% with Ca^{2+}) of the strong acidity, indicating a less acidic pollution component. These factors at the near coastal Florida site are interpreted to represent

- (1) seasalt aerosol that has taken up additional pollution SO_2 before rainfall scavenging, such as by sulfuric acid displacement of chloride,
- (2) sulfuric and nitric acid air pollution from tall stack fuel combustion sources, with little ammonia from its surface sources on land, such as may be due to polluted air mass transport over the sea surface before rainout, and
- (3) more neutralized acid rain such as by a longer residence time over terrestrial sources of ammonia before rainout.

It is important to realize that most of the sulfuric and nitric acids present in rain at Quincy, Florida, are not neutralized by ammonia. The relative importance of the three components

may be related, sample-by-sample, to air flow trajectories, although this comparison was not attempted in the present analysis.

At Coweeta, North Carolina, only two factors were found to explain a significant amount of variance. The most is factor 1 with composition expected for acid air pollution, indicated by high concentrations of SO_4^{2-} and NO_3^- , with additional NH_4^+ sufficient to neutralize 22% of sulfuric and nitric acids. Factor 2 resembles seasalt in composition but also contains smaller concentrations of SO_4^{2-} and NO_3^- , although with relatively less NH_4^+ than in factor 1. As expected from its geographic location, seasalt concentration is lower than in coastal Florida, but the acid rain pollutant concentrations are higher and quite uniform in relative proportions so that only one factor is needed to describe them.

We should take special note of the chemical equivalent ratio $\text{NO}_3^-/\text{xSO}_4^{2-}$ at the two sites, 0.52, 0.32, and 0.39 in the three acid pollution factors just discussed, or about 0.4 overall. These will be compared with the results of principal component analysis of surface water data.

c. Principal components present in surface water

Apalachicola River water has been sampled by the U.S. Geological Survey since the 1960's at a site below the Jim Woodruff dam at Chattahoochee near the confluence of the Chattahoochee and Flint Rivers. Over 200 samples (indicated in the note to Table 2) were collected several times each year, though less frequently during the 1980's, and analyzed for dissolved ions and for total organic nitrogen using procedures summarized by Matraw and Elder [1984]. The results of three different factor analyses of this data set are shown in Table 5. The first shows that factors 1, 2, and 3 are defined by combinations of ions, but that Org N, NH_4^+ , and PO_4^{3-} are each relegated almost completely to their own factors. The second analysis, without the last two ions, confirms this result for Org N, indicating that the concentration of this important constituent varies independently of the major dissolved ions. The third analysis, without Org N, was then carried out in order to include about 50% more samples that did not include Org N data for a more precise definition of the first three factors over the 25 years of record, and its results are similar.

The compositions of the three factors, that explain 84% of data variance, form patterns that we recognize to represent plausible components in a linear mixing model of river water:

- o One (factor 2) is rich in Ca^{2+} and the separate measurement of hardness and may be considered as ground water, i.e. meteoric water that has been exposed to limestone. NO_3^- is virtually absent, although SO_4^{2-} and other ions are present in small concentrations.

- o Another (factor 1) contains most of the SO_4^{2-} and a substantial fraction of the NO_3^- , but the ratio $\text{NO}_3^-/\text{xSO}_4^{2-}$ is lower than in the acid rain components in Table 4 by a factor of almost 10. It is important that NO_3^- is sufficiently well correlated with SO_4^{2-} to be assigned to this factor, suggesting that both ions are the result of atmospheric inputs. But if SO_4^{2-} is a relatively conservative tracer of acid rain in the surface water, its corresponding NO_3^- has been depleted nearly 10-fold. Thus, if it is the result of acid rain, the component is a very aged rain that has lost NO_3^- by chemical transformation or removal from the aquatic system.

- o A third (factor 3) contains SO_4^{2-} and smaller concentrations of other ions, including significant NO_3^- and a ratio $\text{NO}_3^-/\text{xSO}_4^{2-}$ about equal to the acid rain components in Table 4. Thus, NO_3^- is correlated with SO_4^{2-} and assigned to this factor, suggesting an atmospheric deposition source and not depleted below the expected level. Compared to the other river water components, it may represent rather freshly fallen rain, such as in heavy storms, without sufficient time in the watershed for its NO_3^- to be transformed or lost.

4. Comparisons based on patterns of temporal variability

a. Temporal variations in acid precipitation

At any of the NADP sites the amount of rainfall and the concentrations and depositions of the measured ions in rainwater vary over a wide range, and the standard deviation about the mean (range of 68% of the observations) is typically as large as the mean itself. Consequently, a very large number of samples is required to calculate a precise average. The extreme variability is illustrated in Figs. 1-5 for the 5-year record at the Florida Quincy site at which rain was sampled during 60% of the weeks. In Fig. 1, that includes weeks without rain, the weekly rainfall ranged from a few to well over 100 mm, without discernable seasonal pattern or significant change in trend over the 5 years. Fig. 2 shows that the concentration of factor 1 (mainly sea salt) ranges over more than a factor of 10 in relative factor score units, without apparent regularity.

Since concentration of any component is the result of both dilution and the supply of the trace constituent itself, the deposition (concentration x precipitation amount) is plotted in Figs. 3, 4, and 5 for factors 1, 2, and 3, respectively. These also show a wide range of variability, with sporadic peaks a few times each year but without obvious seasonal or longer term pattern. It may be that some of these episodes of peak deposition can be linked to weather conditions, and we have initiated a meteorological investigation of these conditions. But until a means has been developed to forecast acid deposition from weather data, a long term monitoring program, such as NADP, is needed to estimate average deposition at a specific location. Such data can also be used to resolve and define the compositions of principal components as we have seen.

b. Temporal variations in river water composition

The variability over 25 years of monitoring the Apalachicola River is illustrated in Figs. 6-12. Fig. 6 shows that water flow rate in the river exhibits a pronounced seasonal pattern, with highest flow during the winter months early each year, quite unlike rainfall patterns such as in Fig. 1. We believe that river flow is closely linked to seasonal variation of the growth of plants in the watershed, with much less loss of water by evapotranspiration to the atmosphere during winter. Fig. 1 also shows that seasonal winter maxima in water flow have declined in amplitude since 1980, perhaps the effect of increased withdrawal of water for human use in the 3-state region during recent years.

Figs. 7-9 show variation in concentration of the three principal components, in relative factor score units, i.e. (1) aged rain, (2) ground water, and (3) fresh rain, with compositions given in Table 5. All three components exhibit considerable variation in concentration, especially for fresh rain (factor 3) compared to aged rain (factor 1), with intermediate variation for ground water (factor 2). Since about 1980 it appears that the concentrations of all three components have been gradually rising as a longer term trend. If real, this trend could be the result of an interplay of several effects, such as the relative inputs to the river flow from wet and dry deposition and how each of these may be affected by withdrawal of water for human use in the 3-state region.

By close scrutiny of Figs. 6-9 we can compare the timings of peaks in flow and concentrations of the three components. Water flow peaks in the winter months early each calendar year. Aged rain concentrations peak in the fall months late each calendar year at times tending to coincide with minima in water flow. Ground water concentrations show deep

minima during peak winter flow and broad maxima in midsummer when water flow is generally low. (A scatter diagram of river flow vs. ground water component concentration (not shown) shows a significant negative correlation, whereas no overall correlation of other factor concentrations with river flow is found.) Fresh rain concentration maxima tend to occur early each year near times of peak river flow, although with exceptions, and minima usually occur in midsummer when flow rate is low. The aged rain concentration peaks thus tend to precede fresh rain peaks, but with exceptions. In general, the scrutiny reveals these correspondences in timing of concentration and river flow peaks that are consistent with the recognition of principal components as representing ground water, aged rain, and fresh rain. Figs. 10-12 show temporal variations of the fluxes of three components, i.e. concentrations x flow rate. All show high winter maxima, the result of much more prominent maxima in winter flow rates than the peaks in concentrations.

5. Discussion

Some additional comparisons may contribute to our understanding of the relationship between atmospheric deposition and surface water composition. First, if factor 2 represents ground water, we may attempt to estimate the volume of such ground water in the river. Table 6 presents the average concentrations of Ca^{2+} and hardness in well water of northwest Florida counties in comparison with the corresponding concentrations in factor 2. Factor 2 concentrations are expressed per unit of river water and are about 27% and 23% of the well water averages for Ca^{2+} and hardness respectively. Therefore we may reason that about 25% of the river flow is due to ground water, a result that agrees closely with a field study by Mattraw and Elder [1984] and in approximate agreement with estimates of global ground water flow to rivers [World Resources Institute, 1990].

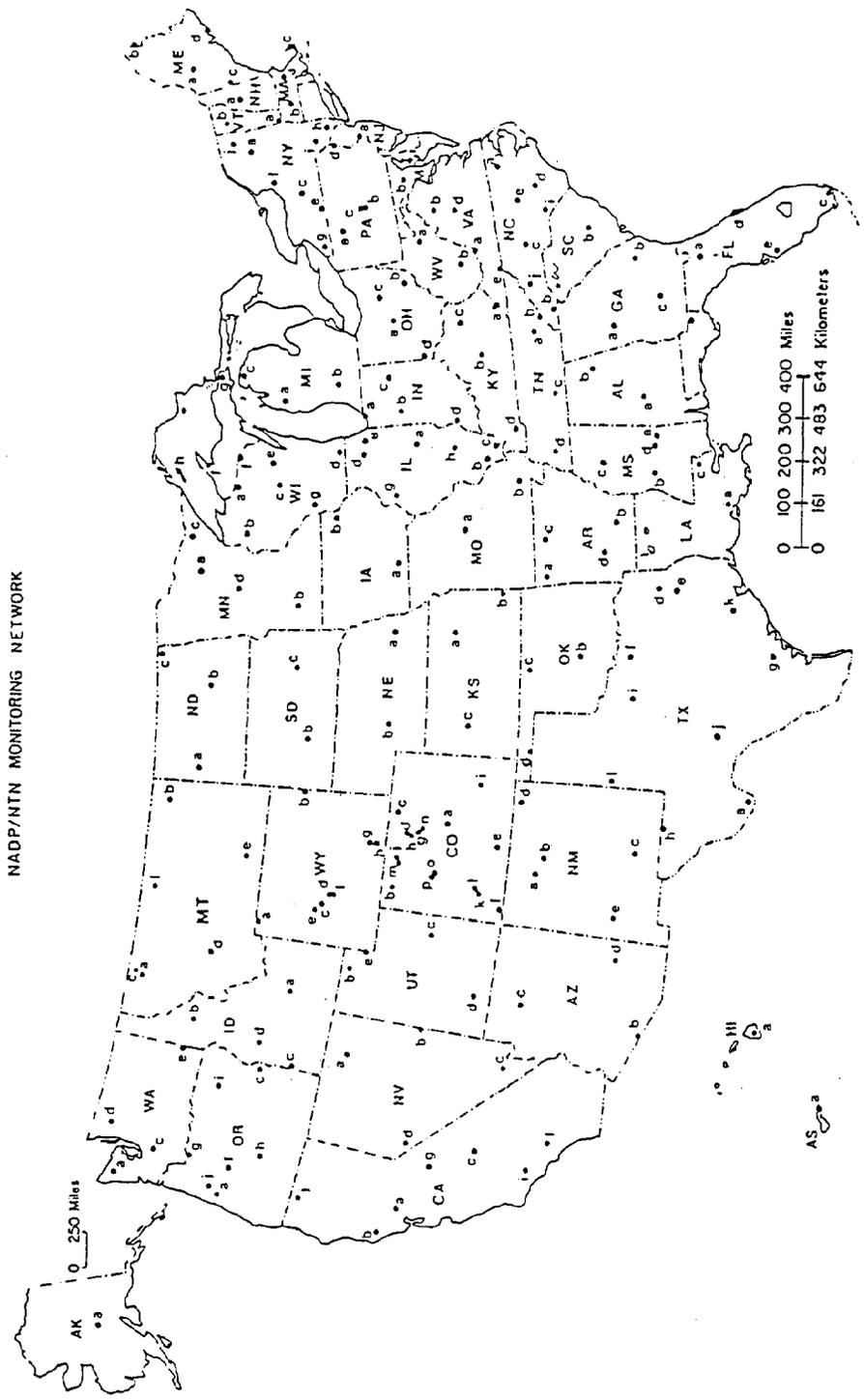
A further comparison of river flow with the study by Mattraw and Elder [1984] indicates general agreement. Table 7 shows that their flow for a one-year study period is identical to the median of USGS measurements for that year and within one standard error of the average. The one-year study also reported flow of total nitrogen (the sum of all dissolved inorganic and the organic nitrogen in unfiltered water). This is again close to the corresponding sum of USGS data. This satisfactory comparison supports the validity of the USGS measurements and our interpretation of them.

The results of this study indicate the great value of long records of atmospheric and surface water monitoring data and the information that can be extracted from them by application of multivariate statistical methods. The present conclusions are, of course, tentative, since not all available data have yet been fully analyzed. Nevertheless, it appears that we are converging onto a means of estimating the extent of nitrate loss or retention by a watershed before transport to an estuary, a challenge that is considered by other experts to be of central importance. For the immediate future, further study of existing data is mandatory, so as to design future measurement programs that will reduce uncertainties in our understanding. These programs could include laboratory experimentation to test the validity of mechanisms suggested by field measurement data, for example mechanisms for NO_3^- transformation, loss, or retention during watershed flow and how these may differ from direct precipitation to a flood plain. Additional field surveys may also be desirable, for example to demonstrate differences between river components that are suggested by the statistical analysis.

Acknowledgements. We are indebted to Curtis Watkins for suggesting that we assess the potential importance of atmospheric nitrate deposition for a north Florida estuary, to J.B. Martin and Linda Geiger for providing U.S. Geological Survey surface water data, and to William Burnett, Peter Cable, Jeffrey Chanton, Paul LaRock, and Jinyou Liang for helpful discussions. Funds for this project were provided by the Florida Department of Environmental Regulation, Office of Coastal Management using funds made available through the National Oceanic and Atmospheric Administration under the Coastal Zone Management Act of 1972, as amended.

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Locations of active sites in the NADP/NTN network as of 10 November, 1989

Table 1. NADP/NTN wet precipitation concentration and deposition summary for eight southeastern states: Florida, Georgia, Alabama, Mississippi, Louisiana, South Carolina, North Carolina, Tennessee

A. Rainwater weekly sampling summary

Site	Location	County	Dates Sampled	Valid Samples	
				Number	% of weeks
<u>Florida</u>					
FLc	Everglades	Dade	800617-890808	253	53
FLe	Verna Well Field	Sarasota	830825-890808	177	57
FLd	Kennedy Space Ctr	Brevard	830802-890808	198	63
FLa	Bradford Forest	Bradford	781010-890725	350	62
FLf	Quincy	Gadsden	840313-890808	168	60
<u>Georgia</u>					
GAb	Bellville	Evans	830426-890815	214	65
GAc	Tifton	Tift	831004-890808	199	65
GAA	Georgia Stn	Pike	781003-890815	371	65
<u>Alabama</u>					
ALb	Sand Mtn	DeKalb	841002-890808	142	56
ALa	Black Belt Substn	Dallas	830831-890815	206	56
<u>Mississippi</u>					
MSa	Meridian	Lauderdale	800415-890808	347	71
MSd	Newton	Newton	861111-890808	---	--
MSc	Coffeeville	Yalobusha	840717-890815	155	58
MSb	Clinton	Hinds	840710-890815	163	61
<u>Louisiana</u>					
LAc	Southeast Res Ctr	Washington	830118-890808	242	71
LAA	Iberia Res Stn	Iberia	821116-890808	244	70
LAB	Hill Farm Res Stn	Claiborne	821116-880126	159	59
<u>South Carolina</u>					
SCb	Santee N Wildlife Ref	Clarendon	841016-890808	141	56
SCa	Clemson	Pickens	790327-860617	270	72
<u>North Carolina</u>					
NCA	Lewiston	Bertie	781031-890815	437	78
NCd	Clinton Crops Res Stn	Sampson	781024-890815	396	70
NCE	Finley Farm	Wake	781003-890815	393	69
NCi	Jordan Creek	Scotland	831018-890801	196	65
NCC	Piedmont Res Stn	Rowan	781114-890808	402	72
NCj	Clingman's Peak	Yancey	851126-890808	96	50
Ncb	Coweeta	Macon	780705-890808	418	72
<u>Tennessee</u>					
TNb	GtSmokyMts N Pk-Elkmont	Sevier	800812-890801	281	60
TNa	Walker Branch Watershed	Anderson	800311-890815	372	76
TNc	Giles County	Giles	841002-890808	151	60
TNd	Hatchie N Wildlife Ref	Haywood	841002-890808	143	57

B. Nitrate and sulfate concentration and deposition averages
 \pm standard error (68% confidence interval)

Site I.D.	NO ₃ ⁻ conc. mg L ⁻¹	NO ₃ ⁻ wet dep. kg ha ⁻¹ yr ⁻¹	NO ₃ ⁻ /SO ₄ ²⁻ wt. ratio
FLc	0.643 \pm .037	4.23 \pm 0.36	0.577 \pm .025
FLe	0.988 \pm .072	6.40 \pm 0.80	0.707 \pm .031
FLd	0.931 \pm .057	6.34 \pm 0.59	0.559 \pm .025
FLa	1.001 \pm .046	7.44 \pm 0.42	0.597 \pm .017
FLf	1.016 \pm .079	6.76 \pm 0.65	0.632 \pm .023
GAb	1.311 \pm .085	6.85 \pm 0.44	0.659 \pm .024
GAc	0.984 \pm .069	5.90 \pm 0.42	0.665 \pm .027
GAa	1.161 \pm .052	7.49 \pm 0.39	0.530 \pm .013
ALb	1.167 \pm .098	6.44 \pm 0.43	0.474 \pm .017
ALa	1.033 \pm .061	7.15 \pm 0.43	0.598 \pm .019
MSa	1.165 \pm .051	10.30 \pm 0.52	0.596 \pm .014
MSd			
MSc	1.118 \pm .072	8.41 \pm 0.57	0.745 \pm .029
MSb	1.163 \pm .077	7.43 \pm 0.52	0.713 \pm .035
LAc	1.140 \pm .070	10.95 \pm 0.65	0.693 \pm .022
LAA	1.230 \pm .066	10.14 \pm 0.69	0.686 \pm .021
LAB	1.221 \pm .073	7.91 \pm 0.56	0.730 \pm .022
SCb	1.034 \pm .070	5.33 \pm 0.49	0.577 \pm .029
SCa	1.579 \pm .075	10.81 \pm 0.60	0.575 \pm .015
NCA	1.491 \pm .073	10.08 \pm 0.47	0.602 \pm .014
NCd	1.408 \pm .067	8.73 \pm 0.42	0.569 \pm .010
NCE	1.618 \pm .074	9.12 \pm 0.42	0.627 \pm .017
NCi	1.318 \pm .085	9.59 \pm 0.67	0.609 \pm .017
NCC	1.689 \pm .065	11.56 \pm 0.55	0.589 \pm .016
NCj	0.986 \pm .184	5.08 \pm 0.52	0.470 \pm .021
NCb	1.107 \pm .045	10.90 \pm 0.46	0.541 \pm .011
TNb	1.254 \pm .061	8.32 \pm 0.43	0.593 \pm .016
TNa	1.580 \pm .063	11.18 \pm 0.48	0.529 \pm .024
TNc	1.212 \pm .073	8.91 \pm 0.64	0.631 \pm .052
TNd	1.033 \pm .061	7.50 \pm 0.54	0.693 \pm .028

Table 2. Comparison of average ion transport in Apalachicola River flow at Chattahoochee with average wet deposition measured at five NADP sites in the Flint and Chattahoochee River basins.

River transport = ion concentration (mg L^{-1}) x measured water flow ($\text{m}^3 \text{sec}^{-1}$).
 Wet deposition = ion concentration (mg L^{-1}) x measured precipitation (mm) x entire basin area (km^2). Units converted to metric kilotons of the ions per year.

Ion		Apalachicola River	NADP Wet Deposition Site					5 Site Averages
			NCb	ALb	GAa	GAc	FLf	
Cl ⁻	Average	86.8	13.9	8.8	12.5	16.0	24.0	15.0
	\pm Std error	± 4.8	± 1.0	± 0.7	± 0.7	± 1.2	± 3.0	± 1.3
	Median	59.4	7.1	5.7	7.4	10.2	12.0	8.5
	Geom. mean	68.7	6.8	5.4	7.2	8.8	11.1	7.9
Na ⁺	Average	98.3	9.3	4.9	8.2	9.0	13.7	8.0
	\pm Std error	± 5.1	± 0.7	± 0.4	± 0.6	± 0.6	± 1.7	± 0.8
	Median	67.0	4.2	3.0	4.5	6.0	6.8	4.9
	Geom. mean	82.4	4.0	2.9	4.4	5.3	6.4	4.6
K ⁺	Average	27.7	1.4	1.0	1.5	3.5	1.5	1.8
	\pm Std error	± 1.7	± 0.1	± 0.1	± 0.2	± 0.9	± 0.2	± 0.3
	Median	17.7	0.8	0.6	0.7	0.9	0.7	0.7
	Geom. mean	21.5	0.7	0.5	0.6	0.9	0.6	0.7
Ca ²⁺	Average	208.5	5.2	3.3	4.4	4.2	4.1	4.2
	\pm Std error	± 8.4	± 0.4	± 0.2	± 0.3	± 0.4	± 0.5	± 0.4
	Median	167.2	3.2	2.1	2.6	2.2	2.3	2.5
	Geom. mean	183.4	3.2	2.3	2.7	2.3	2.1	2.5
Mg ²⁺	Average	22.2	1.5	0.9	1.4	1.6	2.0	1.5
	\pm Std error	± 1.2	± 0.1	± 0.1	± 0.1	± 0.1	± 0.2	± 0.1
	Median	16.1	0.9	0.7	0.9	1.1	1.1	0.9
	Geom. mean	18.5	0.9	0.6	0.9	1.0	0.9	0.9
PO ₄ ³⁻	Average	1.22	<0.51	<0.54	<0.33	<0.66	<0.67	<0.54
	\pm Std error	0.13	0.04	0.05	0.03	0.08	0.07	± 0.05
	Median	0.59	<0.22	<0.37	<0.15	<0.32	<0.30	<0.27
	Geom. mean	0.72	<0.22	<0.31	<0.14	<0.28	<0.30	<0.25

Ion		Apalachicola River	NADP Wet Deposition Site					5 Site Averages
			NCb	ALb	GAa	GAc	FLf	
SO ₄ ²⁻	Average	115.2	100.0	70.3	71.0	46.9	53.8	68.4
	±Std error	±7.6	±4.3	±5.1	±4.1	±3.4	±5.5	±4.5
	Median	77.2	74.2	48.1	44.4	34.2	32.4	46.7
	Geom. mean	87.0	66.6	48.3	44.9	28.5	28.4	43.3
NO ₃ ⁻	Average	26.2	48.3	28.6	33.3	26.2	30.0	33.3
	±Std error	±2.1	±2.1	±1.9	±1.7	±1.8	±2.9	±2.1
	Median	13.8	37.3	22.4	22.2	18.5	17.6	23.6
	Geom. mean	13.8	32.0	20.2	20.0	16.1	15.6	20.8
NH ₄ ⁺	Average	1.18	9.2	8.9	5.9	4.9	4.9	6.8
	±Std error	±0.21	±0.6	±1.3	±0.4	±0.5	±0.6	±0.7
	Median	0.50	5.3	5.1	3.5	2.5	1.9	3.7
	Geom. mean	0.61	4.2	4.5	2.9	2.0	1.7	3.1
Org N (as N)	Average	10.2						
	±Std error	0.8						
	Median	6.4						
	Geom. mean	7.1						
Numbers of samples	*	418	142	371	199	168		

* Numbers of river samples averaged for the different chemical concentrations were Cl⁻ 203, Na⁺ 182, K⁺ 182, Ca²⁺ 182, Mg²⁺ 182, PO₄³⁻ 148, SO₄²⁻ 183, NO₃⁻ 200, NH₄⁺ 94, Org N (organic nitrogen) 152. Wet deposition samples averaged were the same for all ions at each NADP site as indicated.

Water total, km ³ yr ⁻¹ averaged over the period	24.1	75.0	38.6	56.2	45.8	49.0	52.9
	6/79-	6/79- 10/84-	10/84-	6/79- 10/83-	10/83-	3/84-	
	5/80	5/80	8/89	5/80	8/89	8/89	

Table 3. Transport of sulfate and forms of nitrogen in Apalachicola River flow at Chattahoochee compared with atmospheric deposition at five NADP sites. Units: 10^9 moles per year.

Ion	Apalachicola River	Atmospheric Deposition, 5 Site Average		
		Wet only	2xWet = Wet+Dry	
SO ₄ ²⁻	Average	1.20	0.71	1.42
	±Std error	±0.08	0.05	0.09
	Median	0.80	0.49	0.97
	Geom. mean	0.91	0.45	0.90
NO ₃ ⁻	Average	0.42	0.54	1.07
	±Std error	±0.03	0.03	0.07
	Median	0.22	0.38	0.76
	Geom. mean	0.22	0.34	0.67
NH ₄ ⁺	Average	0.066	0.38	0.75
	±Std error	±0.012	0.04	0.07
	Median	0.028	0.20	0.41
	Geom. mean	0.034	0.17	0.34
Org N (as N)	Average	0.73		
	±Std error	0.06		
	Median	0.46		
	Geom. mean	0.51		
ΣN	Average	1.22	0.92	1.82
	Median	0.71	0.58	1.17
	Geom. mean	0.76	0.51	1.01

Table 4. Examples of Factor Analysis of Ion Concentrations at Two NADP Wet Deposition Sites

A. A Florida near coastal site, FLf Quincy, 3 significant factors

Factor loadings (correlation coefficients)				
Variable		Factor 1	Factor 2	Factor 3
Cl ⁻		0.98	0.06	0.07
Na ⁺		0.98	0.08	0.04
Mg ²⁺		0.94	0.27	0.11
Ca ²⁺		0.62	0.64	0.09
SO ₄ ²⁻		0.12	0.87	0.32
NO ₃ ⁻		0.10	0.93	0.21
NH ₄ ⁺		0.11	0.39	0.91
Variance explained, 93%		46%	33%	14%
Factor concentrations (ug L ⁻¹) and ion ratios				
Variable	Const.	Factor 1	Factor 2	Factor 3
Cl ⁻	57±18	1030±13	32±7	29±5
Na ⁺	32±11	607±9	24±4	10±3
Mg ²⁺	-4±2	86±1	12±1	4±1
Ca ²⁺	-20±8	111±46	58±3	6±2
SO ₄ ²⁻	100±68	224±51	843±26	231±20
NO ₃ ⁻	46±34	118±26	562±13	94±10
NH ₄ ⁺	-4±2	21±1	41±1	72±1
Equivalent ratios				
NO ₃ ⁻ /xSO ₄ ²⁻		1.25±0.92	0.52±0.02	0.32±0.04
NH ₄ ⁺ /(NO ₃ ⁻ +xSO ₄ ²⁻)		0.35±0.12	0.085±0.002	0.63±0.05

B. A North Carolina inland site, NCb Coweeta, 2 significant factors

Factor loadings (correlation coefficients)			
Variable		Factor 1	Factor 2
Cl ⁻		0.12	0.91
Na ⁺		0.04	0.86
Mg ²⁺		0.40	0.85
Ca ²⁺		0.68	0.44
SO ₄ ²⁻		0.89	0.10
NO ₃ ⁻		0.89	0.20
NH ₄ ⁺		0.87	0.06
Variance explained, 79%		43%	36%
Factor concentrations (ug L ⁻¹) and ion ratios			
Variable	Const.	Factor 1	Factor 2
Cl ⁻	28±11	52±8	167±3
Na ⁺	23±14	15±10	149±4
Mg ²⁺	-6±1	21±1	19±1
Ca ²⁺	-13±6	106±4	30±2
SO ₄ ²⁻	234±62	1769±44	87±20
NO ₃ ⁻	101±28	887±20	88±9
NH ₄ ⁺	-27±8	204±6	6±2
Equivalent ratios			
NO ₃ ⁻ /xSO ₄ ²⁻		0.39±0.01	1.38±0.56
NH ₄ ⁺ /(NO ₃ ⁻ +xSO ₄ ²⁻)		0.22±0.01	0.14±0.06

Notes: At site NCb several high Ca²⁺ concentrations were not correlated with the factors and were not included in defining them. At both sites K⁺ generally was not strongly correlated with the factors and was not included. xSO₄²⁻ is excess sulfate over 0.25 x Na⁺ (weight), that expected from sea salt. Ion ratios are given as chemical equivalents (+ and - charges).

Table 5. Examples of Factor Analysis of Ion Concentrations in Apalachicola River at Chattahoochee

A. Factor analysis with 11 variables, 6 significant factors

Var.	Factor loadings (correlation coefficients)					
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Cl ⁻	0.78	0.32	0.16	0.12	-0.07	0.05
Na ⁺	0.89	0.25	-0.18	-0.05	-0.03	0.00
Mg ²⁺	0.64	0.65	-0.17	0.03	-0.01	-0.00
SO ₄ ²⁻	0.85	0.06	0.22	-0.15	-0.05	0.16
NO ₃ ⁻	0.08	-0.02	0.98	-0.02	0.13	0.04
K ⁺	0.90	-0.08	0.03	0.00	0.09	0.07
Ca ²⁺	0.09	0.98	0.02	0.06	-0.03	0.05
Hardness	0.14	0.98	-0.00	0.06	-0.03	0.05
OrgN	0.14	0.08	0.05	0.07	-0.02	0.98
NH ₄ ⁺	-0.04	0.10	-0.02	0.99	-0.01	0.07
PO ₄ ³⁻	-0.02	-0.04	0.12	-0.01	0.99	-0.02

B. Factor analysis with 9 variables, 4 significant factors

Variable	Factor loadings (correlation coefficients)			
	Factor 1	Factor 2	Factor 3	Factor 4
Cl ⁻	0.76	0.37	0.19	0.07
Na ⁺	0.89	0.27	-0.05	0.01
Mg ²⁺	0.62	0.53	-0.21	0.07
SO ₄ ²⁻	0.82	0.09	0.23	0.22
NO ₃ ⁻	0.11	-0.08	0.97	0.04
K ⁺	0.86	-0.18	0.02	0.05
Ca ²⁺	0.08	0.98	-0.03	0.03
Hardness (CaCO ₃)	0.14	0.98	-0.04	0.04
OrgN	0.14	0.06	0.04	0.98

C. Factor analysis with 8 variables, 3 significant factors

Variable	Factor loadings (correlation coefficients)			
	Factor 1	Factor 2	Factor 3	
Cl ⁻	0.77	0.30	0.24	
Na ⁺	0.91	0.16	-0.01	
Mg ²⁺	0.67	0.45	-0.24	
SO ₄ ²⁻	0.76	0.10	0.36	
NO ₃ ⁻	0.14	0.02	0.95	
K ⁺	0.83	-0.31	0.09	
Ca ²⁺	0.07	0.98	0.05	
Hardness (CaCO ₃)	0.13	0.98	0.02	
Variance explained, 84%	40%	29%	15%	
Factor concentrations (ug L ⁻¹) and ion ratios				
Variable	Const.	Factor 1	Factor 2	Factor 3
Cl ⁻	-823±225	3936±188	912±114	48±7
Na ⁺	-1492±219	5932±183	650±111	-3±7
Mg ²⁺	185±46	665±38	270±23	-10±2
SO ₄ ²⁻	-2916±475	7717±397	630±241	143±16
NO ₃ ⁻	385±60	387±50	35±31	101±2
K ⁺	550±47	974±40	-222±24	4±2
Ca ²⁺	1194±241	1046±202	9252±122	28±8
(CaCO ₃)	3977±49	5201±410	24152±249	37±16
Equivalent ratios				
NO ₃ ⁻ /xSO ₄ ²⁻		0.048±0.007	0.058±0.059	0.543±0.059
Factor identification		Aged rain	Ground water	Fresh rain

Table 6. Comparison of groundwater component composition in the Apalachicola River with well water in northwest Florida counties (N = number of data averaged)

	River	N	Well	N
Ca ²⁺ ± std error (mg L ⁻¹)	9.94±0.15	141	36.95±0.97	125
Hardness ± std error (mg L ⁻¹) (CaCO ₃)	26.08±0.30	141	114.97±5.42	37

Table 7. Comparison of results calculated from U.S.G.S. Apalachicola River data (June 1979 to May 1980) with published report [Matraw and Elder, 1984]

	Report	U.S.G.S.	
		Median	Average±Std error
Flowrate (km ³ yr ⁻¹)	24.13	24.80	27.98±3.02
Organic and inorganic nitrogen output, kilotons NO ₃ ⁻ yr ⁻¹	82.28	85.19	96.16±8.93

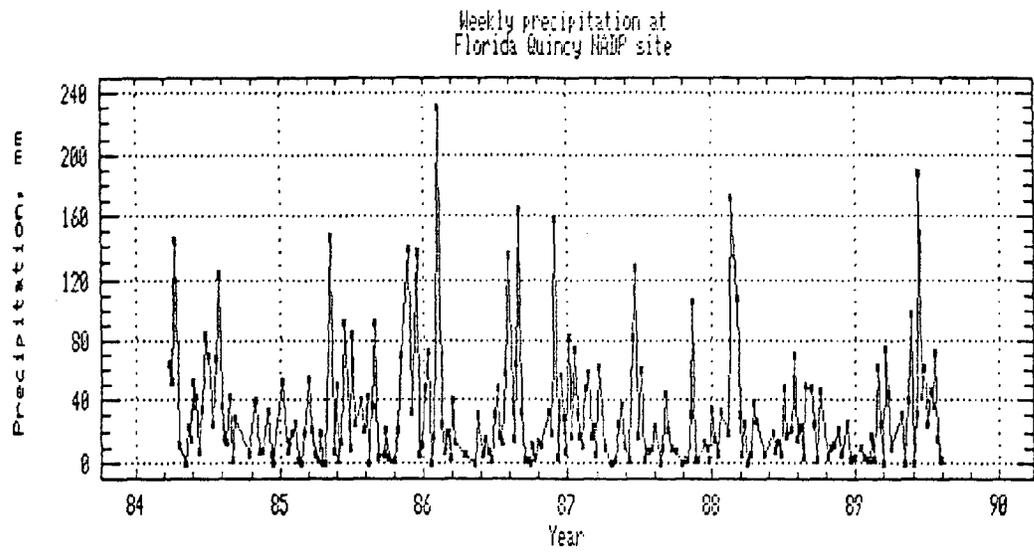


Fig. 1

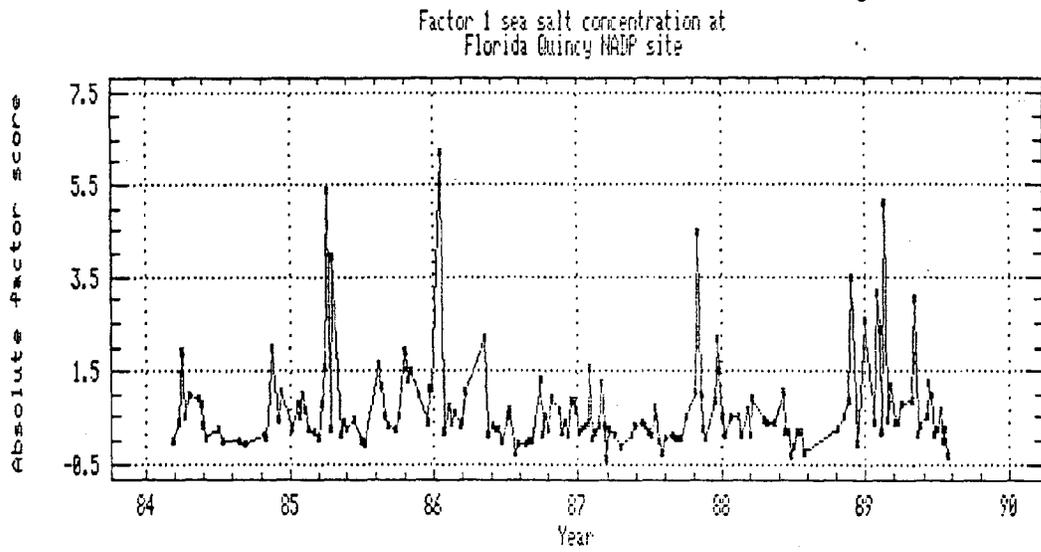


Fig. 2

Factor 1 sea salt deposition at
Florida Quincy NADP site

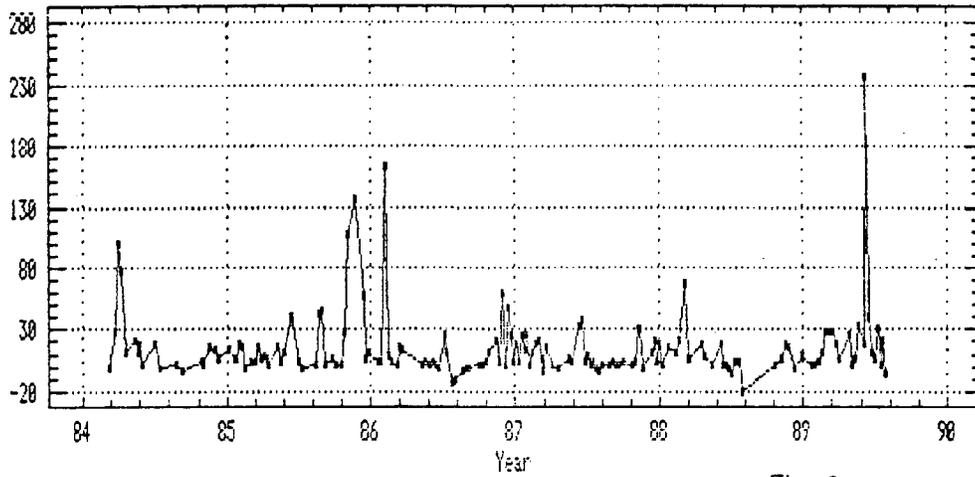


Fig. 3

Factor 2 acid rain deposition at
Florida Quincy NADP site

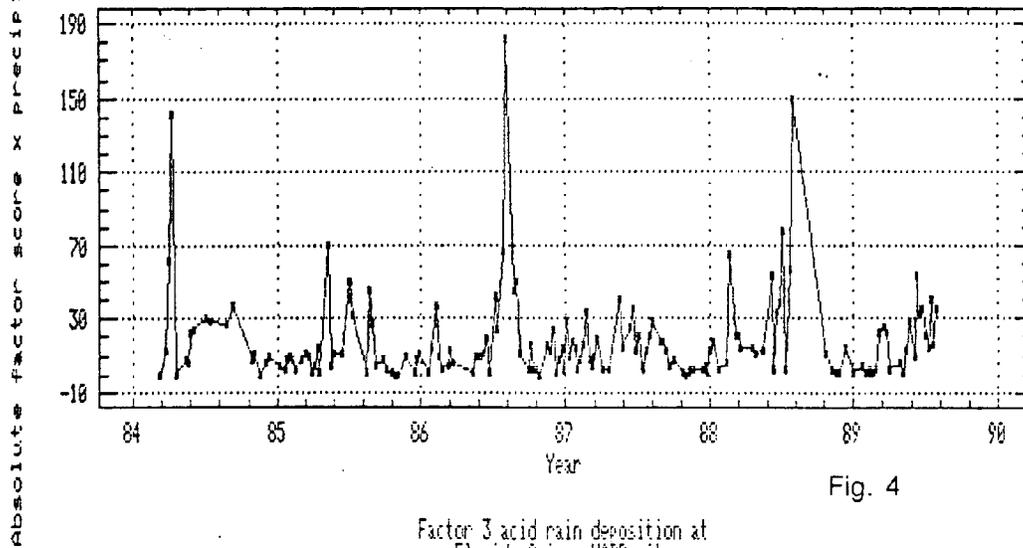


Fig. 4

Factor 3 acid rain deposition at
Florida Quincy NADP site

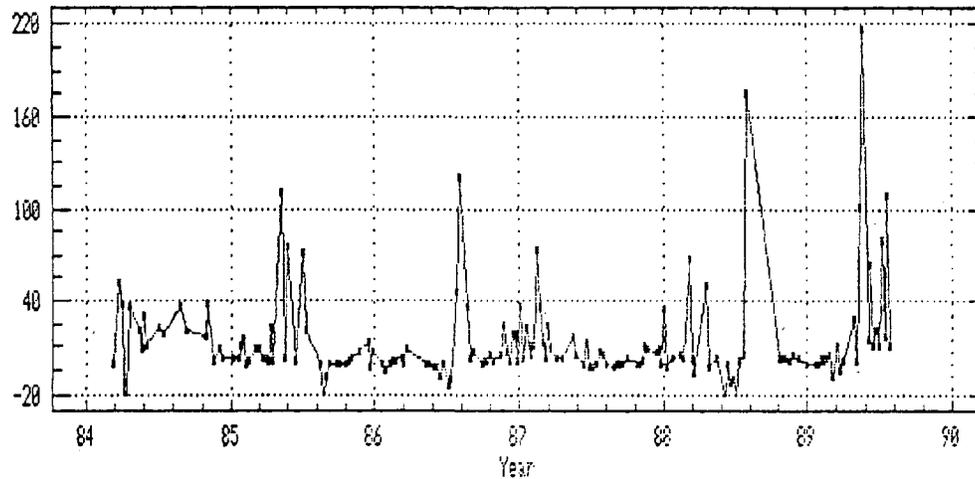


Fig. 5

Apalachicola River flow rate

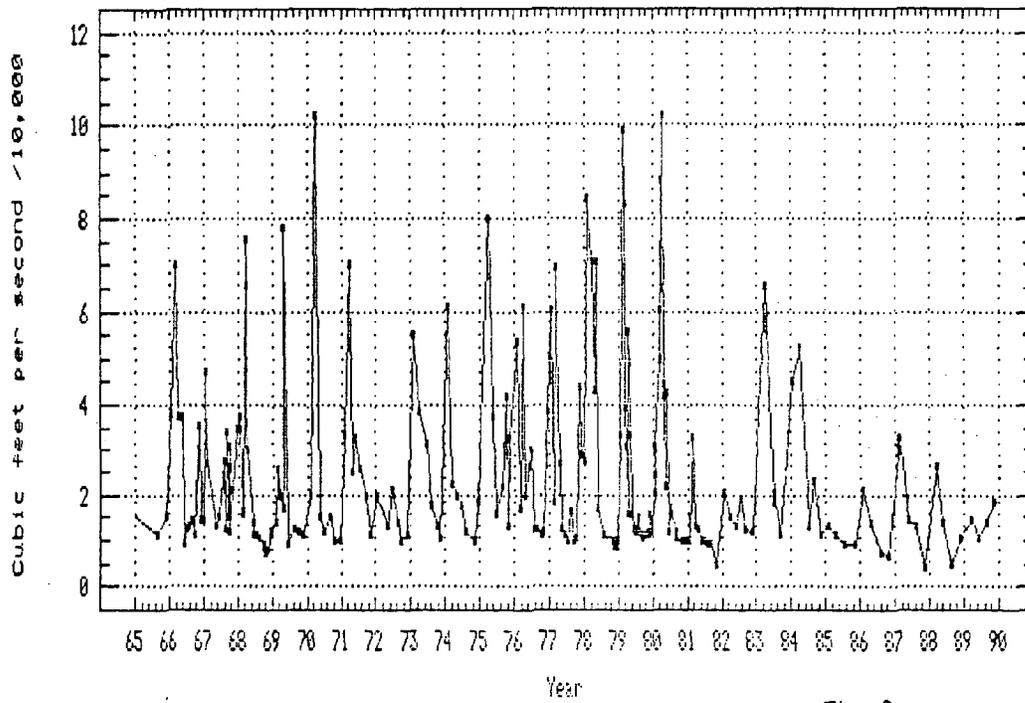


Fig. 6

Apalachicola River factor 1
aged rain concentration

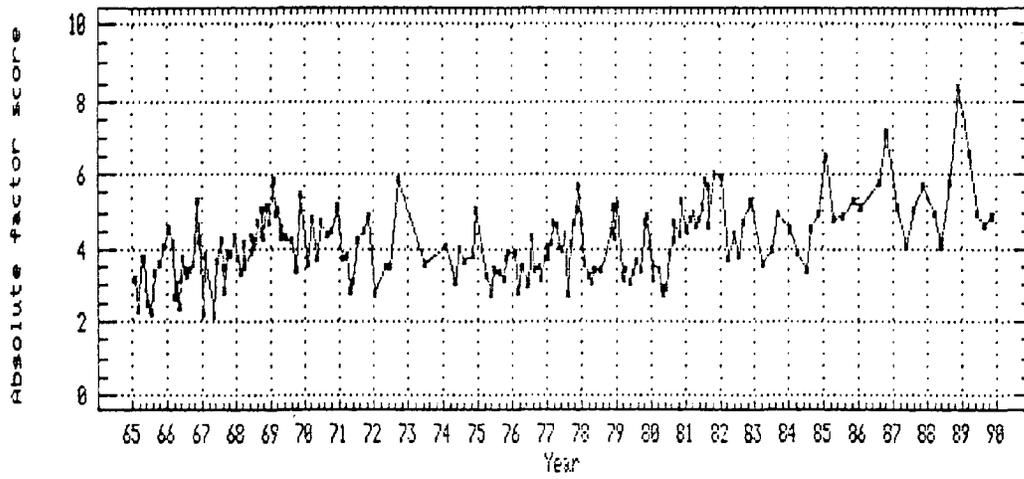


Fig. 7

Apalachicola River factor 2
ground water concentration

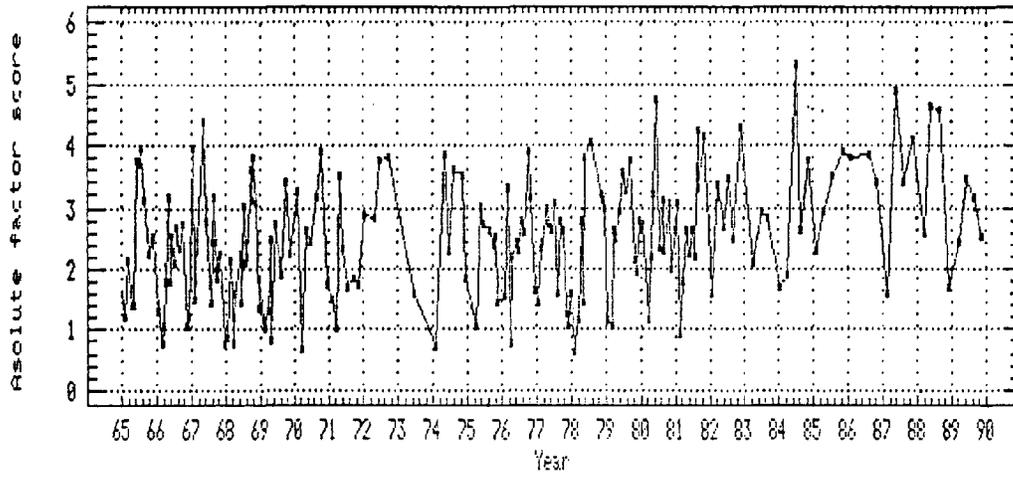


Fig. 8

Apalachicola River factor 3
fresh rain concentration

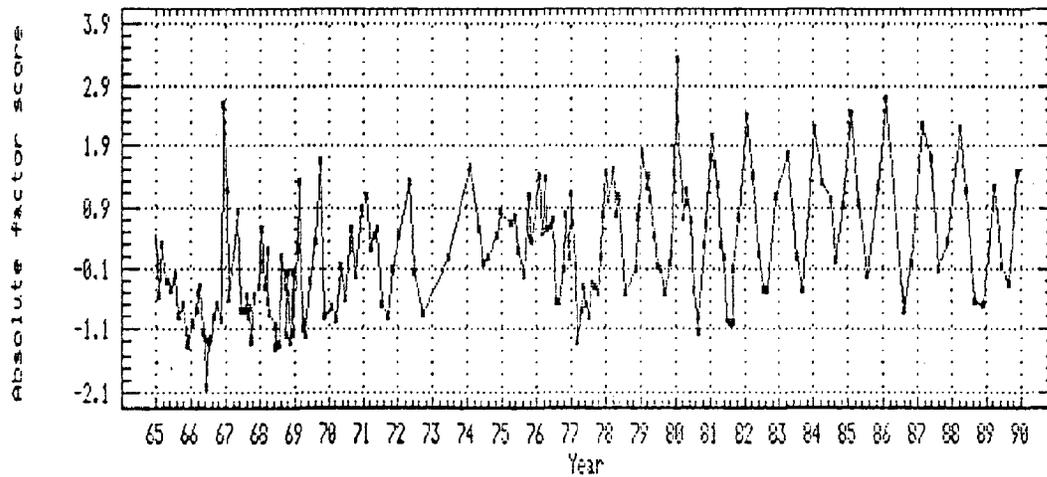


Fig. 9

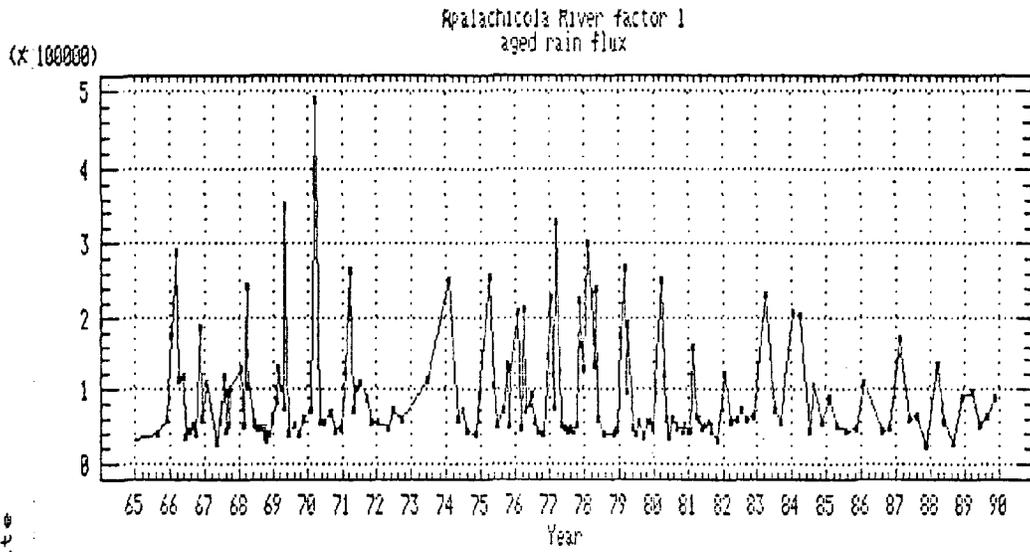


Fig. 10

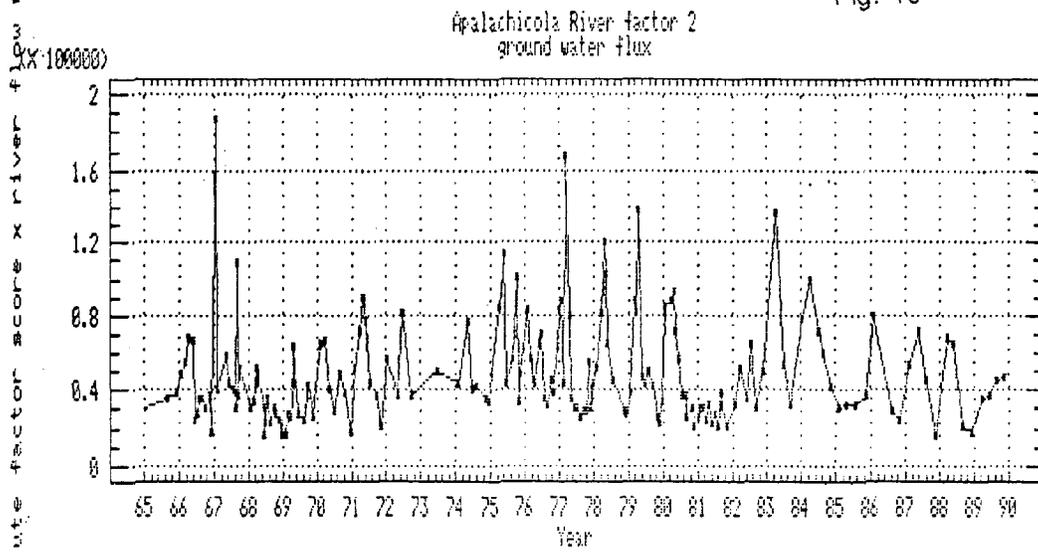


Fig. 11

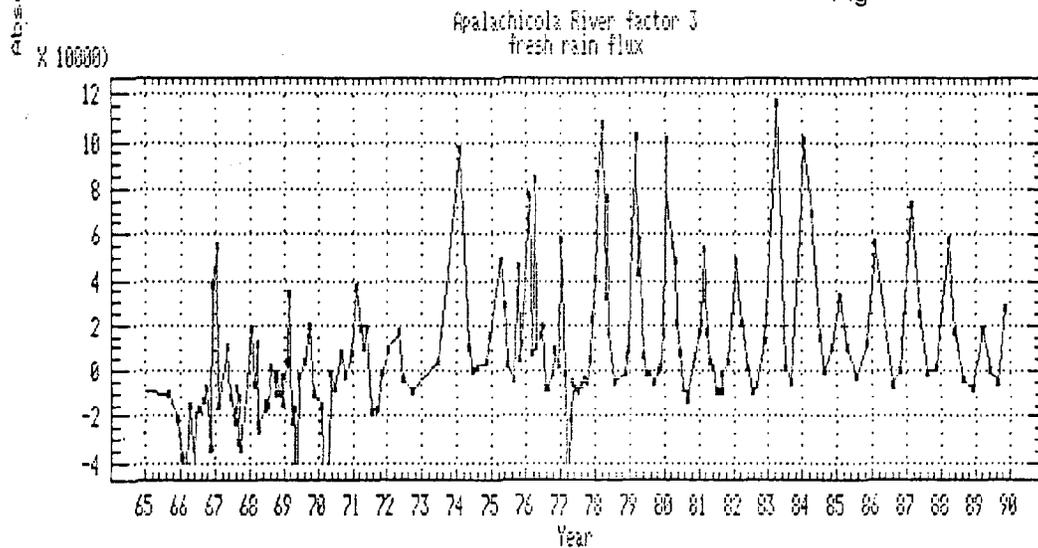


Fig. 12

Acid Deposition Relationships in Florida and Southeastern U.S.A.

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Abstract

The general uniformity of yearly average nitrate and sulfate deposition fluxes from acid air pollution over southeastern U.S.A. obscures possibly important differences on a smaller geographic scale and on seasonal or shorter time scales. A statistical analysis of weekly NADP wet chemical data from 18 sites over most of an eight state region has been carried out. Groupings of sites are identified that indicate uniformity over a state-wide scale, but not larger, in correlations based on short term variability in acid air pollution deposition fluxes. Thus, groups of sites within this geographic scale could serve as predictors of deposition on a shorter time scale than is possible based on long term averages of deposition data. For deposition to the watershed of the Apalachicola River, both meteorological conditions and transport from pollution sources appear to control deposition fluxes of nitrate and sulfate acid air pollutants.

1. Introduction

Rainfall chemistry data from the National Acid Deposition Program can be examined statistically to determine correlations between sites in the magnitudes of their acid air pollutant deposition fluxes. The finding of correlations among groups of sites can facilitate prediction at any location within the area of a group of sites. By comparing correlations in deposition for acid pollutants with those for sea salt or just rainfall, a judgement can be made about the factors that may influence the deposition, for instance meteorological factors that lead to rain or sources of emissions that are scavenged by the rain.

In order to improve prediction of nitrate from acid deposition to the watershed of the Apalachicola River, a statistical comparison of sites in southeastern U.S.A. was carried out. NADP operated 30 sites in eight southeastern states, shown in Table 1 and Fig. 1, the earliest reporting data starting in 1978. As long term averages, the concentrations and deposition fluxes of nitrate and the ratios of nitrate to sulfate do not vary greatly from site to site. Although there is a tendency for sites near urban or industrial centers to be higher than further away, comparing long term averages does not give insights concerning how adjacent sites may be correlated for samples collected concurrently. That is, possible similarities in seasonal or shorter term deposition variations at different sites in the region are not revealed by comparing long term averages. Yet, such similarities may aid in predicting deposition and in judging the relative influences of meteorological and pollution source processes on deposition fluxes.

With special attention to acid deposition in Florida, 18 NADP sites in seven states were compared statistically in a procedure based on factor analysis. The sites, at locations shown in Fig. 1, are listed in Tables 2, 3, and 4. For these sites NADP reported weekly rainfall amounts and chemical concentration measurements for at least 300 weeks (6 years) to mid 1989. Of these weeks, an average \pm standard deviation of 66 ± 7 % had data reported. The remaining weeks of missing data may have been weeks without rain or with operational problems at the sites. Although there were no weeks when all 18 sites reported data, yet for most weeks data were reported for the great majority of sites. This data set was thus suitable for comparison of deposition fluxes between sites.

2. Methods

In order to examine in detail the relationships between sites, we have employed factor analysis in a procedure analogous to that used for resolving principal components of chemical constituents at any one site [Winchester and Fu, 1990]. However, the present procedure, based on a data matrix of variables vs. weeks of data, uses sites rather than chemical constituents as the variables, so that the fluxes of a chosen chemical variable are compared over the 18 sites in 300 weeks of data record. Groupings of sites into principal components express their high degree of correlation in short term variability.

Our procedure contains certain improvements over the only other similar analysis of wet deposition monitoring data known to us [Eder, 1989]. The first improvement is a way to avoid the assumption made by Eder that all sulfate is an acid air pollutant, in view of some sulfate originating with sea salt. In our procedure we perform an initial factor analysis of the chemical data at each site to resolve its principal components and then select one of these (e.g. sea salt or acid pollution) for comparison between sites in the 18 site region by a second factor analysis. In this way, the data for two or more chemical variables are pooled for greater precision of data analysis, and those that may be derived from different sources (e.g. sulfate from sea salt and pollution) are properly apportioned between components. The factor scores from the initial analysis are used as input data for the second analysis.

Another is our use of deposition flux (concentration x rainfall amount) instead of concentration in rain water as input data for the analysis as was done by Eder. Moreover, noting their log-normal distributions, deposition data were logarithmically transformed for the factor analysis of sites vs. weeks of measurements (though not for the initial factor analysis of chemical data at each site, since normal and log-normal distributions described the data equally well).

Still another improvement is devising a procedure that allows use of all weeks of data, including weeks when some sites did not report. Eder pooled his weekly data into months in order to increase the percentage of time that all sites in the network reported data, causing a 4-fold reduction in length of data record. In our procedure we introduced a pseudo detection limit for non-reporting weeks (instead of zero deposition which would preclude logarithmic transformation), choosing a value below the lowest finite data reported at the sites.

In the procedure we carried out separate analyses of three kinds of data:

First, the amount of weekly precipitation at each site was examined in order to identify groups of sites that may vary in similar ways. No initial factor analysis was needed, since the weekly precipitation amounts could be input directly to the factor analysis of 18 site data.

Second, by an initial factor analysis of data at each site, a sea salt component was identified. The factor scores for this component were entered into a data array of 18 sites vs. the 300 weeks of record, and a second factor analysis was performed to identify groups of correlated sites in sea salt deposition. It should be noted that a model is assumed in which correlations between groups are absent, i.e. a linear "mixing" model of independently varying components. Although all sites may to some degree be intercorrelated, the procedure resolves groups of the most highly correlated sites.

Third, the same procedure was applied to a principal component from the initial factor

analysis that resembled acid rain pollutants (mainly nitrate and sulfate), leading by the second factor analysis to identifying groups of correlated sites in acid pollution deposition fluxes.

The first factor analysis of deposition data at each site included a dummy sample with zero deposition for each constituent (variable). The data were standardized by subtracting the mean and dividing by the standard deviation of each variable, then factor analysis was carried out with varimax rotation. The factor scores, having a zero mean for each variable, were increased to "absolute" factor scores by subtracting the (negative) score for the dummy sample. These absolute factor scores were used as input to the second factor analysis. In this case, missing data were replaced by a pseudo detection limit, and all scores were reexpressed as equivalent Na or NO_3^- fluxes (for sea salt and acid pollution components, respectively), before logarithmic transformation for the factor analysis.

By carrying out these three separate analyses of precipitation amount, sea salt deposition, and acid pollution deposition, we are better able to judge whether deposition may be governed mainly by meteorological conditions that lead to rainfall or whether the characteristics of sources, acidic pollution or natural sea salt, also may contribute to the regional variation of deposition fluxes.

3. Results

Tables 2, 3, and 4 present factor loadings for three separate factor analyses of precipitation, sea salt, and acid pollution deposition fluxes at the 18 NADP sites. Calculations for various numbers of factors were carried out, but those for six factors were judged to be the most informative for indicating groups of highly correlated sites. For each analysis, the factors (principal components) are arranged in decreasing order (F1 to F6) in explaining variance. Thus, F1 represents a component that is highly variable in deposition flux, from very high to very low over the 300 weeks of data. In all three analyses F1 is a group of sites in North Carolina, suggesting meteorological control in this state situated between coastal and continental weather influences. In contrast, sites in peninsular Florida are assigned to lower variance factors, suggesting less variable meteorological conditions in its relatively more maritime climate.

Of special interest for acid pollution deposition the Apalachicola River watershed are sites in Georgia, Alabama, and Mississippi. To the extent that they are well correlated they may, as a group, serve as predictors of short term variability in deposition anywhere in their region, not merely of a long term average. For acid deposition fluxes Table 4 shows them mainly assigned to factor F2, quite highly variable and rather well correlated, so that weeks of high deposition fluxes at one are likely to be high at the others as well. The lowest loadings of sites in this group, Ga b and Ms a, lie at the eastern and western extremities of their region as shown in Fig. 1.

Deposition of sea salt also shows high correlation among this group of sites (F2 in Table 3). However, for precipitation itself (the amount of rainfall) the correlation between sites is much weaker (F2, F3, and F4 in Table 2). This distinction between fluxes of precipitation and of the sea salt and acid air pollutants scavenged by precipitation indicates that the deposition fluxes cannot be predicted by rainfall alone. Instead, the concentrations of these chemical substances in air must also be important. Since Tables 3 and 4 show similar factor assignments for sea salt and acid pollution, both may be distributed over the region after transport from their respective sources. Yet this region appears to comprise only parts of two states rather than the southeast as a whole.

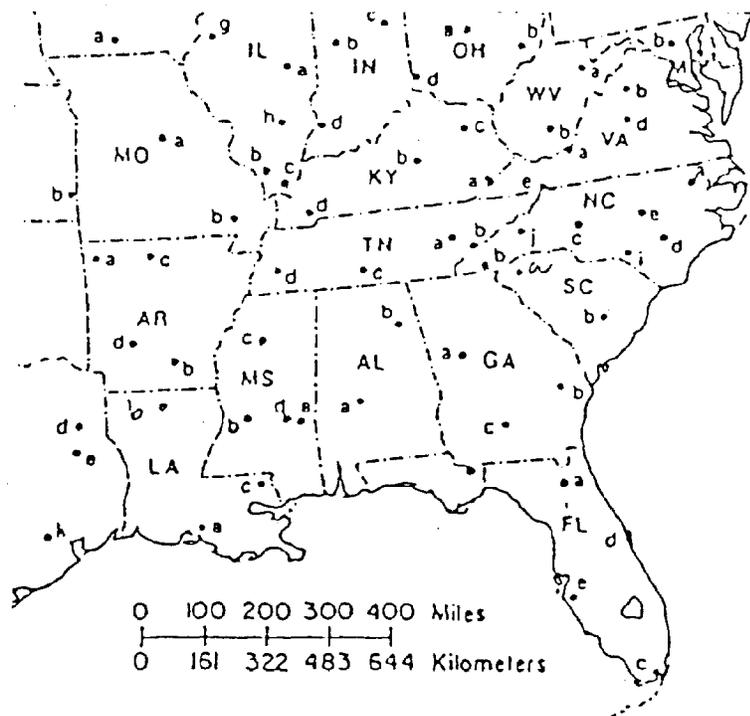
4. Discussion

Comparison of long term average deposition fluxes of nitrate and sulfate pollution shows little variation, although higher than average fluxes are found near urban and industrial centers. But the general uniformity of fluxes over the southeastern U.S.A. obscures possibly important differences on a smaller geographic scale and on seasonal or shorter time scales. The results of the present statistical comparison of wet deposition fluxes from weekly NADP data indicates considerable correlation between sites on a state-wide scale. For estimating likely deposition at a specific locality, for instance of acid air pollution nitrate and sulfate within the watershed of the Apalachicola River system, a group of well correlated sites mainly in western Georgia and Alabama can serve as better predictors than sites over a larger region. However, it is equally clear that smaller scale geographic differences in deposition fluxes within this 2-state region cannot be discerned based on 6 years of weekly NADP wet deposition measurements.

The controlling influences on deposition fluxes may be both meteorological and chemical, i.e. physical processes leading to rainfall and the locations of pollution sources and transport pathways of their emissions. By comparing similar statistical analyses of rainfall, sea salt deposition, and acid pollution deposition, a judgement can be reached that both influences are important for pollution deposition to the watershed of the Apalachicola River system.

5. References

- Eder B. [1989]. A principal component analysis of SO_4^{2-} precipitation concentrations over the eastern United States. *Atmos. Environ.* 23, 2739-2750.
- Winchester J.W. and Fu Ji-Meng [1990]. Atmospheric Deposition of Nitrate and Its Transport to the Apalachicola Bay Estuary in Florida. (This report, Paper 1).



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Fig. 1. NADP sites in the southeastern U.S.A. Of these, 18 with data extending over at least 300 weeks (6 years) were selected for data analysis.

Table 1. Nitrate and sulfate concentration and deposition averages
 \pm standard error (68% confidence interval)

Site I.D.	NO_3^- conc. mg L^{-1}	NO_3^- wet dep. $\text{kg ha}^{-1} \text{yr}^{-1}$	$\text{NO}_3^-/\text{SO}_4^{2-}$ wt. ratio
FL c	0.643 \pm .037	4.23 \pm 0.36	0.577 \pm .025
FL e	0.988 \pm .072	6.40 \pm 0.80	0.707 \pm .031
FL d	0.931 \pm .057	6.34 \pm 0.59	0.559 \pm .025
FL a	1.001 \pm .046	7.44 \pm 0.42	0.597 \pm .017
FL f	1.016 \pm .079	6.76 \pm 0.65	0.632 \pm .023
GA b	1.311 \pm .085	6.85 \pm 0.44	0.659 \pm .024
GA c	0.984 \pm .069	5.90 \pm 0.42	0.665 \pm .027
GA a	1.161 \pm .052	7.49 \pm 0.39	0.530 \pm .013
AL b	1.167 \pm .098	6.44 \pm 0.43	0.474 \pm .017
AL a	1.033 \pm .061	7.15 \pm 0.43	0.598 \pm .019
MS a	1.165 \pm .051	10.30 \pm 0.52	0.596 \pm .014
MS d			
MS c	1.118 \pm .072	8.41 \pm 0.57	0.745 \pm .029
MS b	1.163 \pm .077	7.43 \pm 0.52	0.713 \pm .035
LA c	1.140 \pm .070	10.95 \pm 0.65	0.693 \pm .022
LA a	1.230 \pm .066	10.14 \pm 0.69	0.686 \pm .021
LA b	1.221 \pm .073	7.91 \pm 0.56	0.730 \pm .022
SC b	1.034 \pm .070	5.33 \pm 0.49	0.577 \pm .029
SC a	1.579 \pm .075	10.81 \pm 0.60	0.575 \pm .015
NC a	1.491 \pm .073	10.08 \pm 0.47	0.602 \pm .014
NC d	1.408 \pm .067	8.73 \pm 0.42	0.569 \pm .010
NC e	1.618 \pm .074	9.12 \pm 0.42	0.627 \pm .017
NC i	1.318 \pm .085	9.59 \pm 0.67	0.609 \pm .017
NC c	1.689 \pm .065	11.56 \pm 0.55	0.589 \pm .016
NC j	0.986 \pm .184	5.08 \pm 0.52	0.470 \pm .021
NC b	1.107 \pm .045	10.90 \pm 0.46	0.541 \pm .011
TN b	1.254 \pm .061	8.32 \pm 0.43	0.593 \pm .016
TN a	1.580 \pm .063	11.18 \pm 0.48	0.529 \pm .024
TN c	1.212 \pm .073	8.91 \pm 0.64	0.631 \pm .052
TN d	1.033 \pm .061	7.50 \pm 0.54	0.693 \pm .028

Table 2. Factor loadings based on weekly rainfall amount
(73.2 % of total variance explained)

Site I.D.	Factor					
	<u>F1</u>	<u>F2</u>	<u>F3</u>	<u>F4</u>	<u>F5</u>	<u>F6</u>
NC a	0.85					
NC c	0.73			(0.37)		
NC d	0.81					
NC e	0.85					
NC i	0.77	(0.33)				
AL a		(0.31)	0.57	0.51		
GA a						0.99
GA c		0.79				
MS a			0.50	0.54		
GA b		0.80				
LA c			0.83			
LA a			0.85			
FL d					0.69	
FL a		0.67			0.42	
FL e					0.72	
TN b				0.84		
TN a	0.43			0.67		
FL c					0.82	
Var. %	20.8	12.5	12.0	11.3	10.9	5.7

Note: Factor loadings are correlation coefficients between sites and factors. Loadings >0.4 are most significant, 0.3-0.4 may be marginally significant (indicated by parentheses) and <0.3 are least significant and are indicated by blanks in the table.

Table 3. Factor loadings based on weekly deposition flux of sea salt component
(62.3 % of total variance explained)

Site I.D.	Factor					
	<u>F1</u>	<u>F2</u>	<u>F3</u>	<u>F4</u>	<u>F5</u>	<u>F6</u>
NC a	0.76					
NC c	0.64	(0.31)				
NC d	0.81					
NC e	0.80					
NC i	0.76					
AL a		0.44	0.46	(0.34)		
GA a		0.50		(0.30)		
GA c		0.76				
MS a		(0.38)	0.56			
GA b		0.69				
LA c		(0.31)	0.66			
LA a			0.85			
FL d						0.63
FL a		0.48			0.56	
FL e					0.77	
TN b				0.81		
TN a				0.78		
FL c						0.82
Var. %	16.8	11.7	10.5	9.4	7.2	6.8

Note: See caption to Table 2.

Table 4. Factor loadings based on weekly deposition flux of acid rain component
(61.6 % of total variance explained)

Site I.D.	Factor					
	<u>F1</u>	<u>F2</u>	<u>F3</u>	<u>F4</u>	<u>F5</u>	<u>F6</u>
NC a	0.77					
NC c	0.67					
NC d	0.74					
NC e	0.71					
NC i	0.72					
AL a		0.69	(0.38)			
GA a		0.65				
GA c		0.64		(0.35)		
MS a		0.52	0.46			
GA b	(0.36)	0.47				
LA c			0.79			
LA a			0.78			
FL d				0.74		
FL a				0.74		
FL e				0.53		0.45
TN b					0.78	
TN a	(0.33)				0.66	
FL c						0.88
Var. %	16.8	11.0	9.8	8.9	8.3	6.7

Note: See caption to Table 2.

Comparison of Acid Deposition and Surface Transport in Three Watersheds of North Florida

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Abstract

Comparison of sulfate, different forms of nitrogen, and other chemical compositions between atmospheric deposition and surface transport has been made for the Apalachicola, Sopchoppy, and Ochlockonee Rivers in north Florida by mass balance and multivariate statistical methods. The results show that the chemical compositions of all rivers, in general, can be represented as a mixture of three groups of dissolved constituents. One, containing nitrogen and sulfate, resembles the composition of rain water; another, containing calcium, resembles ground water; and a third, containing chloride and sodium, resembles sea salt. Total mass flow of nitrogen in all three rivers agrees well with the average atmospheric deposition to their watersheds, suggesting that the atmosphere is the major source of nitrogen to their watersheds. However, for Cl^- , Na^+ , Mg^{2+} , Ca^{2+} , K^+ , PO_4^{3-} , the calculated atmospheric contribution is much less than their river fluxes, implying that surface processes, including urban, agricultural, and industrial releases and weathering of soil, are dominant. The three rivers differ considerably in types of watersheds. The finding that atmospheric nitrogen deposition fluxes agree well with transport of nitrogen by river flow and that river nitrate is largely correlated with non-seasalt sulfate implies that on the average the watersheds are in a quasi steady state and that additional surface sources or sinks are relatively small. Moreover, the high relative river flow of organic nitrogen, which is not present in rain water, suggests that it may be a watershed transformation product of atmospheric inorganic nitrogen.

1. Introduction

The present study represents an extension of our previous analysis of Apalachicola River composition data [Winchester and Fu, 1990]. The results from that single watershed system leave unresolved a question whether surface sources of nitrate or other nitrogen species could be large, but by coincidence a mass balance agreement between atmospheric deposition and river flux could still be achieved. Therefore, we have undertaken similar analyses of two additional north Florida rivers that have very different watershed characteristics, the Sopchoppy, that drains a wetland without agricultural, urban, or industrial activity, and the Ochlockonee upstream of Lake Talquin, where agricultural activity may be present. Although we have not yet carried out a survey of various kinds of human activity in these or the Apalachicola River watersheds, qualitatively they differ considerably, and a comparison may indicate whether these differences could lead to observable differences in their flows of nitrogen compounds toward estuaries of the Gulf of Mexico.

2. Methods

Two methods have been used for comparison of the three watersheds, a mass balance between atmospheric deposition and river flow and resolution of principal components by factor analysis according to a linear mixing model. In our previous study of the Apalachicola River system, the first method indicated that atmospheric deposition was sufficiently large to account

for nitrogen in the river, and the second indicated that most river nitrate was correlated with sulfate, suggesting that both are principally of atmospheric origin. We have now applied these two methods to two additional rivers.

In all three rivers, mainly three chemical forms of nitrogen have been routinely measured several times per year for more than 20 years by the U.S. Geological Survey (USGS): NO_3^- , NH_4^+ , and organic nitrogen. The flows of these and other chemical species can be compared with the record of atmospheric deposition at sites in or near the watersheds, especially at five sampling sites of the National Atmospheric Deposition Program (NADP) that have operated mainly during the 1980's. The NADP data show that NO_3^- and NH_4^+ are the major forms of nitrogen in atmospheric wet deposition, but the river data show substantial amounts of organic nitrogen, usually in excess of inorganic nitrogen concentrations. From the river and atmospheric data the deposition and river surface transport fluxes can be calculated:

$$\text{River surface transport} = \text{ion concentration (mg L}^{-1}\text{)} \\ \times \text{river flow (m}^3 \text{sec}^{-1}\text{)}$$

$$\text{Wet deposition} = \text{ion concentration (mg L}^{-1}\text{)} \\ \times \text{measured precipitation (mm)} \\ \times \text{entire basin area (km}^2\text{)}$$

The methods used for factor analysis of both rain water and river water have been described previously [Winchester and Fu, 1990]. Factors (principal components) are resolved into groups of measured chemical variables that are highly correlated. These groups may be recognized as representing components in the atmosphere or surface water that have been mixed in varying proportions in the different samples but otherwise are relatively constant in their individual compositions. In the Apalachicola River we recognized the three significant components to represent ground water (high in Ca), aged rain water (containing sulfate and smaller amounts of nitrate than measured in rain water), and relatively fresh rain water (with nitrate and sulfate in proportions closer to that in rain water).

3. Results

In Table 1, mass flows of ions in two rivers, Sopchoppy and Ochlockonee, are compared with atmospheric deposition fluxes at the nearest NADP site. As for the Apalachicola River [Winchester and Fu, 1990], the first six ions show greater flows in river water than can be accounted for by atmospheric deposition, wet + dry estimated to be twice wet only. For SO_4^{2-} atmospheric deposition is similar to river flow and for NO_3^- and NH_4^+ atmospheric deposition is much greater.

Table 2 shows the comparison of sulfate and forms of nitrogen for the three rivers more explicitly after conversion of metric kiloton to mole units. For sulfate, considering the standard errors of the mean values listed, no significant difference is seen between atmospheric deposition and river flow. For total nitrogen in all its chemical forms the same is true, with agreement well within a factor of 2 between atmospheric deposition and river flow. However, in all three rivers organic nitrogen greatly exceeds nitrate and ammonium ion concentrations, whereas in the atmosphere organic nitrogen is undetectable and therefore not routinely monitored by NADP. The mass balance suggests that much of the atmospheric input of inorganic nitrogen undergoes transformation to organic nitrogen in the watershed.

Further insights into relationships among species of nitrogen and other ions in the

watershed can be gained from correlations revealed by factor analysis. Tables 3 and 4 present results for the Sopchoppy and Ochlockonee Rivers that may be compared with those of the Apalachicola [Winchester and Fu, 1990]. In each river three significant factors are found that account for most of the concentration of each ion and for most of overall data variance. These factors resemble those for the Apalachicola River and suggest that they represent mixing of ground water (high Ca), relative saline water (high Cl and Na), and rainwater (high sulfate and nitrate, though nitrate being lower than in rain water implies aging in the watershed).

4. Discussion

The three rivers show agreement in mass balance and factor analysis relationships that support our previous conclusion that river borne nitrogen can be accounted for largely by atmospheric deposition. They also show that organic nitrogen always exceeds inorganic forms. The temporal variation in the ratio organic nitrogen to total nitrogen in the Apalachicola River from 1970 through 1989 is shown in Fig. 1 to exhibit marked summer maxima. By factor analysis we find that organic nitrogen is not well correlated with inorganic nitrogen, as pointed out previously for the Apalachicola River, implying time delays or seasonal dependence in biochemical transformations that can remove correlations.

The most "natural" of the three rivers, the Sopchoppy, often has nitrate below detection limit, but factor analysis shows a ratio of river nitrate to excess non-seasalt sulfate of 0.042 in the most sulfate-rich component, in good agreement with the Apalachicola. However, the Ochlockonee ratio is larger. Further study of specific differences between watersheds that could underlie these observations should be carried out.

This study has shown that a judgement can be made whether additional surface sources of nitrogen to the rivers is likely to be large compared to atmospheric deposition. The agreement among three rivers, having different watershed characteristics in mass balance and ionic correlations revealed by factor analysis, suggests that additional surface sources of nitrogen are likely to be small. However, a research program to measure their magnitudes directly, as well as to survey land use and other practices in the watersheds that may affect nitrogen transport to coastal estuaries in Florida, would be desirable.

5. Reference cited

Winchester J.W. and Fu Ji-Meng [1990]. Atmospheric Deposition of Nitrate and Its Transport to the Apalachicola Bay Estuary in Florida. (This report, Paper 1).

Table 1. Comparison of average ion transport in flow of Sopchoppy River, Wakulla County, with wet deposition measured at Quincy, Florida, NADP site (FLf).

River transport = ion concentration (mg L⁻¹) x measured water flow (m³ sec⁻¹).

Wet deposition = ion concentration (mg L⁻¹) x measured precipitation (mm) x entire basin area (km²).

Units converted to metric kilotons of the ions per year.

Ion		Sopchoppy River	NADP Wet Deposition	Ochlockonee River	NADP Wet Deposition
Cl ⁻	Average	0.66	0.14	11.2	1.59
	±Std error	±0.08	±0.02	±0.85	±.20
	Median	0.28	0.07	6.3	0.80
Na ⁺	Average	0.27	0.08	6.96	0.91
	±Std error	±0.03	±0.01	±0.51	±0.11
	Median	0.11	0.04	4.00	0.45
K ⁺	Average	0.020	0.009	1.51	0.10
	±Std error	±0.002	±0.001	±0.15	±0.02
	Median	0.007	0.004	0.69	0.04
Ca ²⁺	Average	0.66	0.024	3.19	0.27
	±Std error	±0.08	±0.003	±0.22	±0.03
	Median	0.28	0.013	2.06	0.15
Mg ²⁺	Average	0.05	0.012	1.30	0.13
	±Std error	±0.005	±0.001	±0.09	±0.02
	Median	0.03	0.007	0.84	0.07
PO ₄ ³⁻	Average	0.008	<0.0040	0.066	<0.044
	±Std error	±0.002	±0.0004	±0.008	±0.005
	Median	0.002	<0.0018	0.043	<0.020
SO ₄ ²⁻	Average	1.03	0.32	4.62	3.57
	±Std error	±0.19	±0.03	±0.55	±0.37
	Median	0.62	0.19	2.14	2.15
NO ₃ ⁻	Average	0.008	0.18	1.34	1.99
	±Std error	±0.002	±0.02	±0.12	±0.19
	Median	0.002	0.10	1.01	1.16
NH ₄ ⁺	Average	0.006	0.029	0.079	0.32
	±Std error	±0.001	±0.004	±0.008	±0.04
	Median	0.002	0.011	0.046	0.12
Org N as N	Average	0.12		0.68	
	±Std error	±0.02		±0.08	
	Median	0.04		0.28	

Table 2. Transport of sulfate and forms of nitrogen in Apalachicola, Sopchoppy, and Ochlockonee River flows compared to atmospheric deposition to their watersheds (Units are 10^9 or 10^6 moles yr^{-1} ; total deposition = 2 x wet deposition)

	NO_3^-	NH_4^+	Org N	Total N	SO_4^{2-}
<u>Apalachicola</u> (10^9 moles yr^{-1})					
Wet Deposition					
Average	0.54	0.38		0.92	0.71
\pm Std err	± 0.03	± 0.04		± 0.05	± 0.05
Median	0.38	0.20		0.58	0.49
Total Deposition					
Average	1.07	0.75		1.82	1.42
\pm Std err	± 0.07	± 0.07		± 0.10	± 0.09
Median	0.76	0.41		1.17	0.97
River Flux					
Average	0.42	0.066	0.73	1.22	1.20
\pm Std err	± 0.03	± 0.012	± 0.06	± 0.07	± 0.08
Median	0.22	0.028	0.46	0.71	0.80
<u>Sopchoppy</u> (10^6 moles yr^{-1})					
Wet Deposition					
Average	2.90	1.61		4.51	3.33
\pm Std err	± 1.11	± 0.22		± 1.12	± 0.31
Median	1.61	0.61		2.22	1.99
Total Deposition					
Average	5.80	3.62		9.02	6.66
\pm Std err	± 2.22	± 0.44		± 2.24	± 0.62
Median	3.22	1.22		4.44	3.98
River Flux					
Average	0.13	0.33	8.57	9.03	10.7
\pm Std err	± 0.03	± 0.06	± 1.43	± 1.43	± 1.98
Median	0.03	0.11	2.86	3.00	6.46
<u>Ochlockonee</u> (10^6 moles yr^{-1})					
Wet Deposition					
Average	32.1	17.8		49.9	37.2
\pm Std err	± 3.06	± 2.22		± 3.78	± 3.85
Median	18.7	6.67		25.4	22.4
Total Deposition					
Average	64.2	55.6		99.8	74.4
\pm Std err	± 6.12	± 4.44		± 7.56	± 7.70
Median	37.4	13.34		50.8	44.8
River Flux					
Average	21.6	4.33	48.6	74.5	48.1
\pm Std err	± 1.94	± 0.44	± 5.71	± 6.05	± 5.73
Median	16.3	2.56	20.0	38.9	22.3

Table 3. Factor Analysis of Ion Concentrations in Sopchoppy River, Florida,
with 8 Variables and 3 Significant Factors

Variable	Factor loadings (correlation coefficients)		
	Factor 1	Factor 2	Factor 3
Cl ⁻	-0.088	0.92	0.035
Na ⁺	0.60	0.57	0.018
Mg ²⁺	0.98	-0.004	-0.091
Ca ²⁺	0.97	-0.02	-0.10
Hardness	0.98	-0.02	-0.10
NO ₃ ⁻	0.082	0.25	0.75
SO ₄ ²⁻	-0.24	-0.22	0.78
K ⁺	0.81	0.15	-0.0005
Variance explained, 81%	49%	16%	15%

Variable	Factor concentrations (ug L ⁻¹) and ion ratios (equivalents)			
	Const.	Factor 1	Factor 2	Factor 3
Cl ⁻	391±390	-101±36	4302±147	59±54
Na ⁺	367±123	342±27	1314±110	15±40
Mg ²⁺	95±92	1164±20	-21±82	-161±30
Ca ²⁺	242±941	11546±206	-1206±841	-1795±307
Hardness	1210±2521	33762±552	-3341±2253	-5169±821
NO ₃ ⁻	-357±55	21±12	259±49	291±18
SO ₄ ²⁻	6998±1052	-1166±231	-4257±940	5391±343
K ⁺	-3±30	103±6	75±25	-0.1±9
Ion equivalent ratios				
NO ₃ ⁻ /xSO ₄ ²⁻		-0.013±0.008	-0.044±0.012	0.042±0.004

Table 4. Factor Analysis of Ion Concentration with 8 Variables, 3 Significant Factors in Ochlockonee River.

Variable	Factor loadings (correlation coefficients)		
	Factor 1	Factor 2	Factor 3
Cl ⁻	0.29	0.91	0.30
Na ⁺	0.36	0.87	0.32
Mg ²⁺	0.82	0.36	0.41
Ca ²⁺	0.90	0.30	0.30
Hardness(CaCO ₃)	0.87	0.32	0.35
NO ₃ ⁻	0.64	0.27	0.54
SO ₄ ²⁻	0.42	0.35	0.79
K ⁺	0.38	0.35	0.79
Variance explained, 93%	40%	28%	25%

Variable	Factor concentrations (ug L ⁻¹) and ion ratios (equivalents)			
	Const.	Factor 1	Factor 2	Factor 3
Cl ⁻	716±225	3224±79	7442±57	8238±186
Na ⁺	-914±157	2904±54	5072±40	6053±130
Mg ²⁺	17±51	953±18	300±13	1151±43
Ca ²⁺	629±95	2605±32	639±24	2105±79
Hardness	1630±302	10427±104	2810±76	10088±250
NO ₃ ⁻	957±84	1065±214	326±156	2148±514
SO ₄ ²⁻	-2289±482	1732±166	1052±121	7354±399
K ⁺	506±60	250±21	170±15	1252±49
Ion equivalent ratios				
NO ₃ ⁻ /xSO ₄ ²⁻		0.82±0.21	-1.17±0.82	0.28±0.07

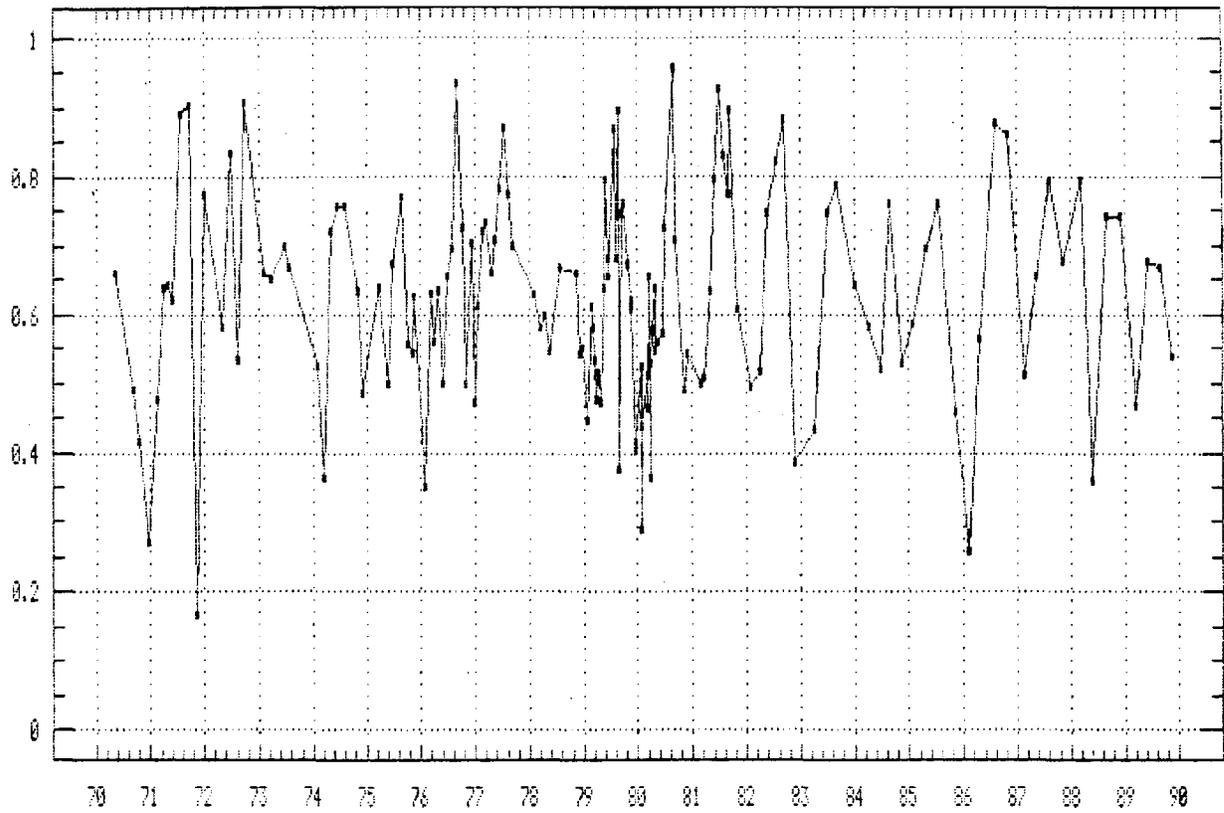


Fig. 1. Variation of ratio of organic nitrogen to total organic plus inorganic forms of nitrogen in the Apalachicola River at Chattahoochee, plotted vs. year from 1970 through 1989.

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