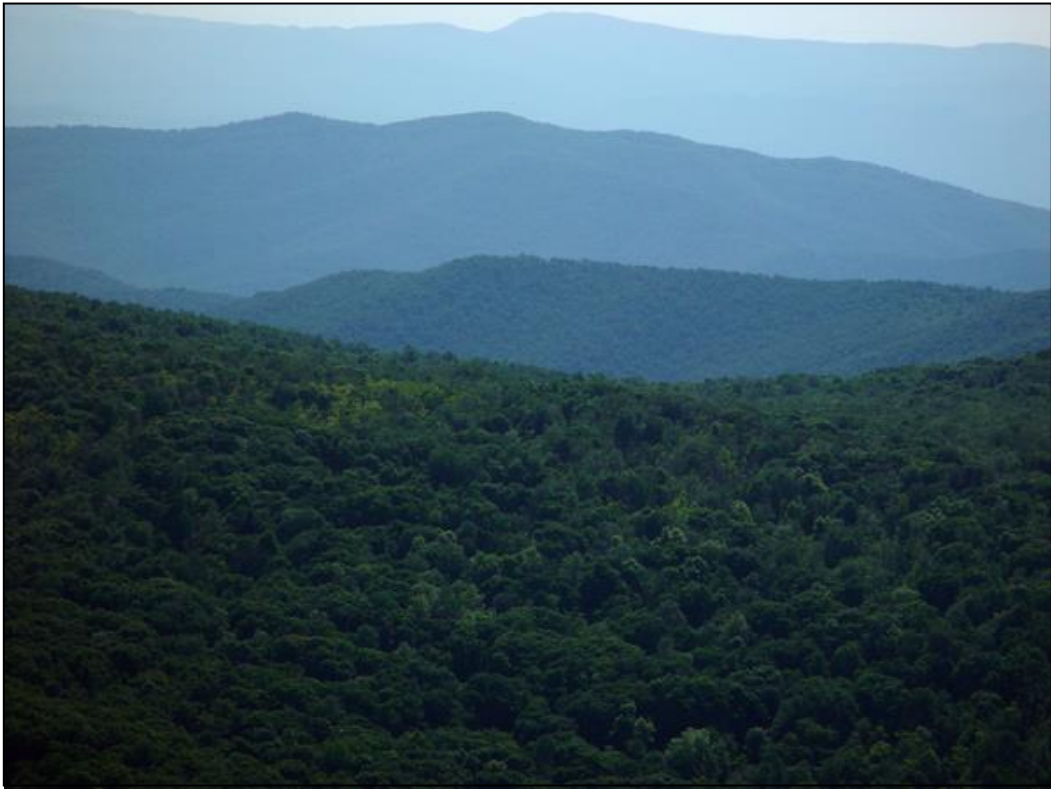


SHENANDOAH NATIONAL PARK  
**SHENANDOAH WATERSHED STUDY (SWAS)**  
**Annual Report for 2004**



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**11/21/05**

# Shenandoah Watershed Study (SWAS)

## Annual Report for 2004

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# **Shenandoah Watershed Study (SWAS)**

## **Annual Report for 2004**

Start and End Dates: ongoing (1979-present)

Reporting Period Dates: 07/01/03-06/30/04

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### **1. Executive Summary**

The Department of Environmental Sciences at the University of Virginia maintains the Shenandoah Watershed Study (SWAS) program in cooperation with the National Park Service. Over the preceding 26 years, the SWAS program has developed a monitoring framework designed to account for the spatial and temporal variability of hydrologic and biogeochemical conditions in the watershed ecosystems of the Shenandoah National Park (SHEN). The SWAS program is a component of SHEN's Long Term Ecological Monitoring Program. The SWAS framework includes 14 study watersheds selected to represent the major bedrock types in SHEN. Data collection includes quarterly, weekly and hourly sample collection for analysis of stream water composition, discharge gauging, and collection and analysis of precipitation. This data collection allows detection of biogeochemical change in SHEN watersheds and supports research to advance understanding of factors and processes that govern current conditions and determine response to stressors.

This report references the SWAS data and quality assurance report for 07/01/03–06/30/04. We propose a periodic schedule for annual reports in which statistical analysis of trends are reported every three to five years, or as warranted by notable observations or other important considerations. The 2003 annual report provided trend analysis for stream water composition based on quarterly and weekly sample collection, for both flow-adjusted and unadjusted data, and for both the SHEN region and for individual sites. The current report provides descriptive information for sample collection and data obtained in 07/01/03–06/30/04.

The major program recommendations submitted with this report are consistent with previous recommendations concerning the need for increased emphasis on the more-sensitive headwater reaches of SHEN streams, characterization and monitoring of soils and springs, and investigation of the fate and transport of atmospherically deposited mercury. We further recommend that recent work to model the frequency, duration, and magnitude of episodic acidification be extended to better address the effects of discharge-related extreme conditions on aquatic biota in SHEN. In addition to these scientific questions, we provide recommendations concerning the

need for funds to replace equipment. Also, in response to anticipated reduced funding availability we recommend a reduction in the scope of the monitoring effort.

## **2. Significant Findings**

*Expanded discussions of the following findings are provided in Section 8.*

- In contrast to long-term trends reported in the previous annual report, which indicated decreasing acidification, most of the SWAS study streams in SHEN were more acidic during the 2004 data report period than in the 2003 data report period.
- Concentrations of the sum of base cations ( $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$ ) were lower in all SWAS study streams, accounting for most of the increase in acidity.
- Conforming to previously reported trends, precipitation was less acidic at the two SWAS precipitation monitoring sites in 2004 than in previous years.
- Stream discharge levels in the 2004 water year were generally high in relation to previous years.

## **3. Recommendations for SHEN Management and SWAS Program**

*The following recommendations arise from the above-listed significant findings and other material provided in this report. Expanded discussions of the recommendations are provided in Section 9.*

- Obtain water composition and biological data to characterize upper stream reaches, springs, seepage areas, and other stream waters that are not presently sampled as part of SWAS or other components of the SHEN Long-Term Ecological Monitoring program.
- Investigate the fate and transport of atmospherically deposited mercury in SHEN surface waters.
- Investigate the relationship between episodic discharge-related extremes in SHEN stream water quality and the status of aquatic biota.
- Establish a program to monitor change in the availability of base-cations (e.g., calcium and magnesium ions) in SHEN soils.
- Prioritize and seek resources for replacement of dated and unreliable laboratory instruments used for water quality analysis.

- In response to anticipated reduced funding availability, reduce the scope of the monitoring program by discontinuing SWAS precipitation monitoring.

#### **4. Introduction/Background**

Over the preceding 25 years, the Department of Environmental Sciences at the University of Virginia and the Shenandoah National Park (SHEN) have collaborated to develop the SWAS research and monitoring program. The SWAS program is a component of SHEN's Long Term Ecological Monitoring Program. As described below, the primary objectives of the SWAS program are to identify and understand change that is occurring in SHEN's forested mountain watersheds. A partial listing of causes of significant ecosystem change presently facing SHEN includes forest growth, insect infestation, climatic change, and air pollution. These causal factors may all in some way affect the hydro-biogeochemical environment of SHEN watersheds and thus come within the purview of the SWAS program.

The solute composition of stream waters is a critical environmental parameter in forested mountain watersheds. It directly affects the distribution and productivity of fish and other aquatic biota. Moreover, because stream-water composition is determined by a complex integration of hydro-biogeochemical inputs and processes in watersheds, change in stream-water composition provides a measurable indication of ecosystem change that is occurring on a watershed scale. For these reasons, stream-water composition is monitored at a number of locations in SHEN. Current SWAS data collection in SHEN includes a combination of quarterly, weekly, and higher-frequency water quality sampling on 14 streams and continuous discharge measurement on five streams, as well as determination of precipitation amount and composition at two locations.

The selection of the 14 watersheds for SWAS data collection was based on a number of factors, including: representation of major geologic formations and range of stream sensitivity in SHEN, coordination with the Park's Long-Term Ecological Monitoring System (LTEMs), degree of direct human alteration of watershed conditions, and site accessibility. Coordination with the LTEMs program provides routine monitoring of aquatic biota for most of these watersheds.

A regional context for SWAS program findings is provided through coordination with the Virginia Trout Stream Sensitivity Study (VTSSS), which extends quarterly water quality sampling to an additional 51 streams located mostly in the George Washington and Jefferson National Forests. The streams studied by both the SWAS and VTSSS programs provide habitat for native brook trout.

Additional information about the SWAS program, including a listing and timeline of associated research projects, interpretive reports, a bibliography of publications associated with the program, and the Standard Operations Procedure for laboratory analysis, can be accessed from the program website: <http://swas.evsc.virginia.edu>.

## 5. Objectives

The SWAS program has both scientific and resource-management objectives. The underlying scientific objective of the SWAS program has been to improve understanding of hydro-biogeochemical processes and factors that govern ecosystem conditions in SHEN mountain watersheds. This scientific objective complements a resource management objective that has been defined by the need to document and assess change that is occurring in SHEN streams and watershed ecosystems.

## 6. Study Area Description

SWAS data collection and interpretive analyses are designed to provide information about the status of stream and watershed ecosystems in SHEN as a whole. Provision of information on this geographic scale has been accomplished by development of a stratified monitoring framework that substantially partitions the inherent spatial and temporal variability that exists among SHEN watersheds. This monitoring framework is designed to:

- (1) account for differences in watershed properties that determine biogeochemical conditions and stressor-response relationships, and
- (2) allow identification and understanding of change that occurs on different time scales.

A map showing the location of the 14 SWAS study watersheds in relation to SHEN's three major bedrock classes is provided in Figure 1. A diagram depicting the spatial and temporal components of the SWAS watershed-monitoring framework is provided in Figure 2.

Important aspects of spatial variability among SHEN watersheds are captured by the distribution of the study watersheds among SHEN's three major bedrock types. Previous studies in SHEN have shown close associations between watershed bedrock type and stream water composition, the distribution of aquatic biota, the acid-base status of soils, and the distribution of forest cover (see Lynch and Dise, 1985; Bulger et al., 1999). SHEN landscape includes three major bedrock types, siliciclastic (quartzite and sandstone), granitic, and basaltic.

Watersheds underlain by siliciclastic formations are associated with low pH and low acid neutralizing capacity in streams, fewer invertebrate and fish taxa in streams, lower base-saturation in soils, and forest cover consistent with poor site quality. In contrast, watersheds underlain by basaltic formations are associated with relatively high pH and high acid neutralizing capacity in streams, greater numbers of invertebrate and fish taxa in streams, relatively high base-saturation in soils, and forest cover consistent with good site quality. Watersheds underlain by granitic formations are intermediate in these respects. Each of these bedrock types influence about one-third of SHEN's stream miles and land area.

Important aspects of temporal variability are captured by stream water sampling at different frequencies, including quarterly, weekly, and hourly. This allows identification and understanding of both chronic and episodic change in stream water composition. By maintenance

of continuing long-term data collection, misinterpretation that might otherwise result due to transient changes can be avoided.

Table 1 provides a listing of the SWAS study watersheds, with descriptive information including geographic coordinates and elevation of stream water sampling sites, watershed area above the stream water sampling sites, watershed bedrock, and stream water sampling frequency.

## **7. Methods**

### **Field and Laboratory Methods**

As indicated above, SWAS data collection in SHEN includes a combination of quarterly, weekly, and higher-frequency water quality sampling on 14 streams and continuous discharge measurement on five streams, as well as determination of precipitation amount and composition at two locations. The routine field work schedule involves weekly visits (requiring two to three days per week) to six stream sites for water quality sampling, maintenance of discharge gauges, and maintenance of, and retrieval of samples from, automatic high-runoff sampling systems. Two precipitation sampling sites are also visited on a weekly basis for maintenance, collection of data, and retrieval of samples. Stream water samples are also collected on a quarterly basis by SHEN staff at an additional eight sites.

### **Chemical Analysis**

Chemical analysis of all stream water and precipitation samples is performed at the SWAS program laboratory at the University of Virginia. Analyses are conducted for all major chemical properties and constituents, including pH, acid neutralization capacity (ANC), conductivity, sulfate, nitrate, chloride, ammonium, calcium ion, magnesium ion, sodium ion, potassium ion, silica, and dissolved aluminum. The accompanying data report describes analytical methods and lists chemical composition and quality assurance data. The complete Standard Operating Procedure document for sample analysis can be accessed from the SWAS program website: <http://swas.evsc.virginia.edu>.

## **8. Findings and Discussion**

### **Number of Samples Collected**

Figure 3 indicates the total number of stream water samples collected for analysis through the SWAS program during each of the years during the period of record, as well as the number of weekly grab samples and episodic (ISCO) samples collected at the intensively studied sites established in 1993. The total number of samples increased in the late 1980s with initiation of weekly sampling on North Fork Dry Run and quarterly sampling of geologically representative streams throughout SHEN. The number of samples increased in the early 1990s with initiation of

additional weekly sampling and episodic sampling on three sites (Paine Run, Piney River, and Staunton River) selected for intensive study. The somewhat lower number of samples collected in recent years is due to less-frequent sampling during high-discharge conditions.

## Discharge

Figure 4 provides time series plots of discharge for the five SWAS study streams with continuous discharge gauging. The time series plots indicate that most of the extreme high-flow events occurred late in the water year. As evidenced by the compared cumulative frequency distributions, discharge levels in the 2004 water year were generally high in relation to previous years. This may explain some of the observed differences in stream water composition, discussed in following sections, between the 2004 and 2003 water years.

## Acid-Base Status of Stream Water

Figure 5 provides time series plots of major acid-base constituents for the six SWAS study streams with weekly sample collections. More-intensive sampling is conducted during episodic high-discharge conditions on Paine Run, Piney River, and Staunton River. The data obtained during these high-discharge conditions are indicated.

Figure 7 provides time series plots of major acid-base constituents for the 14 primary SWAS study for the period of record. Data for quarterly sample collections are presented. For those streams with more-frequent sampling, the data were subsampled to provide quarterly data.

Table 2 indicates differences between mean values of the major acid-base constituents for all 14 of the primary SWAS study watersheds for the 2003 and 2004 data report periods. With respect to the acid-base status of SHEN surface waters, the most significant differences between the two report periods include:

- Most of the study streams were more acidic in 2004 than in 2003, based on ANC and pH.
- For all of the study streams, the concentrations of base cations ( $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+}$ ) were lower in 2004 than in 2003.
- For most of the study streams, sulfate concentrations were lower in 2004 than in 2003.
- For most of the study streams, nitrate concentrations were higher in 2004 than in 2003.

The observed increase in stream water acidity between 2003 and 2004 contrasts with previous long-term trend analysis reported for the period ending in 2003. This difference is can be largely explained by the sharp decrease in base cation concentrations among all streams. Sulfate concentrations decreased between 2003 and 2004 and thus were not associated with the increase in acidity. However, nitrate concentrations, which should also be associated with increased acidity, increased between 2003 and 2004.

The decrease in concentrations of base cations between 2003 and 2004 is consistent with trends reported for the period ending in 2003, but the magnitude of the decrease is generally greater. This observation may be explained by long-term depletion of base cations in watershed soils, a

factor that may affect both forest productivity and prospects for recovery from stream water acidification.

The general decrease in sulfate concentrations between 2003 and 2004 was consistent with long-term trends reported for the period ending in 2003, and consistent with expectations given recent reductions in sulfur emissions and deposition. The decrease in sulfate or total strong-acid anion concentration in stream water, however, was evidently insufficient to offset the concurrent decrease in the sum of base cations.

The general increase in nitrate concentrations between 2003 and 2004 contrasts with previous long-term trend analysis reported for the period ending in 2003. Although this increase may partly explain the increase in stream water acidity, the more likely explanation is the decrease in base-cation concentrations because, as stated above, the total strong-acid anion concentration in stream water generally decreased. The cause of the observed increase in nitrate concentrations is unknown, though it may be related to continuing effects of forest defoliation by gypsy moth larva or other forest disturbance.

As indicated in Figures 5 and 6, temporal variation in acid base status (indicated by ANC and pH) occurs on both seasonal and shorter-term scales, in addition to time-scales represented by long-term trend analysis. Examination of the plots indicates that ANC and pH follow the well-known season cycle, in which the most acidic conditions are present in the colder part of the year. Superimposed on this repeated cycle are the transient more-extreme acidity levels associated with high-discharge conditions, as indicated in Figure 5 for the intensively studied sites. This is a persistent pattern as indicated in Figure 6, which compares ANC distributions for weekly samples and episodic, high-discharge, samples collected at the intensively studied sites.

## Precipitation Composition

Figure 8 provides time series plots for concentrations of major acid-base constituents measured in precipitation at the two SWAS precipitation monitoring sites, and compares cumulative frequency distributions for these constituents for the 2004 data reporting period and all other years in the record. Consistent with expectations based on emission reductions and past observations, SHEN precipitation was less acidic in 2004 than in previous years. pH was significantly greater and concentrations of sulfate and nitrate were significantly lower. Concentrations of ammonium, a component of total nitrogen deposition, were not different in 2004 than in previous years. Base cation concentrations in precipitation were significantly lower in 2004 than in previous years. Consistent with the decreasing acidity of precipitation, the decrease in concentrations of base cations in precipitation was less than the decrease in the acid anions, sulfate and nitrate. It is also possible that the decrease in base cations in precipitation contributed to the reduced concentrations of base cations observed in SHEN streams, although this is speculative, given uncertainty concerning the base-cation contribution of dry deposition.

## 9. Current Recommendations

*Obtain water composition and biological data to characterize upper stream reaches, springs, seepage areas, and other stream waters that are not presently sampled as part of SWAS or other components of the SHEN Long-Term Ecological Monitoring program.*

This recommendation responds to the SHEN Water Resources Scoping Report (WRSR; Vana-Miller and Weeks, 2004) in which it was observed that most of the data for SHEN water resources have been obtained for lower-elevation stream reaches, and that data are regularly collected for only a fraction of SHEN streams. For example, the streams monitored through the SWAS component of the SHEN Long-Term Ecological Monitoring System (LTEMs), were selected to represent the major bedrock types in SHEN and thereby account for the inherent spatial variability among SHEN watersheds. SWAS data, however, are routinely obtained for only 14 streams among the approximately 72 streams in SHEN, and no springs or seepage areas are monitored. The WRSR thus recommended: (1) investigation to identify the locations of springs and seeps, followed by characterization of baseline conditions; and (2) sampling other streams and lower-order reaches to evaluate the park-wide applicability of stream status determined through data obtained for the SWAS watersheds. The information obtained would provide a basis for revision of the SHEN water resources inventory and monitoring program to ensure collection of data necessary to protect all of the water resources in SHEN.

*Establish a program to monitor change in the availability of base-cations (e.g., calcium and magnesium ions) in SHEN soils.*

The continuing decrease in concentrations of base cations in watershed soils is apparently a result of prolonged exposure to acidic deposition. Base cations provide acid neutralization through soil exchange and serve as critical nutrients for aquatic fauna and terrestrial vegetation. Because natural replenishment of base cation supplies in watershed soils is a slow process, the depletion of base cations may limit recovery from surface water acidification despite recent reductions in sulfur emissions and deposition. The loss of base supplies in watershed soils should thus be considered the fundamental, long-term impact of acidic deposition on watershed ecosystems.

Given the importance of base-cation supplies in watershed soils with respect to both streams and forests, a program to monitor base status in soils is important for understanding current and future ecosystem conditions in SHEN. Monitoring would be most informative if conducted within the established SWAS study watersheds and by protocols established for evaluating acidic deposition effects on soils (e.g., Webb et al., 2004)

*Investigate the fate and transport of atmospherically deposited mercury in SHEN surface waters.*

Atmospheric deposition of mercury (Hg) associated with long-range transport has led to increased concentrations in freshwater systems and biota, in some cases exceeding thresholds for fish consumption. However, total Hg deposition has not been found to be an effective predictor of bioaccumulation in aquatic species. Recent investigations in SHEN have shown that despite relatively high deposition levels, Hg concentration levels in fish and salamanders in SHEN

streams are relatively low by comparison with some other areas with relatively low deposition levels. Although low, Hg concentration levels in SHEN fish vary among streams for undetermined reasons, and long-term effects of Hg deposition are thus unknown.

Again, responding to recommendations in the WRSR, we suggest initiation of studies to identify the processes and landscape factors that govern this variation in SHEN. Studies should be designed to build on recent and current studies of Hg mobility in SHEN. A study of Hg concentrations in fish (conducted by USGS Biological Resources Division, SHEN Natural Resource Management, and the SWAS investigator team) is nearing completion. Preliminary findings indicate associations between Hg levels in brook trout and both bedrock type and elevation. Another study is underway (UVA graduate thesis project) to investigate longitudinal and temporal variation of Hg in SHEN stream waters and sediments. Given the known link between bioaccumulation and the presence of organic matter in low oxygen environments, upper reaches of streams and seepage areas represent a logical focus for further investigation.

*Investigate the relationship between episodic discharge-related extremes in SHEN stream water quality and the status of aquatic biota.*

As discussed above, the most acidic conditions in SHEN streams occur episodically during high-discharge conditions. Previous investigations in SHEN have substantially increased our understanding of both the hydrochemical parameters of episodic acidification and biological response to episodic acidification in SHEN. The Fish in Sensitive Habitats project, for example, established that episodic acidification is a major factor associated with both recruitment failure for brook trout and mortality of adult blacknose dace (Bulger et al., 1999). Although general relationships are observed in SHEN streams between fish diversity and base-flow ANC, the predictive power of such relationships is limited. It seems probable that the distributions of fish and other aquatic species can be better explained by also considering the occurrence of episodic acidification.

A recent cooperative project of the USGS and the SWAS team (Rice et al., in review) has provided a model to predict the magnitude, frequency, and duration of episodic acidification in SHEN streams as a function of bedrock type, watershed size, and elevation. We suggest further development of this model as a tool for predicting and explaining distributions of aquatic species in SHEN. This would be a logical and productive response to the WRSR recommendation for better integration between the hydrochemical components and biological components of the SHEN LTEMs program.

*Prioritize and seek resources for replacement of dated and unreliable laboratory instruments used for water quality analysis.*

A problem facing the SWAS program is the lack of resources for analytical and field instrumentation. The inability to maintain adequate equipment is a continuing difficulty and a source of program inefficiency. Equipment funds have not been included in the SWAS budget for a number of years. Although the SWAS program has recently moved into dedicated state-of-the-art lab facilities in a newly constructed addition to UVA's Department of Environmental Sciences building, the program still relies on dated and increasingly unreliable analytical equipment.

In response to this problem, the SWAS team has submitted a proposal to the National Science Foundation (NSF) to upgrade and acquire laboratory equipment. If funded, this proposal will allow the SWAS program to move up to a new level of analytical capability which will allow not only a more efficient analysis of water samples (more automation, less down time for repairs) but will give the programs increased capabilities for exploring new scientific questions concerning the biogeochemistry of mountain watersheds.

Decisions on the NSF proposal are expected within the next few months, and at this point, the prospects for funding are unknown. We therefore recommend that the National Park Service continue to prioritize and seek resources to upgrade and replace the critical SWAS laboratory equipment.

*In response to anticipated reduced funding availability, reduce the scope of the monitoring program by discontinuing SWAS precipitation monitoring.*

Given the projected reduction in funding availability for the SWAS program, we have considered means whereby the scope of monitoring activity can be reduced while maintaining critical aspects of the program. We have concluded that the precipitation monitoring component of the program can be discontinued with the least impact on the information value of the program, while providing a meaningful reduction in field and laboratory work. This will end a 26-year record at the White Oak Run site and a 19-year record at the North Fork Dry Run site.

In lieu of the data provided by these sites, the SWAS program will be dependent upon the precipitation data provided for the Big Meadows site through the National Acid Deposition Program/National Trends Network (NADP/NTN). Although the Big Meadows site is centrally located in SHEN, loss of the data provided by the other two sites will result in reduced spatial coverage, both in terms of geographic coverage and elevation coverage. Moreover, the NADP/NTN program has experienced at least one temporary shut-down in the past due to funding problems. Nonetheless, a reduction in SWAS monitoring activity is necessary if additional funding is not obtained.

## 10. Citations

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- Webb, J.R., T.S. Sullivan, and B. Jackson. Assessment of Atmospheric Deposition Effects on National Forests: Protocols for Collection of Supplemental Stream Water and Soil Composition Data for the MAGIC Model. Prepared for USDA Forest Service, Asheville, NC, 2004.

## **Tables and Figures**

Table 1: SWAS study watersheds

| Site      | Stream Name       | Streamwater Sampling Frequency | ELEV (ft) | AREA (km <sup>2</sup> ) | UTM Coordinates |         | Percent Bedrock Coverage |                   |                   |
|-----------|-------------------|--------------------------------|-----------|-------------------------|-----------------|---------|--------------------------|-------------------|-------------------|
|           |                   |                                |           |                         |                 |         | SILI <sup>1</sup>        | GRAN <sup>2</sup> | BASA <sup>3</sup> |
| DR01      | DEEP RUN          | weekly                         | 1360      | 3.12                    | 695591          | 4238919 | 100.0                    | 0.0               | 0.0               |
| NFDR      | NF OF THE DRY RUN | weekly                         | 1600      | 2.31                    | 729933          | 4279183 | 0.0                      | 100.0             | 0.0               |
| PAIN VT35 | PAINE RUN         | weekly and episodic            | 1390      | 12.39                   | 693243          | 4229927 | 100.0                    | 0.0               | 0.0               |
| PINE VT60 | PINEY RIVER       | weekly and episodic            | 1140      | 12.59                   | 737939          | 4286960 | 0.0                      | 31.3              | 68.7              |
| STAN VT59 | STAUNTON RIVER    | weekly and episodic            | 1010      | 10.50                   | 729380          | 4258243 | 0.0                      | 100.0             | 0.0               |
| VT36      | MEADOW RUN        | quarterly                      | 1480      | 8.86                    | 691758          | 4225462 | 100.0                    | 0.0               | 0.0               |
| VT51      | JEREMYS RUN       | quarterly                      | 930       | 21.97                   | 727652          | 4288251 | 31.0                     | 0.0               | 69.0              |
| VT53      | TWO MILE RUN      | quarterly                      | 1220      | 5.56                    | 703527          | 4245225 | 100.0                    | 0.0               | 0.0               |
| VT58      | BROKENBACK RUN    | quarterly                      | 1080      | 9.86                    | 735102          | 4272372 | 0.0                      | 93.4              | 6.6               |
| VT61      | NF THORNTON RIVER | quarterly                      | 1100      | 19.08                   | 736982          | 4286022 | 5.2                      | 27.0              | 67.8              |
| VT62      | HAZEL RUN         | quarterly                      | 1080      | 13.24                   | 738348          | 4277397 | 0.0                      | 100.0             | 0.0               |
| VT66      | ROSE RIVER        | quarterly                      | 1120      | 23.73                   | 729550          | 4266066 | 0.0                      | 9.1               | 90.9              |
| VT75      | WHITE OAK CANYON  | quarterly                      | 1160      | 14.08                   | 730905          | 4268968 | 0.0                      | 14.1              | 85.9              |
| WOR1      | WHITE OAK RUN     | weekly                         | 1480      | 5.13                    | 696960          | 4235772 | 100.0                    | 0.0               | 0.0               |

<sup>1</sup> SILI = siliciclastic (Harper, Antietam, and Weverton Formations)

<sup>2</sup> GRAN = granitic (Pedlar and Old Rag Formations)

<sup>3</sup> BASA = basaltic (Catocin Formation)

Table 2: Difference and confidence interval between 2003 and 2004 mean concentration (weekly grab samples only)

| unique identifier<br>for the site | Analyte | LowerCL     | Difference Between<br>Means | UpperCL    |
|-----------------------------------|---------|-------------|-----------------------------|------------|
| DR01                              | NO3     | -2.273226   | -0.426438                   | 1.420349   |
| DR01                              | PH      | -0.034966   | 0.007121                    | 0.049209   |
| DR01                              | SO4     | 1.134533    | <b>5.025696</b>             | 8.916859   |
| DR01                              | anc     | 1.279866    | <b>2.949183</b>             | 4.618500   |
| DR01                              | sbc     | 6.978711    | <b>9.779292</b>             | 12.579872  |
| NFDR                              | NO3     | 9.449433    | <b>14.592212</b>            | 19.734990  |
| NFDR                              | PH      | -0.008628   | 0.059615                    | 0.127859   |
| NFDR                              | SO4     | -2.140188   | 1.049673                    | 4.239534   |
| NFDR                              | anc     | -7.756457   | 4.269231                    | 16.294918  |
| NFDR                              | sbc     | 9.714177    | <b>20.569385</b>            | 31.424592  |
| PAIN                              | NO3     | -2.544772   | -0.415910                   | 1.712952   |
| PAIN                              | PH      | 0.049546    | <b>0.132279</b>             | 0.215012   |
| PAIN                              | SO4     | 2.351666    | <b>4.312368</b>             | 6.273071   |
| PAIN                              | anc     | 3.324342    | <b>5.238728</b>             | 7.153113   |
| PAIN                              | sbc     | 8.475636    | <b>11.297001</b>            | 14.118367  |
| PINE                              | NO3     | -9.661393   | <b>-5.108262</b>            | -0.555130  |
| PINE                              | PH      | 0.066674    | <b>0.128002</b>             | 0.189330   |
| PINE                              | SO4     | 1.085806    | <b>5.359733</b>             | 9.633659   |
| PINE                              | anc     | -14.265689  | 11.608583                   | 37.482855  |
| PINE                              | sbc     | -10.787146  | 9.505685                    | 29.798516  |
| STAN                              | NO3     | -1.188012   | -0.050317                   | 1.087379   |
| STAN                              | PH      | 0.030577    | <b>0.127090</b>             | 0.223603   |
| STAN                              | SO4     | -3.118398   | -1.133917                   | 0.850565   |
| STAN                              | anc     | -3.068055   | 3.869485                    | 10.807025  |
| STAN                              | sbc     | -0.993568   | 4.521294                    | 10.036155  |
| VT36                              | NO3     | -6.424775   | -1.029000                   | 4.366775   |
| VT36                              | PH      | -0.023217   | 0.200000                    | 0.423217   |
| VT36                              | SO4     | -23.689594  | -6.937300                   | 9.814994   |
| VT36                              | anc     | 0.854948    | <b>5.645000</b>             | 10.435052  |
| VT36                              | sbc     | -12.527206  | 1.785300                    | 16.097806  |
| VT51                              | NO3     | -15.691433  | -2.483250                   | 10.724933  |
| VT51                              | PH      | -0.273431   | 0.057500                    | 0.388431   |
| VT51                              | SO4     | -23.424416  | 5.137500                    | 33.699416  |
| VT51                              | anc     | -132.239676 | 2.825000                    | 137.889676 |
| VT51                              | sbc     | -94.300959  | 12.634500                   | 119.569959 |
| VT53                              | NO3     | -6.383777   | -0.853500                   | 4.676777   |
| VT53                              | PH      | -0.280369   | -0.057500                   | 0.165369   |
| VT53                              | SO4     | -11.944380  | 8.575000                    | 29.094380  |
| VT53                              | anc     | -8.419167   | 4.525000                    | 17.469167  |
| VT53                              | sbc     | 2.311174    | <b>13.660000</b>            | 25.008826  |
| VT58                              | NO3     | -5.932379   | 0.064500                    | 6.061379   |
| VT58                              | PH      | -0.491678   | -0.117500                   | 0.256678   |
| VT58                              | SO4     | -2.674121   | 8.429250                    | 19.532621  |
| VT58                              | anc     | -39.649022  | 0.850000                    | 41.349022  |
| VT58                              | sbc     | -24.954929  | 7.651250                    | 40.257429  |
| VT61                              | NO3     | -23.653567  | -1.468750                   | 20.716067  |
| VT61                              | PH      | -0.566635   | -0.182500                   | 0.201635   |
| VT61                              | SO4     | -15.656322  | 11.393250                   | 38.442822  |
| VT61                              | anc     | -128.257943 | -2.475000                   | 123.307943 |

| unique identifier<br>for the site | Analyte | LowerCL    | Difference Between<br>Means | UpperCL   |
|-----------------------------------|---------|------------|-----------------------------|-----------|
| VT61                              | sbc     | -72.222209 | 11.308500                   | 94.839209 |
| VT62                              | NO3     | -8.081359  | -1.229250                   | 5.622859  |
| VT62                              | PH      | -0.408352  | -0.035000                   | 0.338352  |
| VT62                              | SO4     | -5.252464  | 7.451250                    | 20.154964 |
| VT62                              | anc     | -38.086693 | 0.050000                    | 38.186693 |
| VT62                              | sbc     | -23.584989 | 6.766750                    | 37.118489 |
| VT66                              | NO3     | -17.146994 | -3.078750                   | 10.989494 |
| VT66                              | PH      | -0.236210  | 0.010000                    | 0.256210  |
| VT66                              | SO4     | -3.016086  | 8.489250                    | 19.994586 |
| VT66                              | anc     | -68.398379 | -7.900000                   | 52.598379 |
| VT66                              | sbc     | -36.525328 | 11.190250                   | 58.905828 |
| VT75                              | NO3     | -19.566789 | -5.169000                   | 9.228789  |
| VT75                              | PH      | -0.206751  | 0.020000                    | 0.246751  |
| VT75                              | SO4     | -3.796424  | 8.860500                    | 21.517424 |
| VT75                              | anc     | -53.272775 | 5.400000                    | 64.072775 |
| VT75                              | sbc     | -45.686459 | 8.414750                    | 62.515959 |
| WOR1                              | NO3     | -2.918808  | 0.235574                    | 3.389957  |
| WOR1                              | PH      | 0.035553   | <b>0.130175</b>             | 0.224797  |
| WOR1                              | SO4     | -1.736319  | 2.161407                    | 6.059133  |
| WOR1                              | anc     | -6.196073  | 1.235895                    | 8.667863  |
| WOR1                              | sbc     | -5.586978  | 5.602313                    | 16.791605 |

- Difference Between Means = 2003-2004 data report periods (July 1 to Jun 30)
- Differences indicated in bold text are significant at  $p = 0.05$

Figure 1: Distribution of SWAS study watersheds in relation to major bedrock classes in SHEN

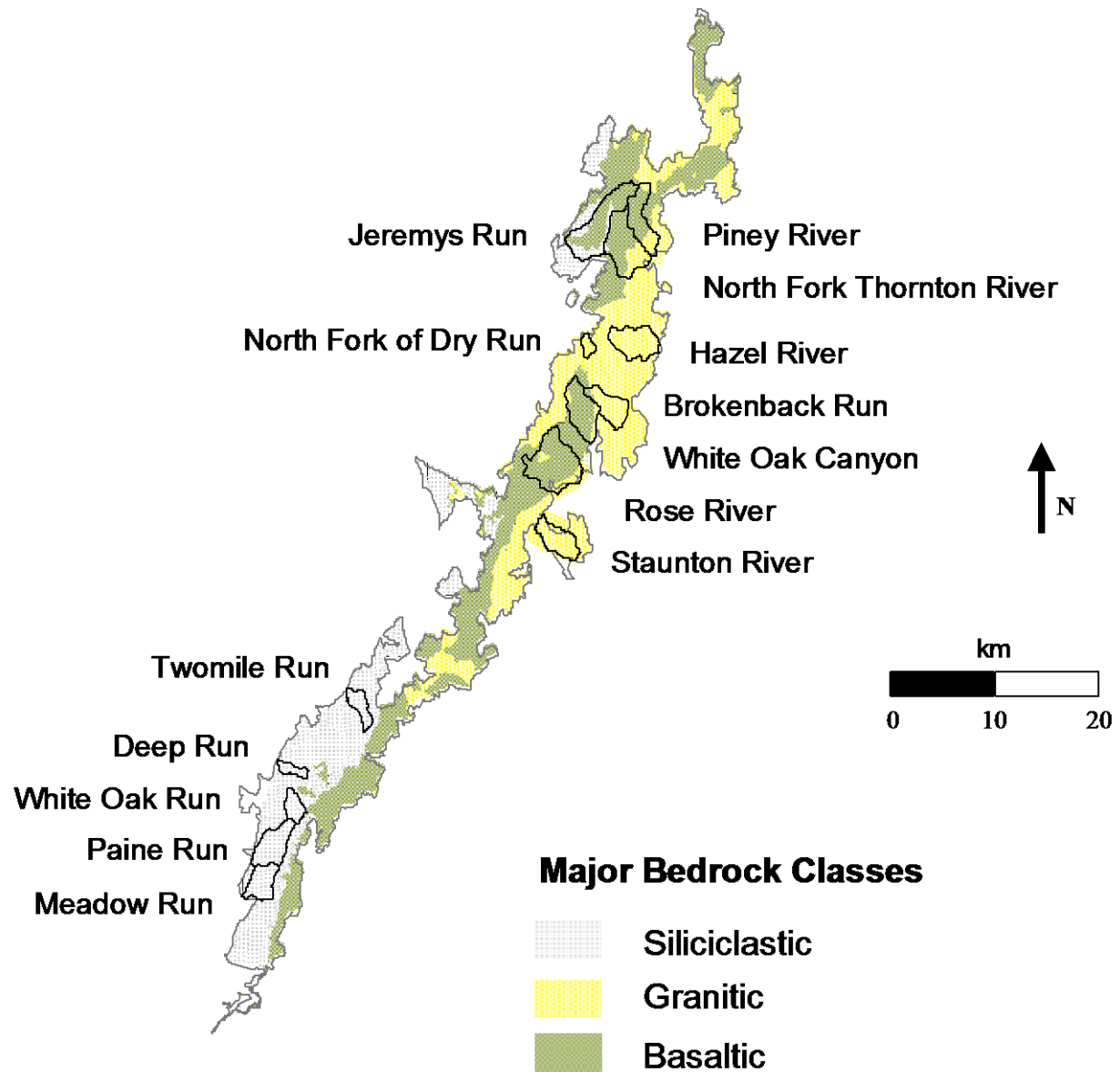
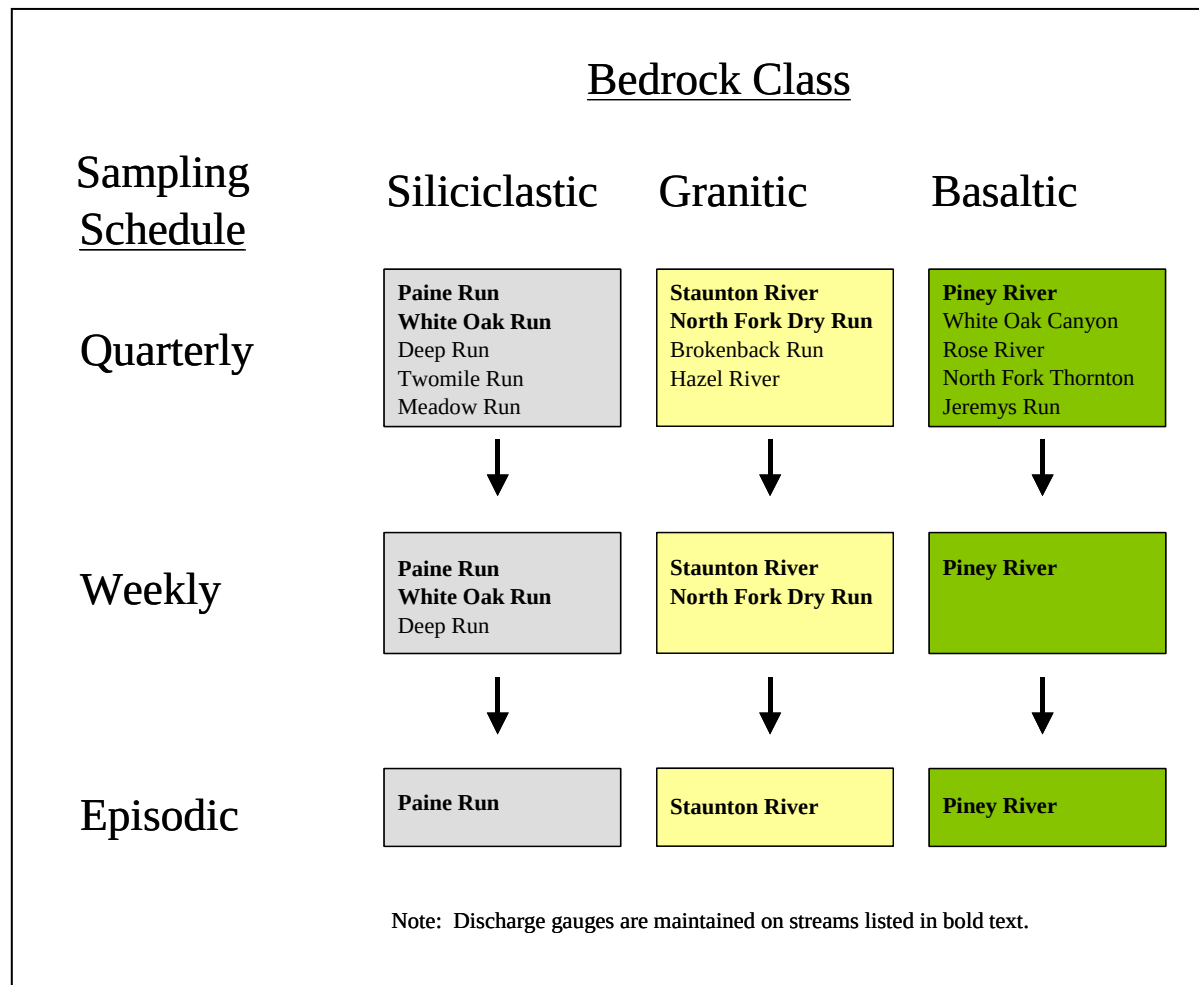
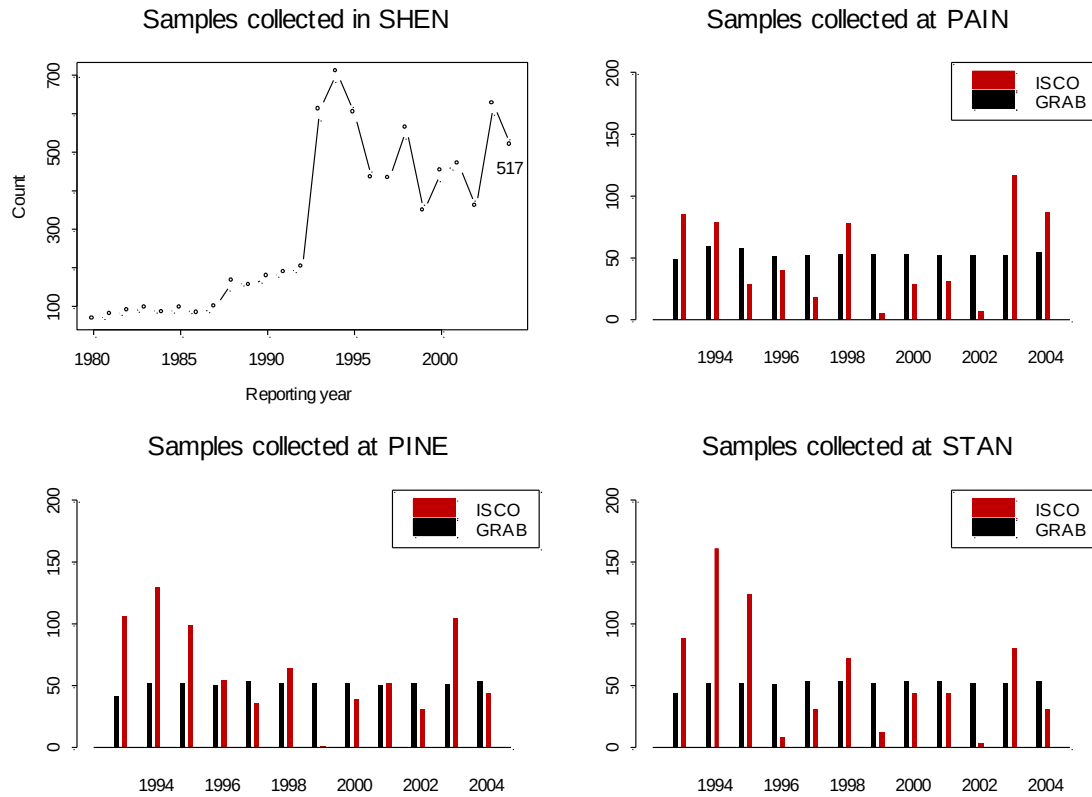


Figure 2: Schematic of SWAS watershed monitoring framework, indicating stratification by bedrock class and sampling frequency for study watersheds



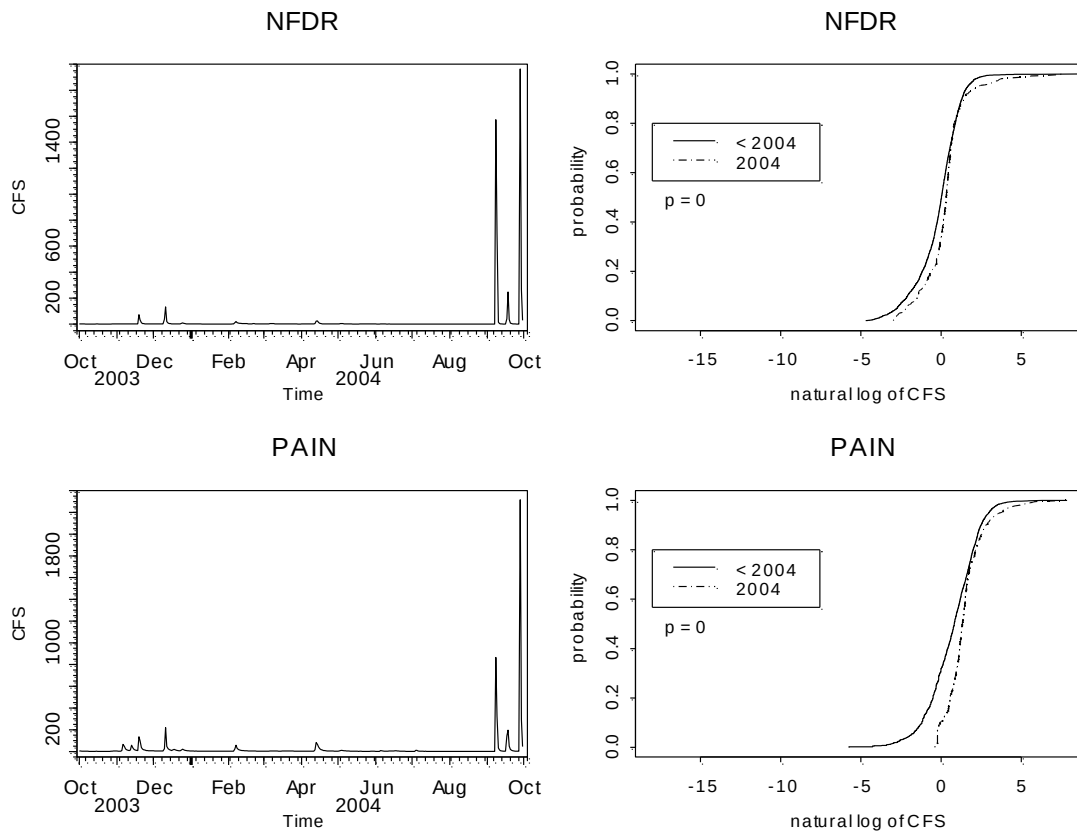
- Episodic sampling is conducted at 2-hour intervals during periods of discharge exceeding the 95<sup>th</sup> flow-duration percentile determined separately for cold and warm seasons.

Figure 3: Number of stream water samples collected



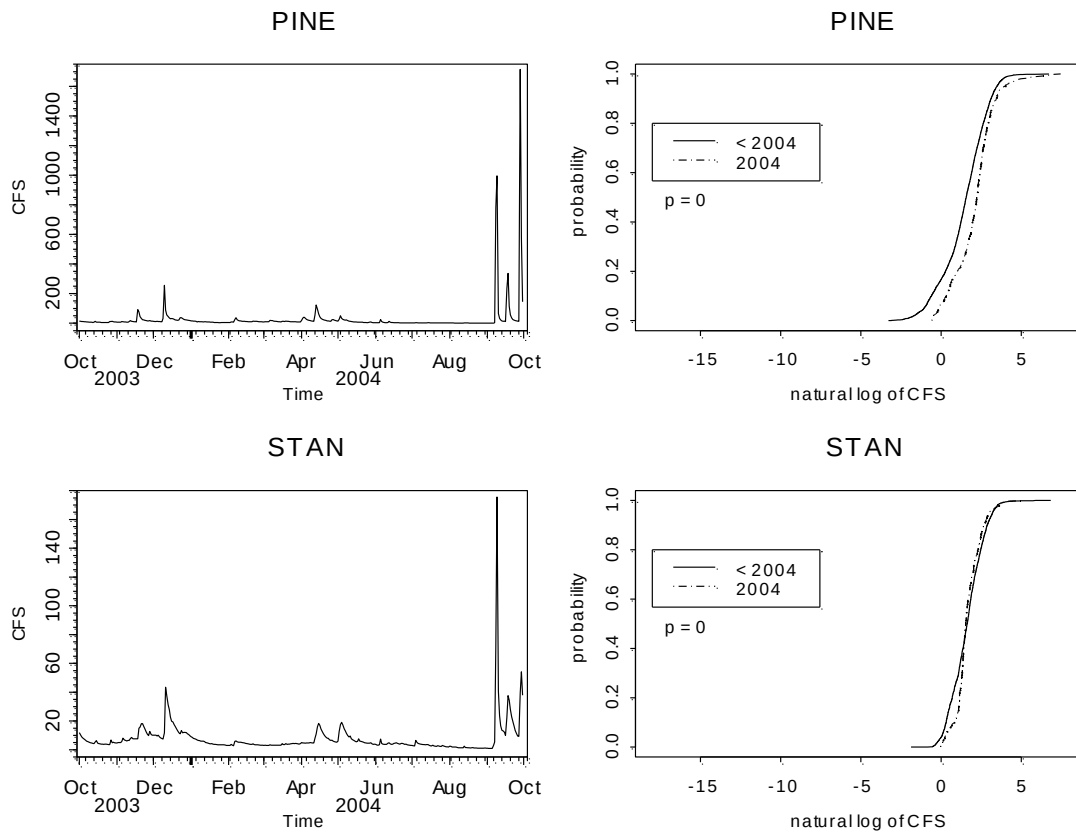
- The upper-left plot indicates the number of stream water samples collected for all sites in SHEN.
- The bar graphs indicate the number of weekly grab samples and the number of episodic (ISCO) samples collected at the intensively studied Paine Run, Piney River, and Staunton River sites.

Figure 4a: Discharge for 2004 water year (October 1, 2003 – September 30, 2004) and comparison of cumulative frequency distributions for discharge in 2004 with discharge in previous years.



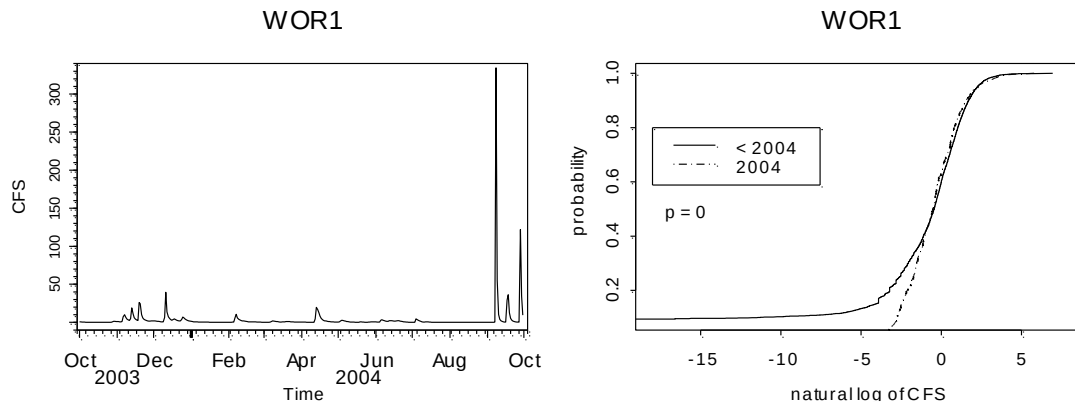
- p value = 2-tailed probability (based on the Kolmogorov-Smirnov statistic) that the current year's distribution of discharge values is the same as the distribution of all previous years' discharge values

Figure 4b: Discharge for 2004 water year (October 1, 2003 – September 30, 2004) and comparison of cumulative frequency distributions for discharge in 2004 with discharge in previous years.



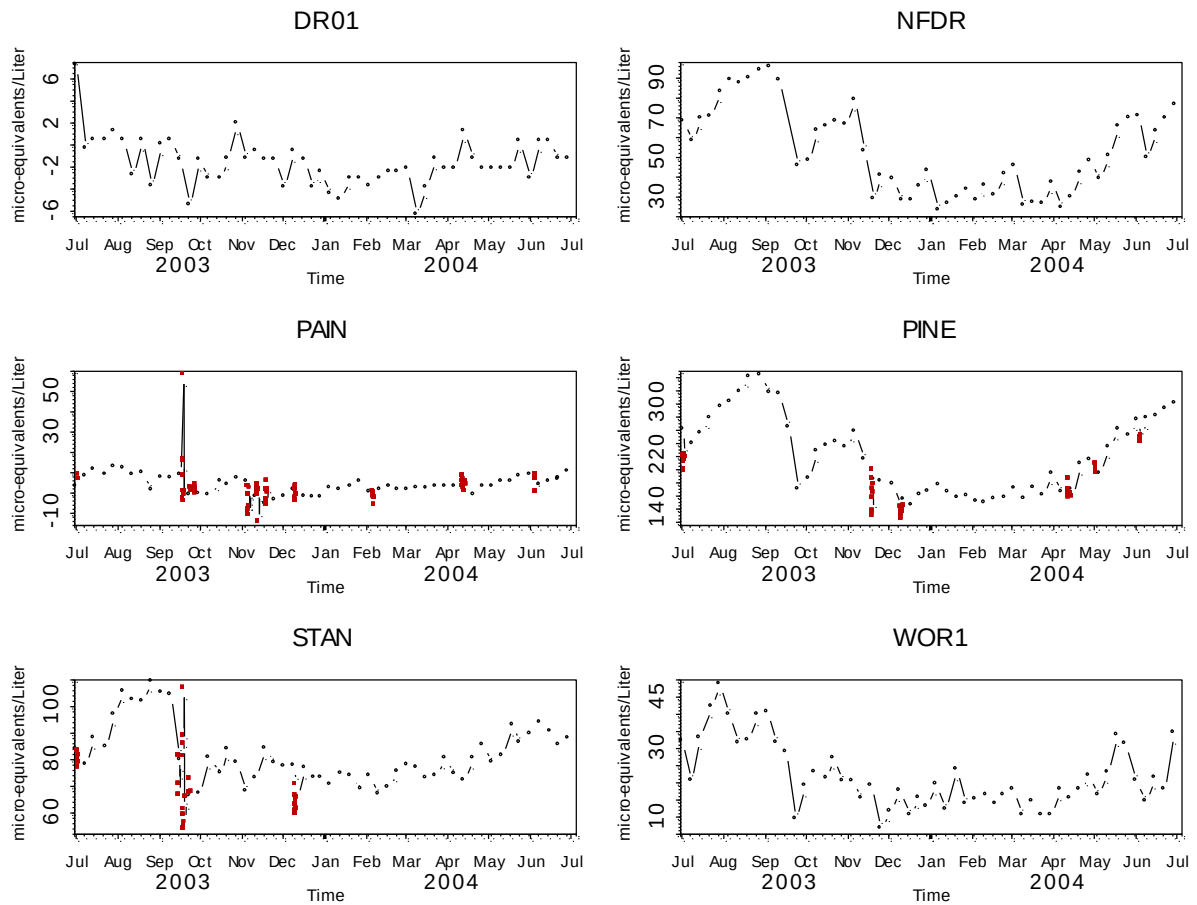
- p value = 2-tailed probability (based on the Kolmogorov-Smirnov statistic) that the current year's distribution of discharge values is the same as the distribution of all previous years' discharge values

Figure 4c: Discharge for 2004 water year (October 1, 2003 – September 30, 2004) and comparison of cumulative frequency distributions for discharge in 2004 with discharge in previous years.



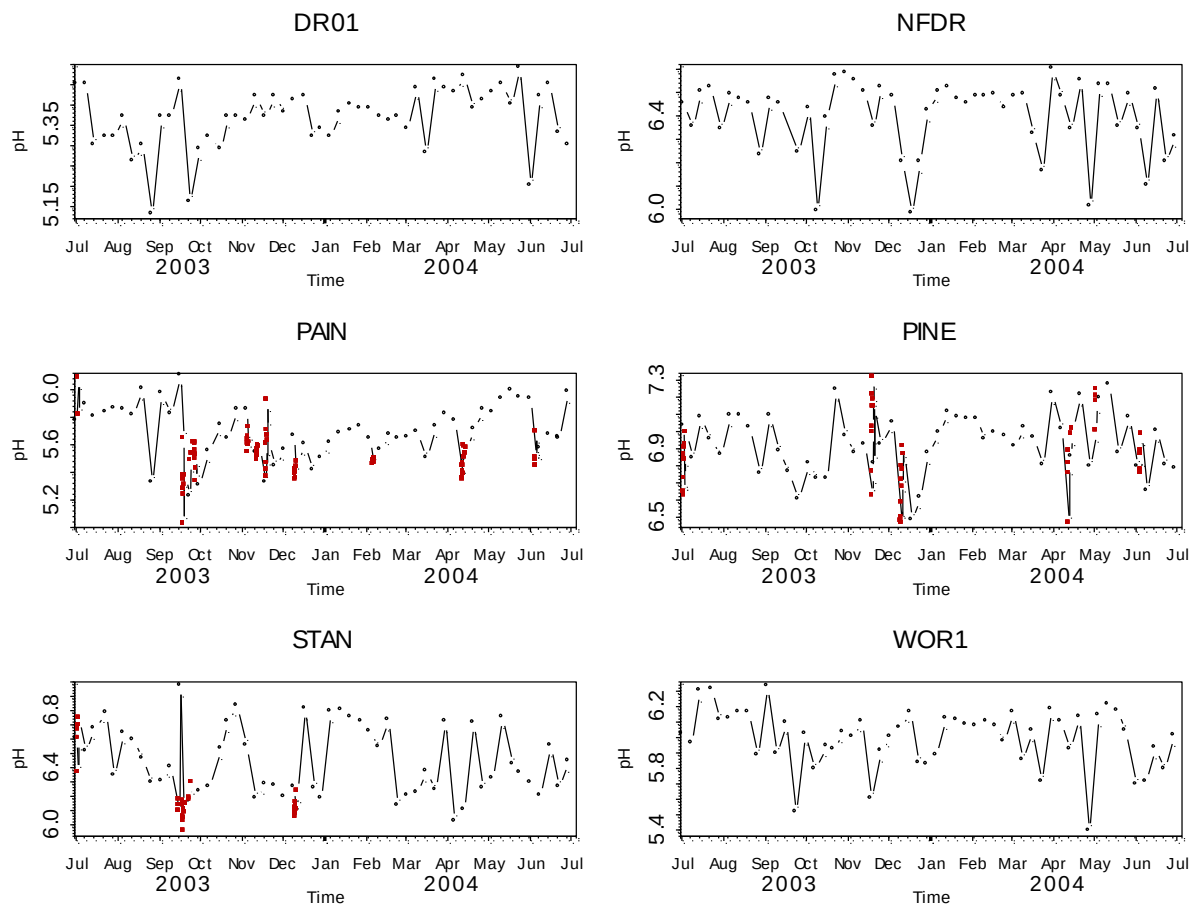
- p value = 2-tailed probability (based on the Kolmogorov-Smirnov statistic) that the current year's distribution of discharge values is the same as the distribution of all previous years' discharge values

Figure 5a: Time-series for intensively studied sites (ANC)



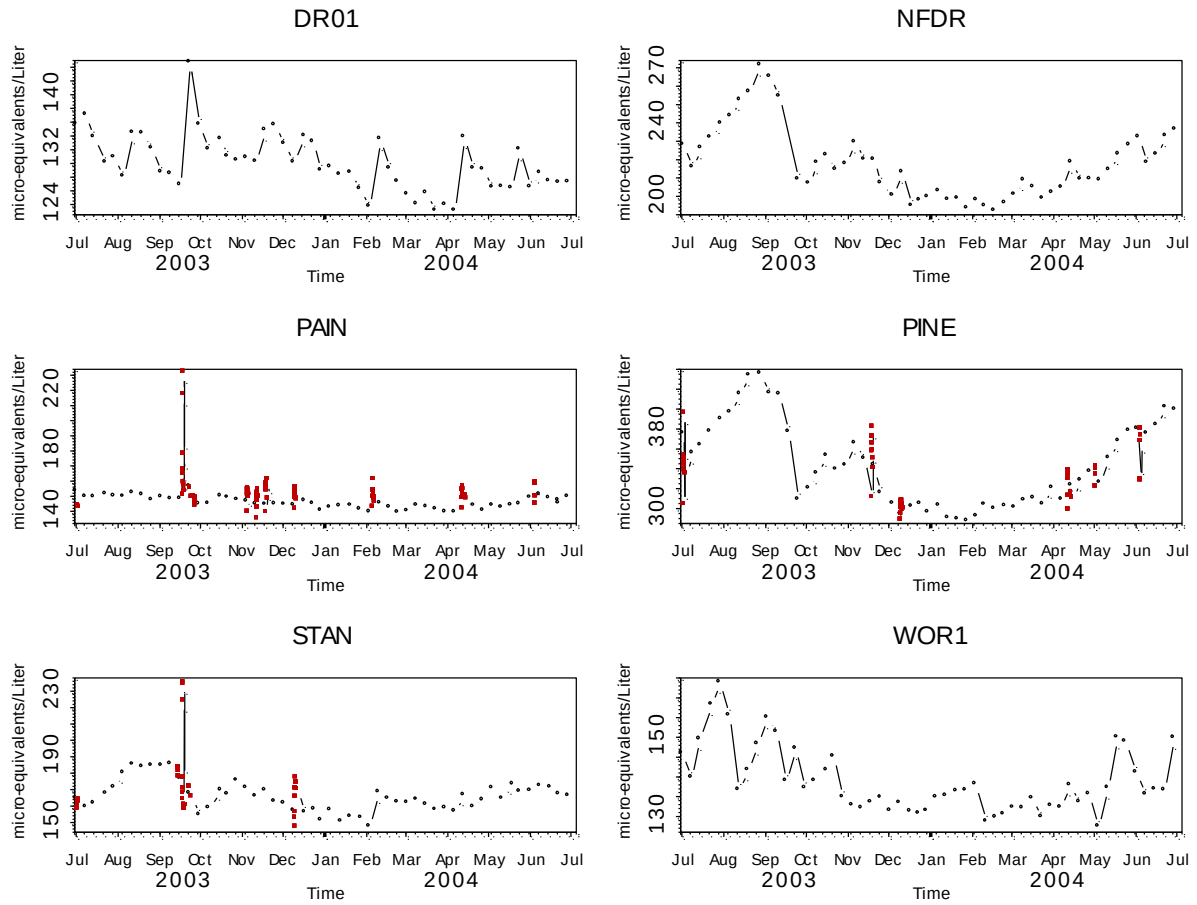
- open points represent weekly grab samples
- closed red points represent episodic (ISCO) samples

Figure 5b: Time-series for intensively studied sites (pH)



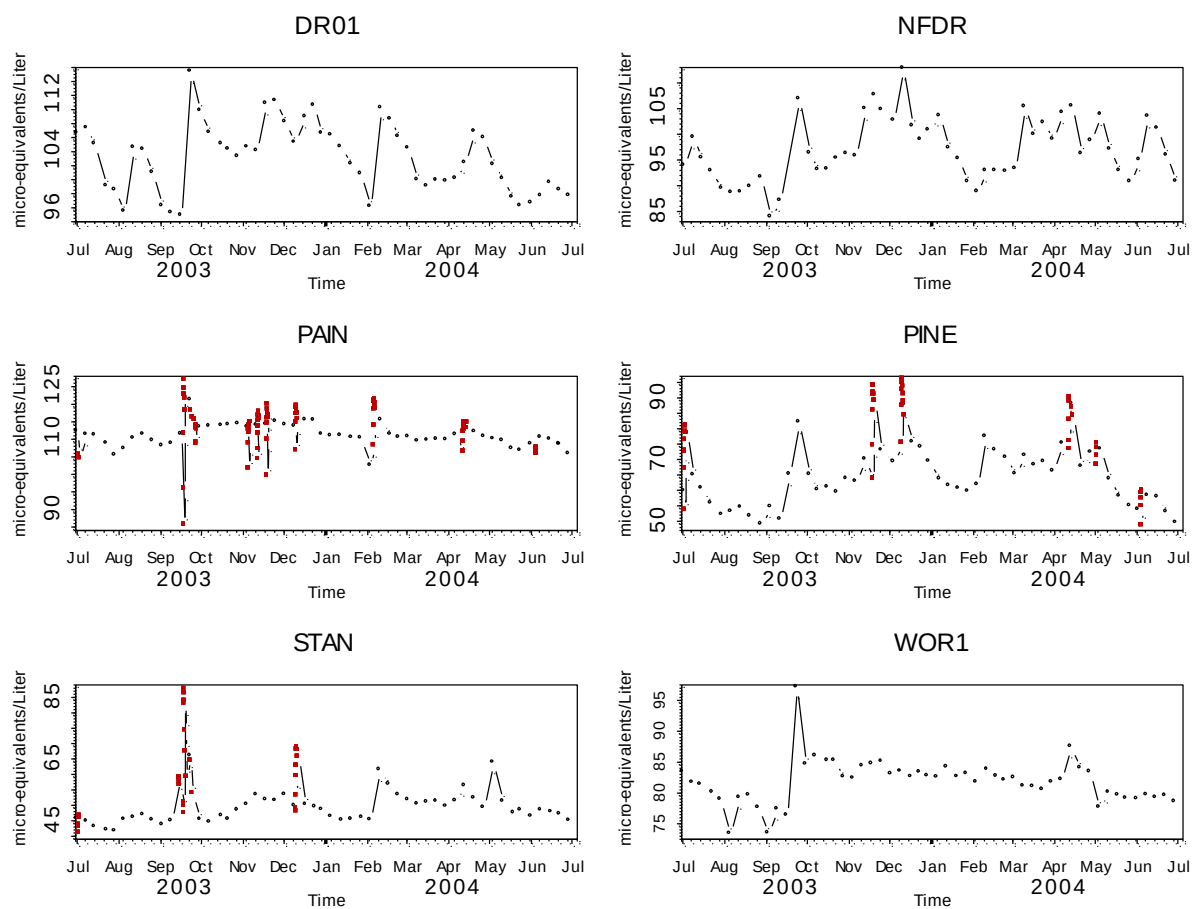
- open points represent weekly grab samples
- closed red points represent episodic (ISCO) samples

Figure 5c: Time-series for intensively studied sites (sum of base cations)



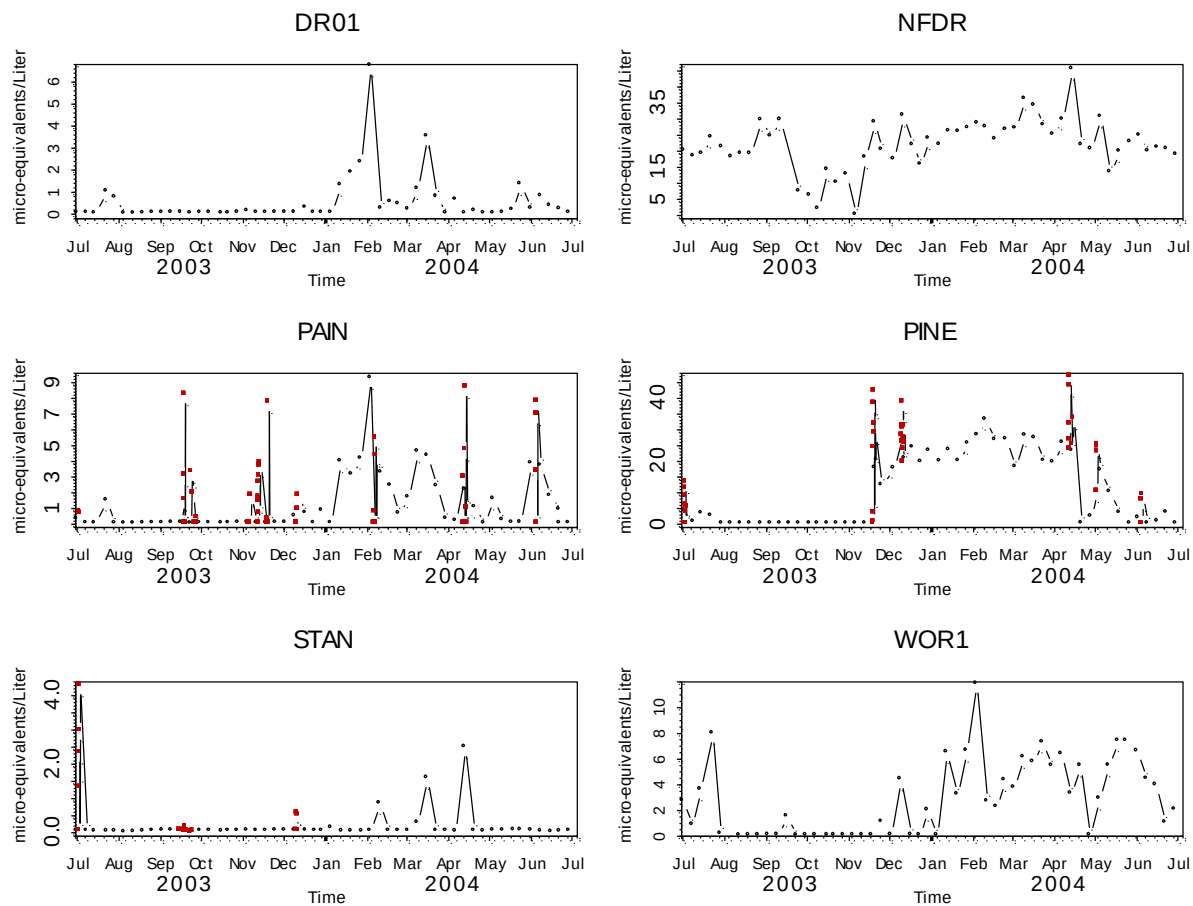
- open points represent weekly grab samples
- closed red points represent episodic (ISCO) samples
- sum of base cations =  $(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+})$

Figure 5d: Time-series for intensively studied sites ( $\text{SO}_4^{2-}$ )



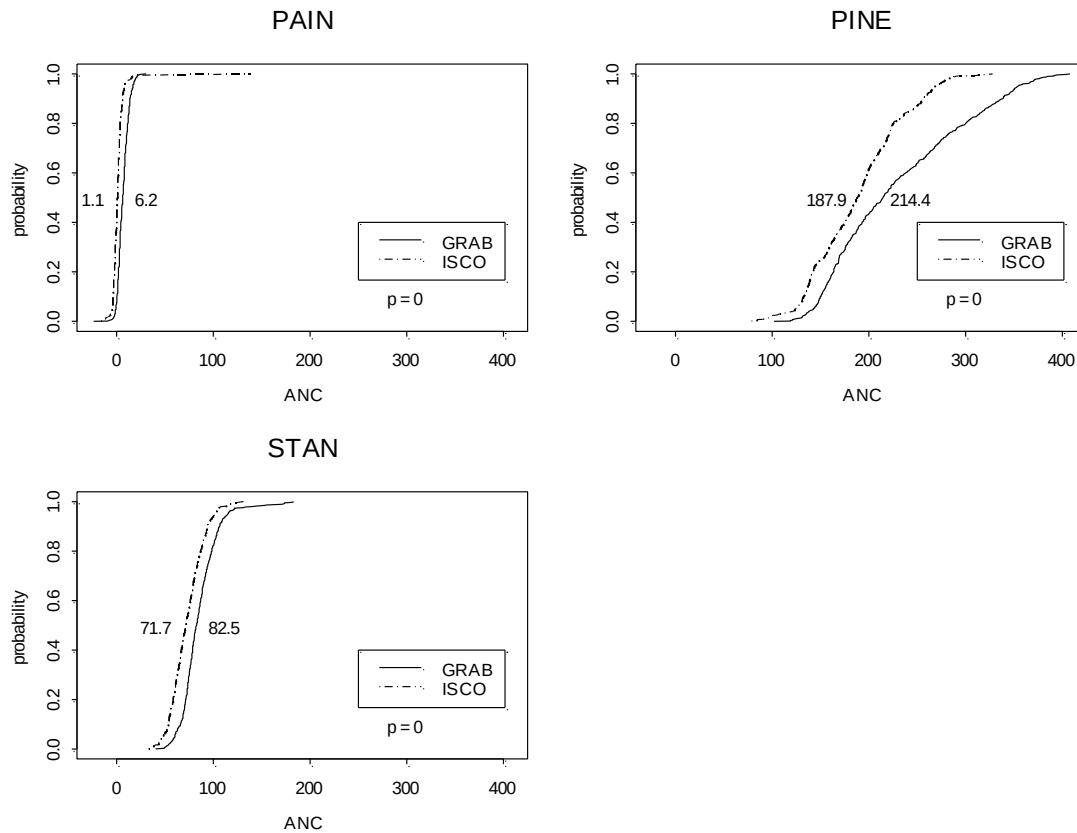
- open points represent weekly grab samples
- closed red points represent episodic (ISCO) samples

Figure 5e: Time-series for intensively studied sites ( $\text{NO}_3^-$ )



- open points represent weekly grab samples
- closed red points represent episodic (ISCO) samples

Figure 6: Comparison of cumulative frequency distributions for ANC associated with weekly grab samples and episodic (ISCO) samples for intensively studied sites



- period of record: 1993-2004 water years
- ANC concentrations =  $\mu\text{eq/L}$
- median values are indicated adjacent CDF lines
- p value = 2-tailed probability (based on the Kolmogorov-Smirnov statistic) that the current year's distribution of concentration values is the same as the distribution of all previous years' concentration values

Figure 7a: Time-series for quarterly sites; 1988-2003 (ANC)

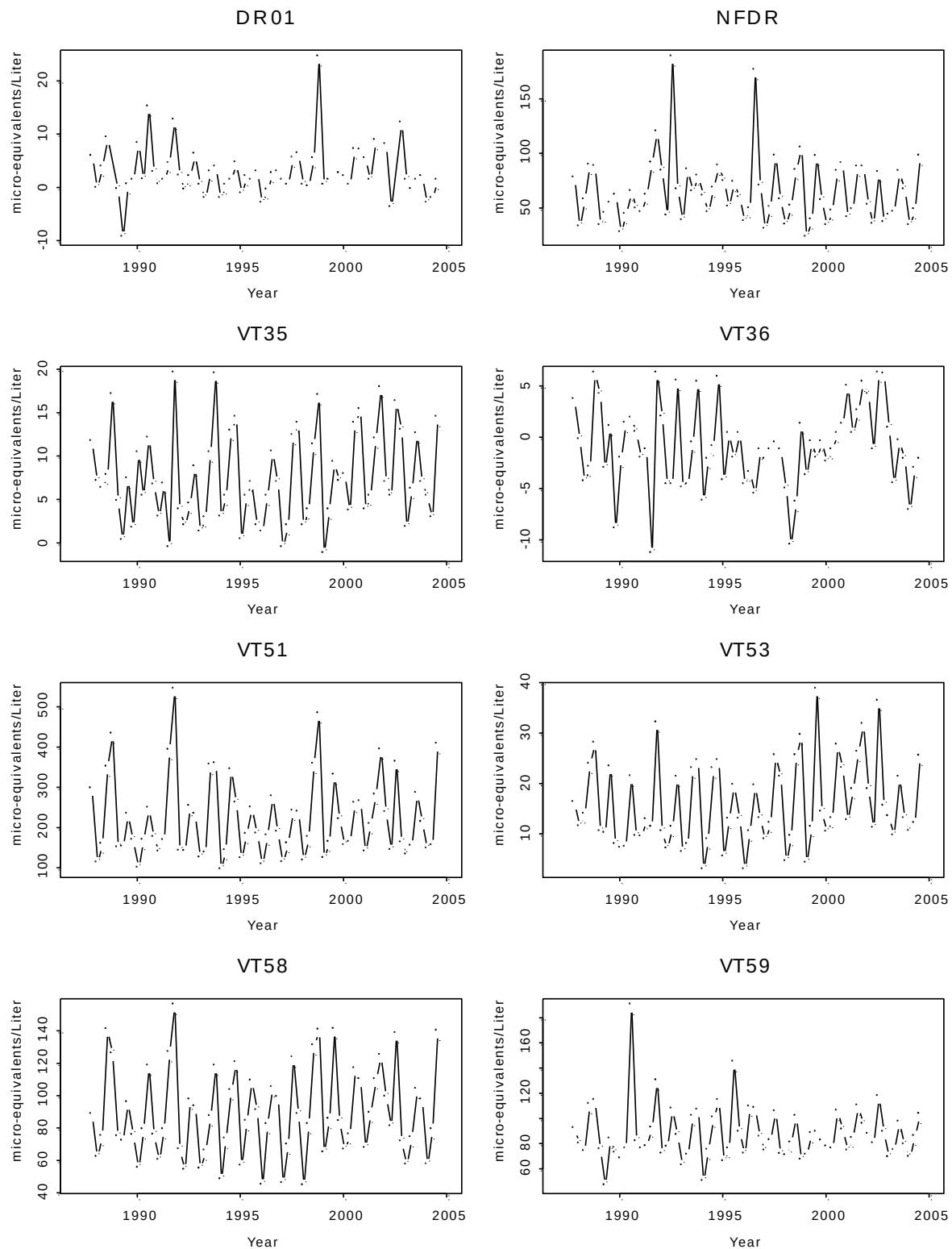


Figure 7a: Time-series for quarterly sites; 1988-2004 (ANC continued)

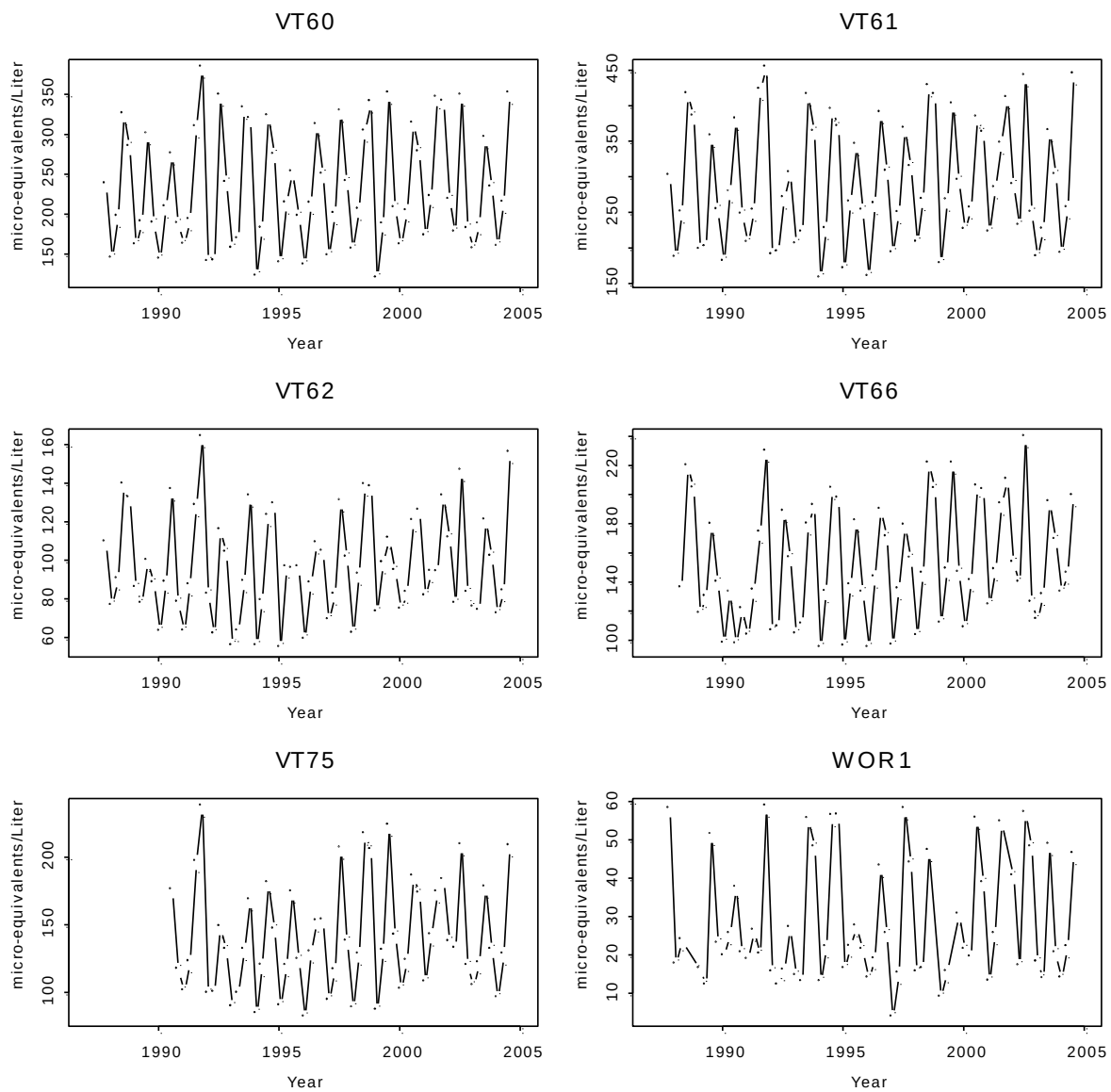


Figure 7b: Time-series for quarterly sites; 1988-2004 (pH)

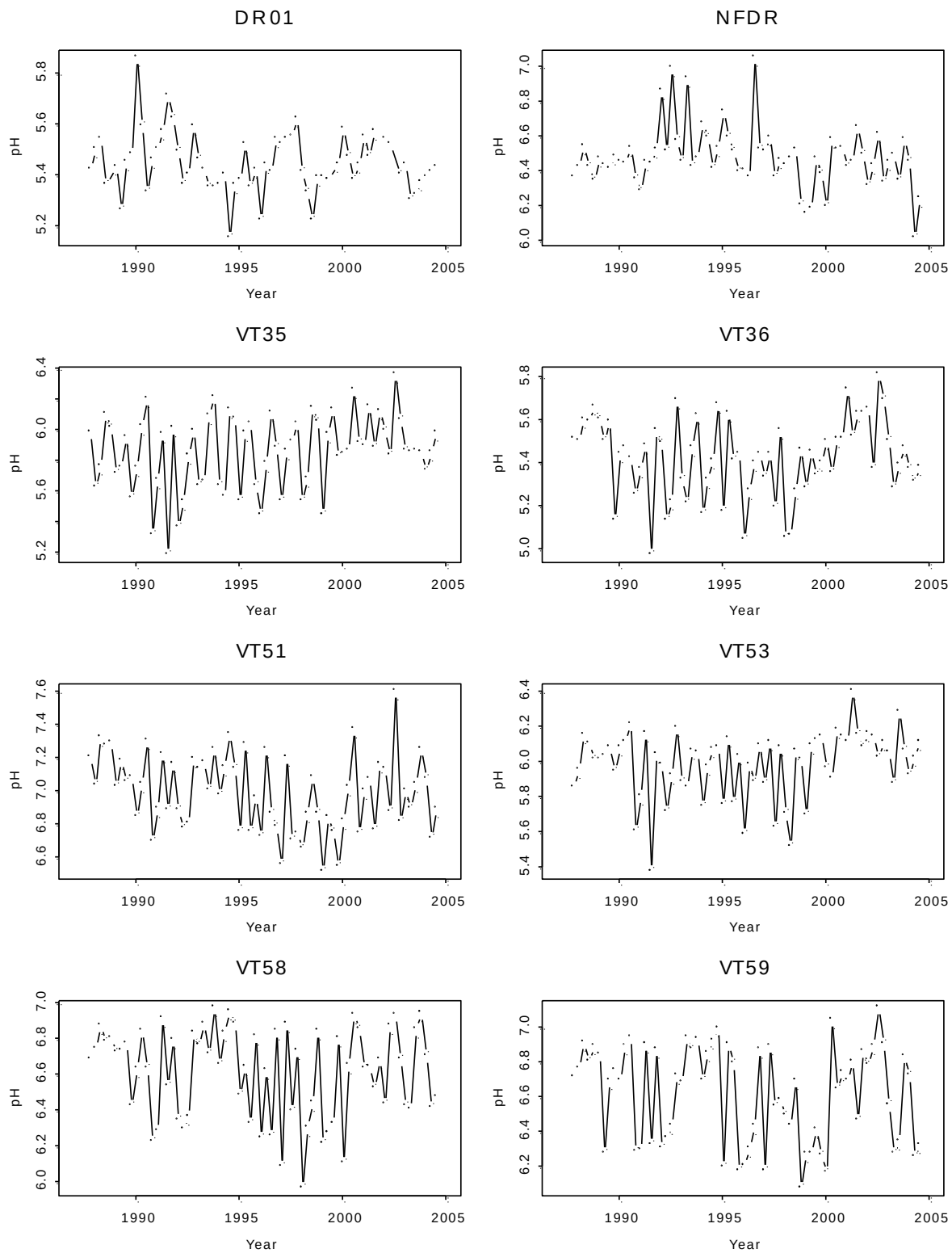


Figure 7b: Time-series for quarterly sites; 1988-2004 (pH continued)

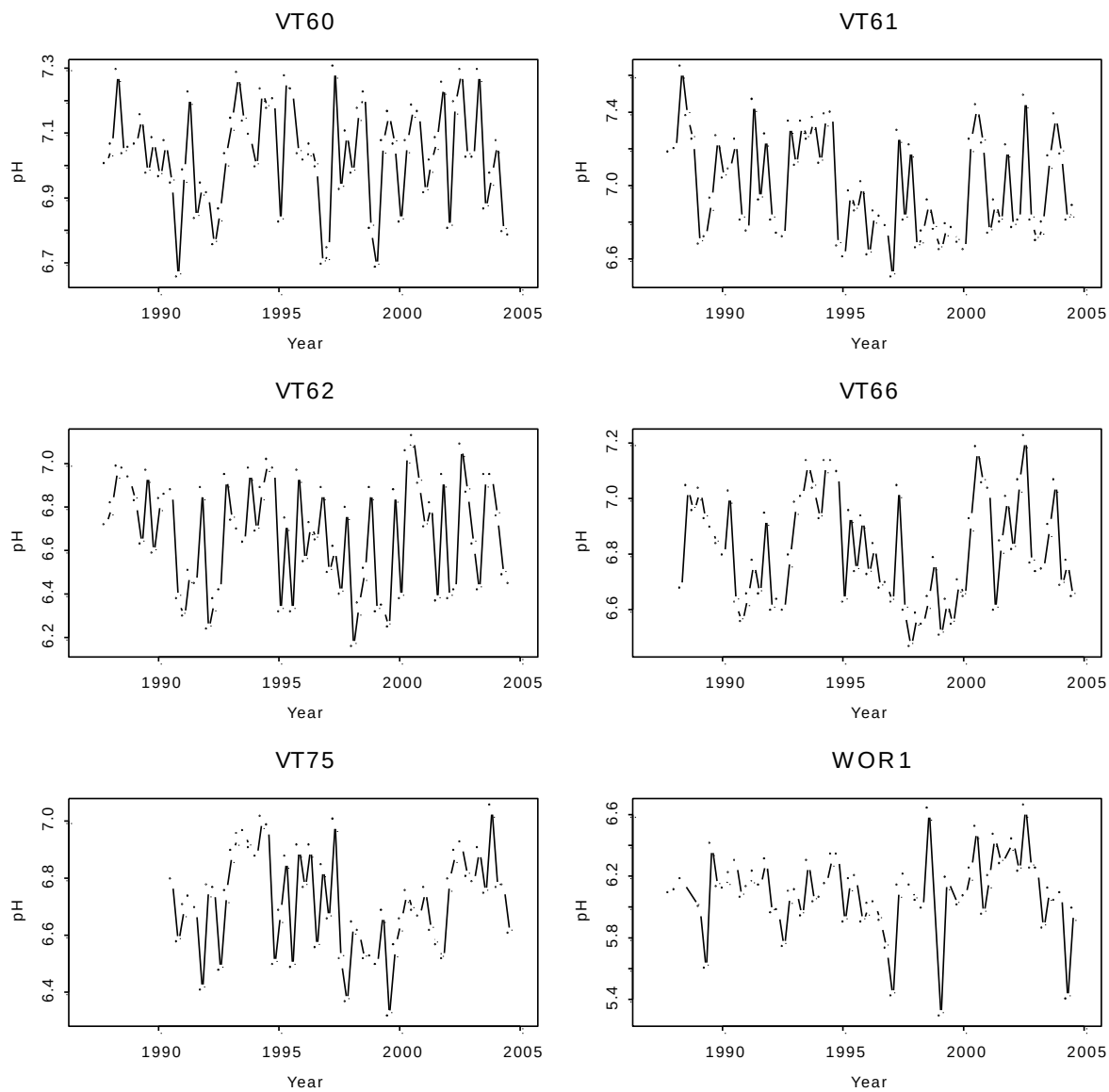


Figure 7c: Time-series for quarterly sites; 1988-2004 (sum of base cations)

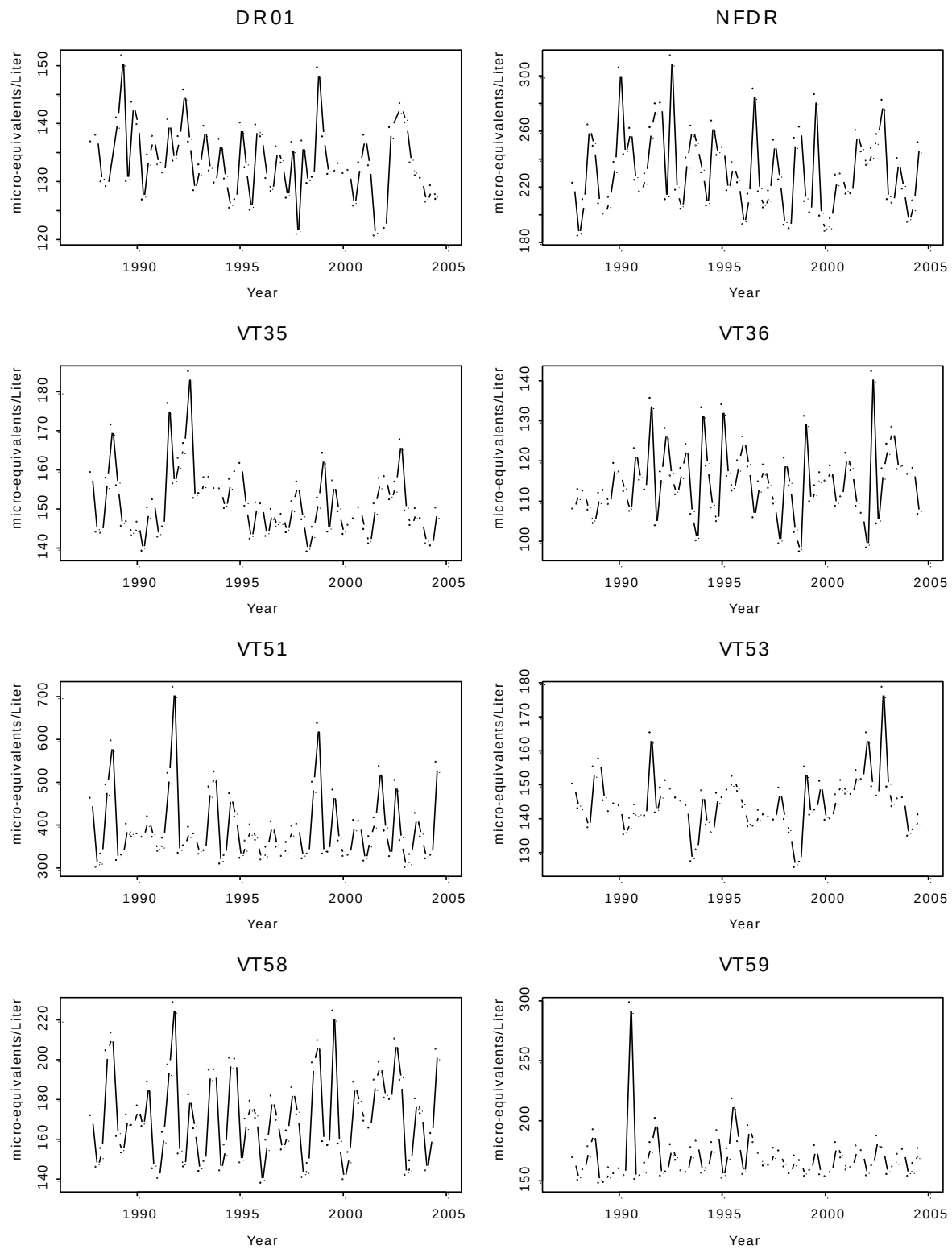
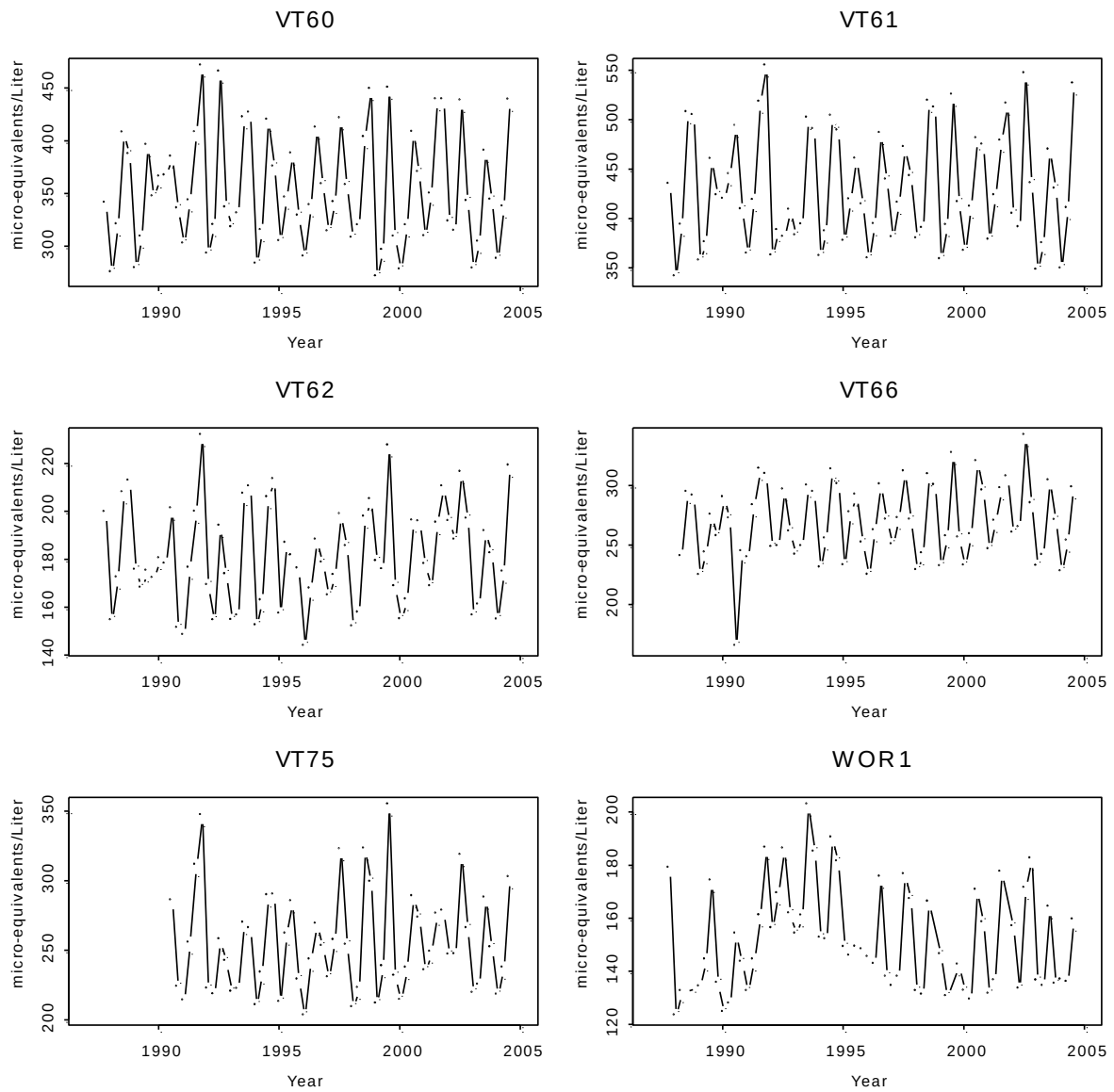


Figure 7c: Time-series for quarterly sites; 1988-2004 (sum of base cations continued)



- sum of base cations =  $(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)$

Figure 7d: Time-series for quarterly sites; 1988-2004 ( $\text{SO}_4^{2-}$ )

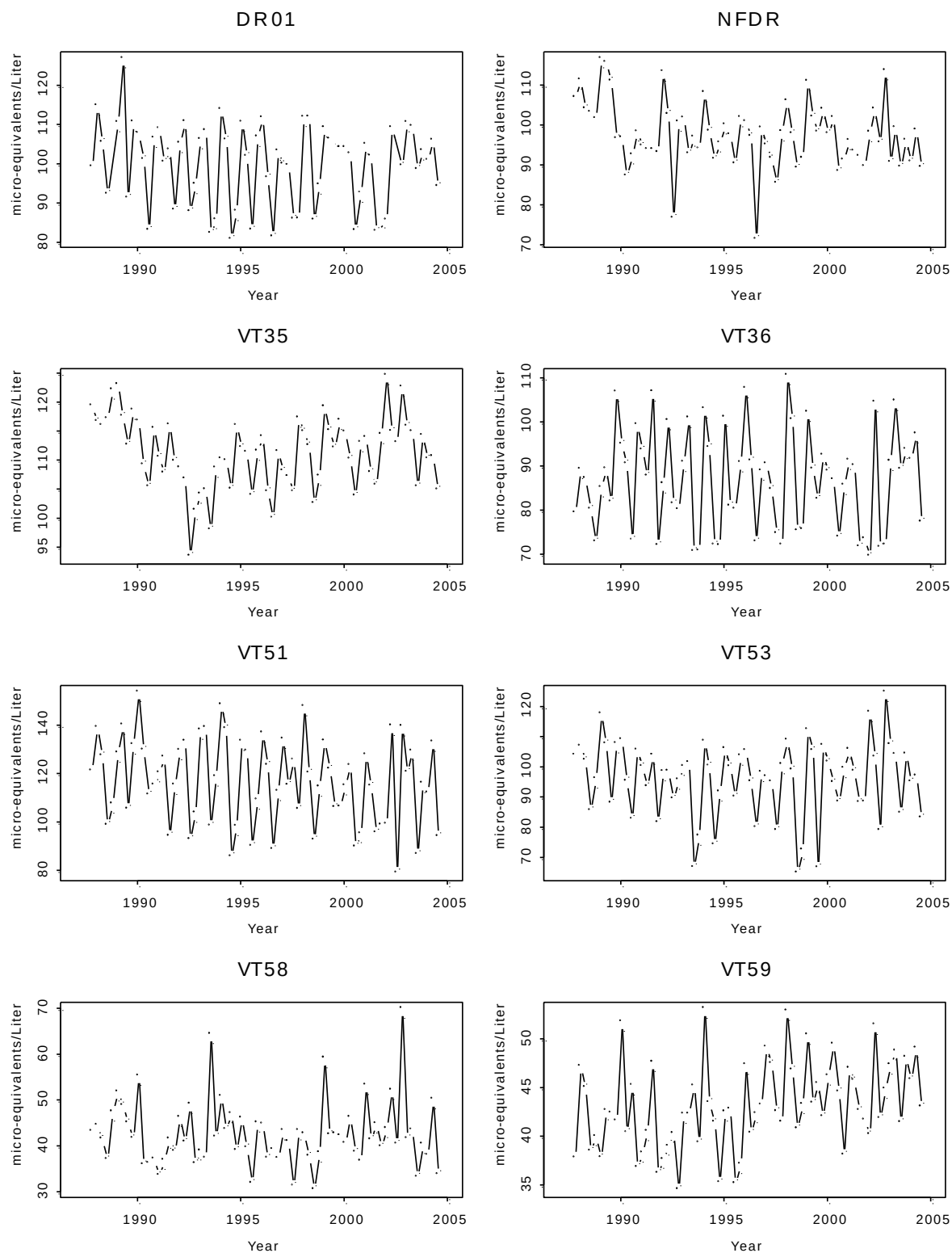


Figure 7d: Time-series for quarterly sites; 1988-2004 ( $\text{SO}_4^{2-}$ -continued)

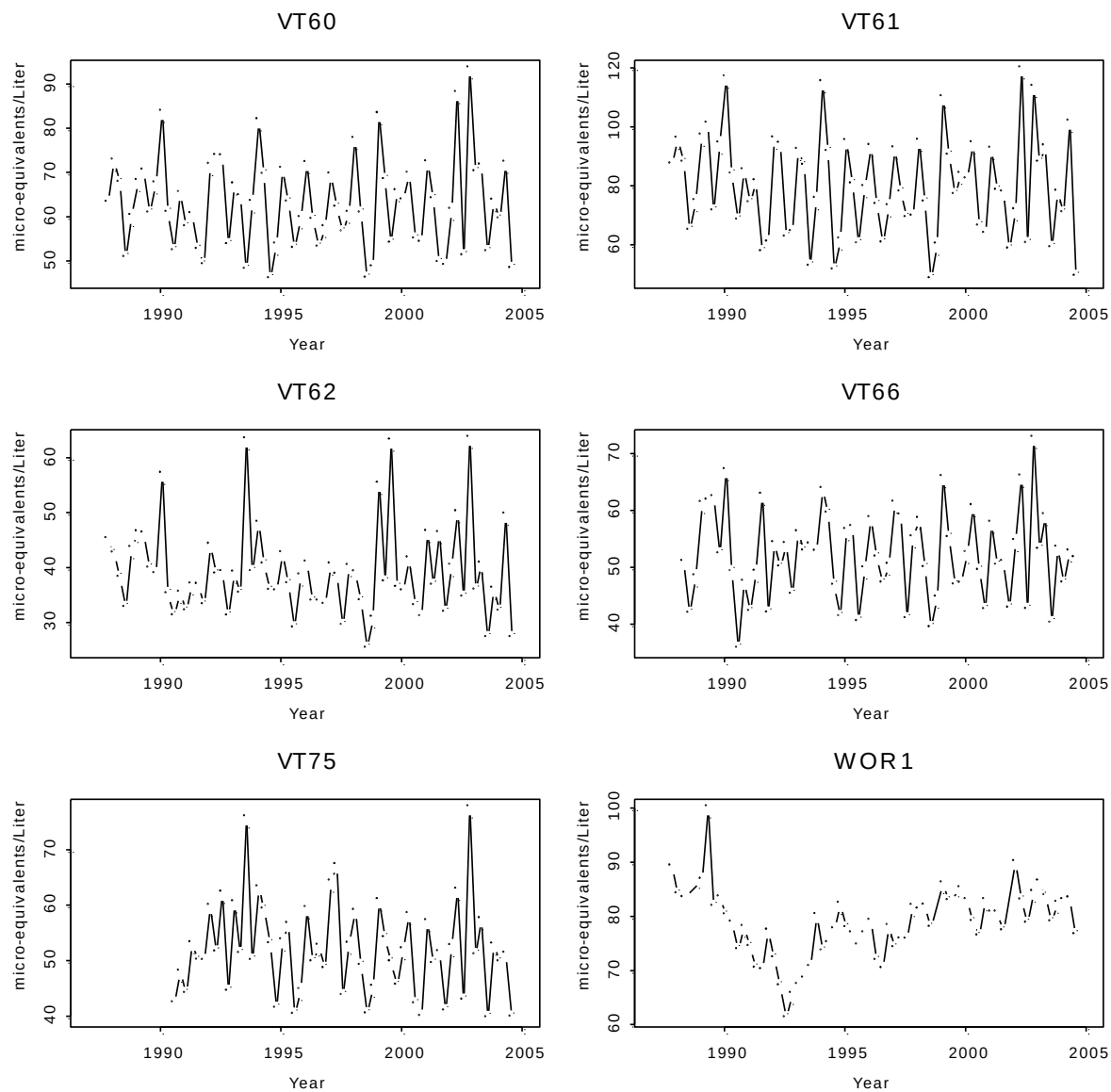


Figure 7e: Time-series for quarterly sites; 1988-2004 ( $\text{NO}_3^-$ )

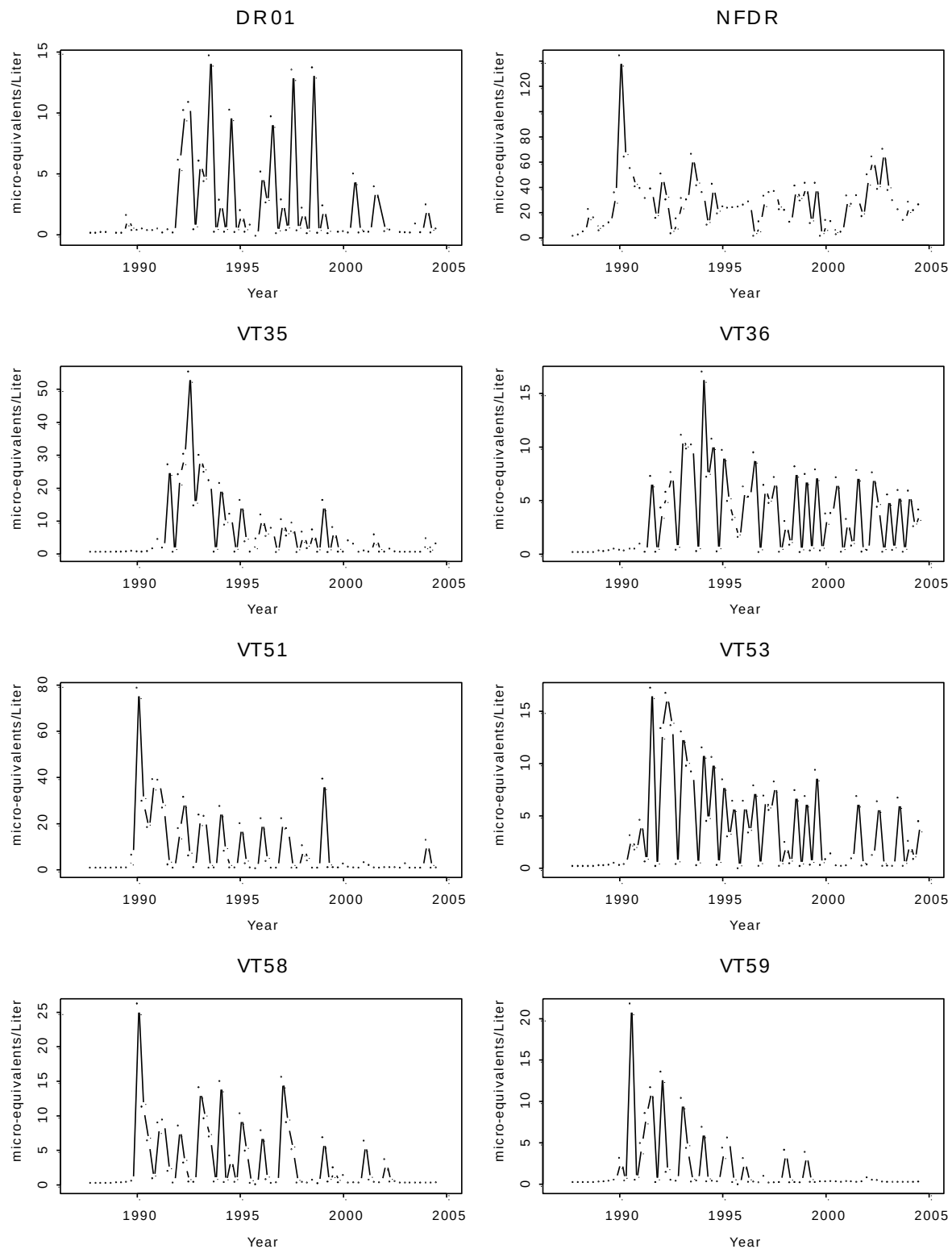


Figure 7e: Time-series for quarterly sites; 1988-2004 ( $\text{NO}_3^-$  continued)

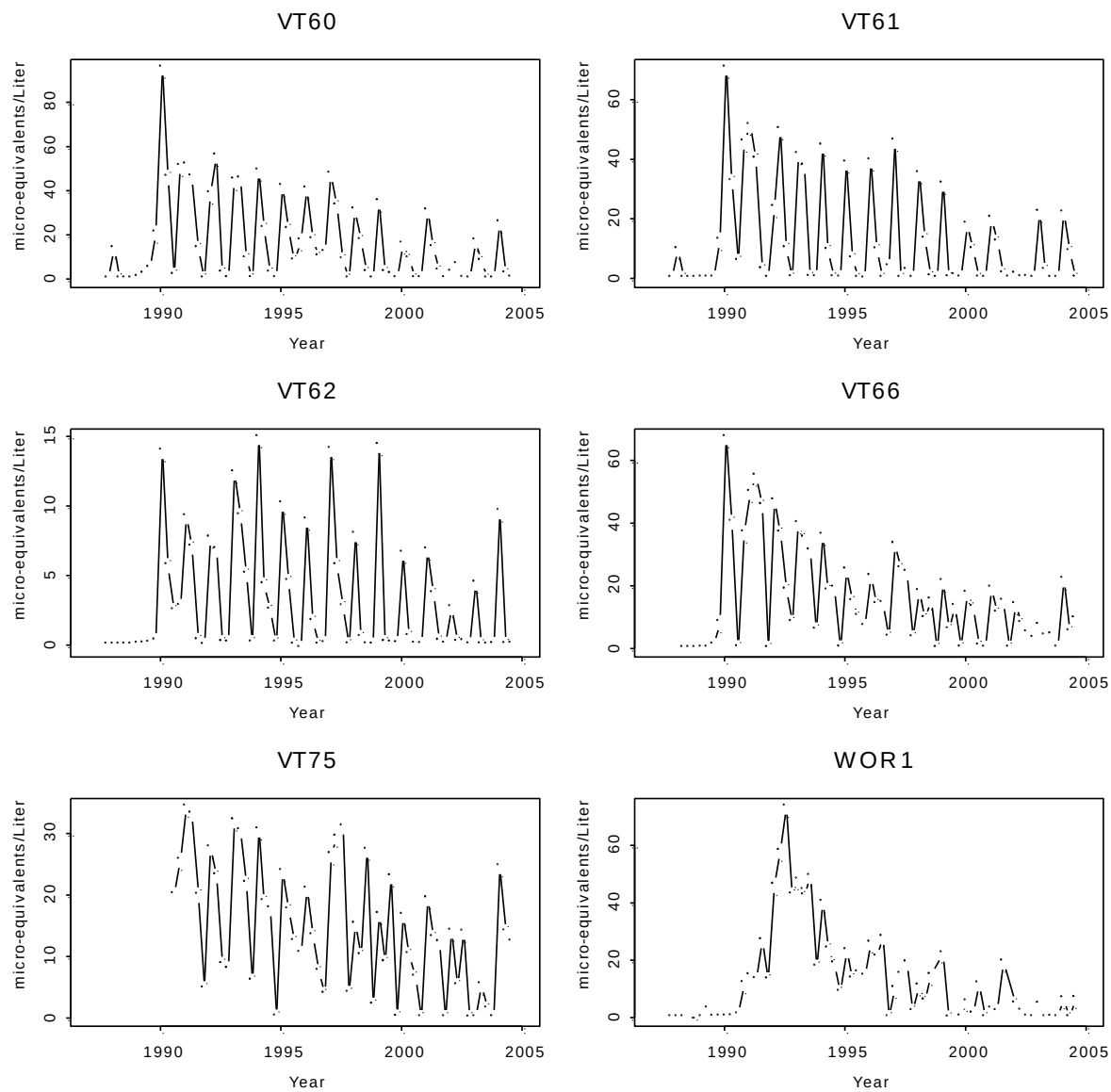
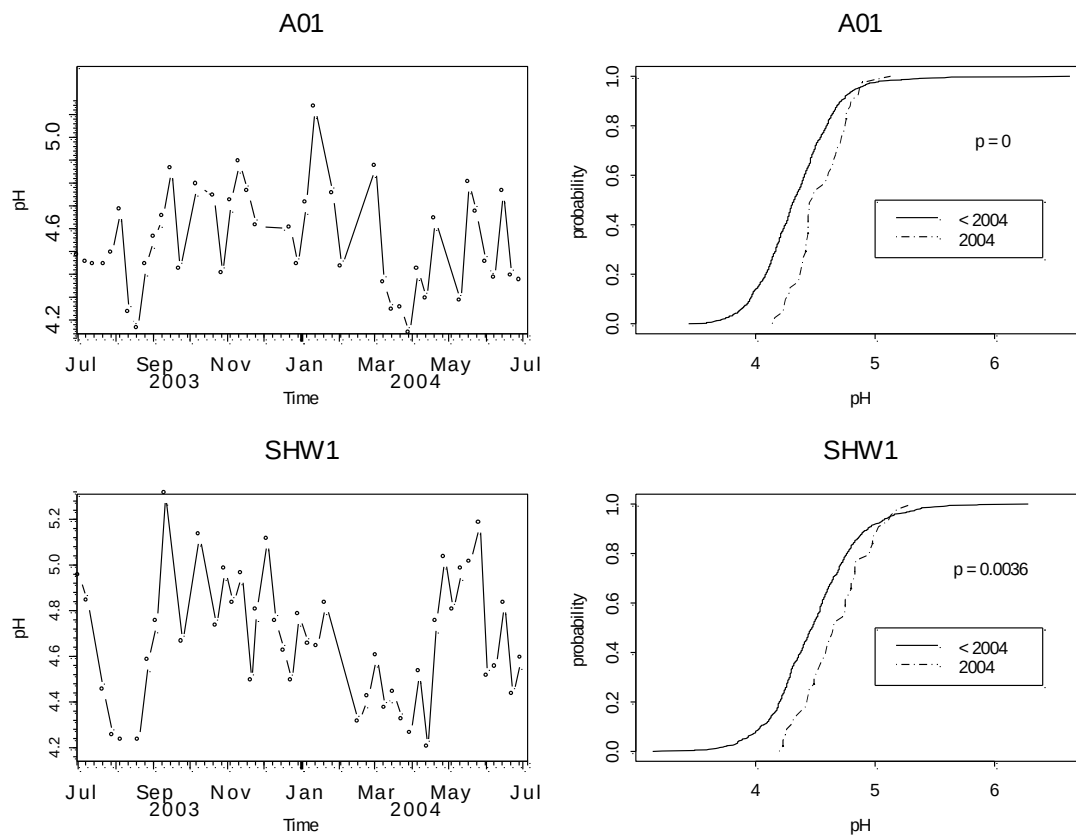
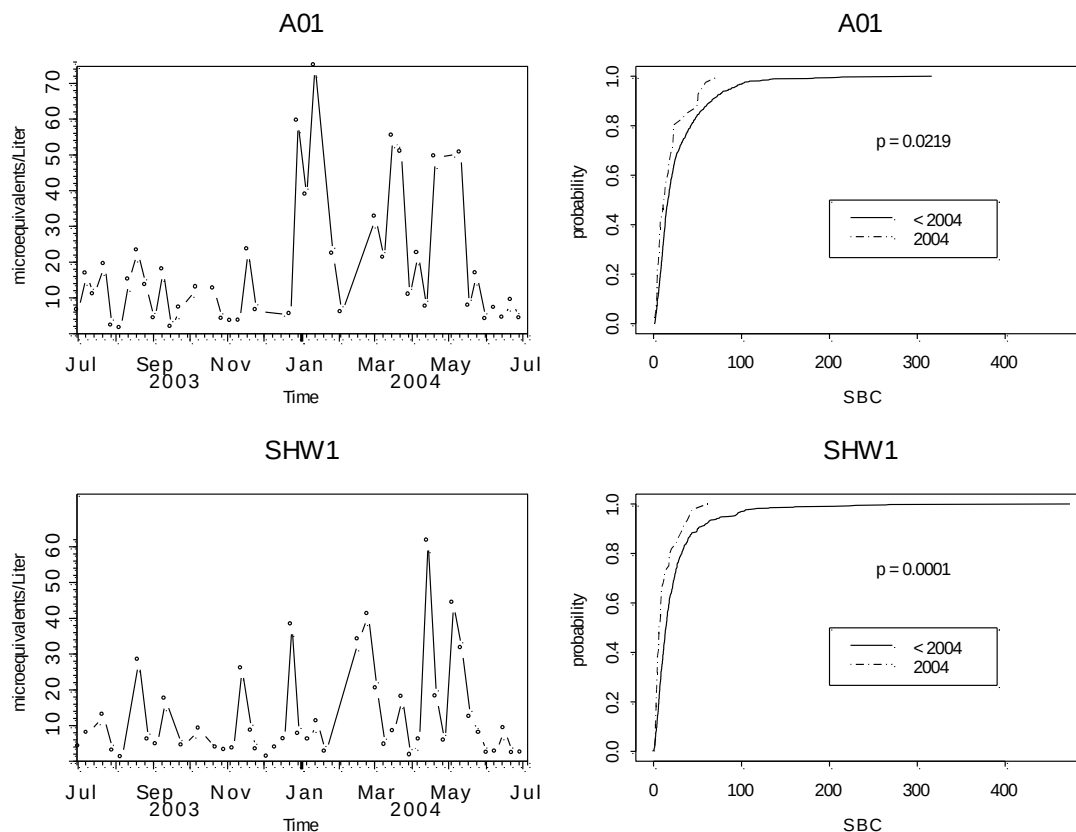


Figure 8a: Precipitation composition; 2004 time series and comparison of cumulative frequency distributions for pH for 2004 and prior record



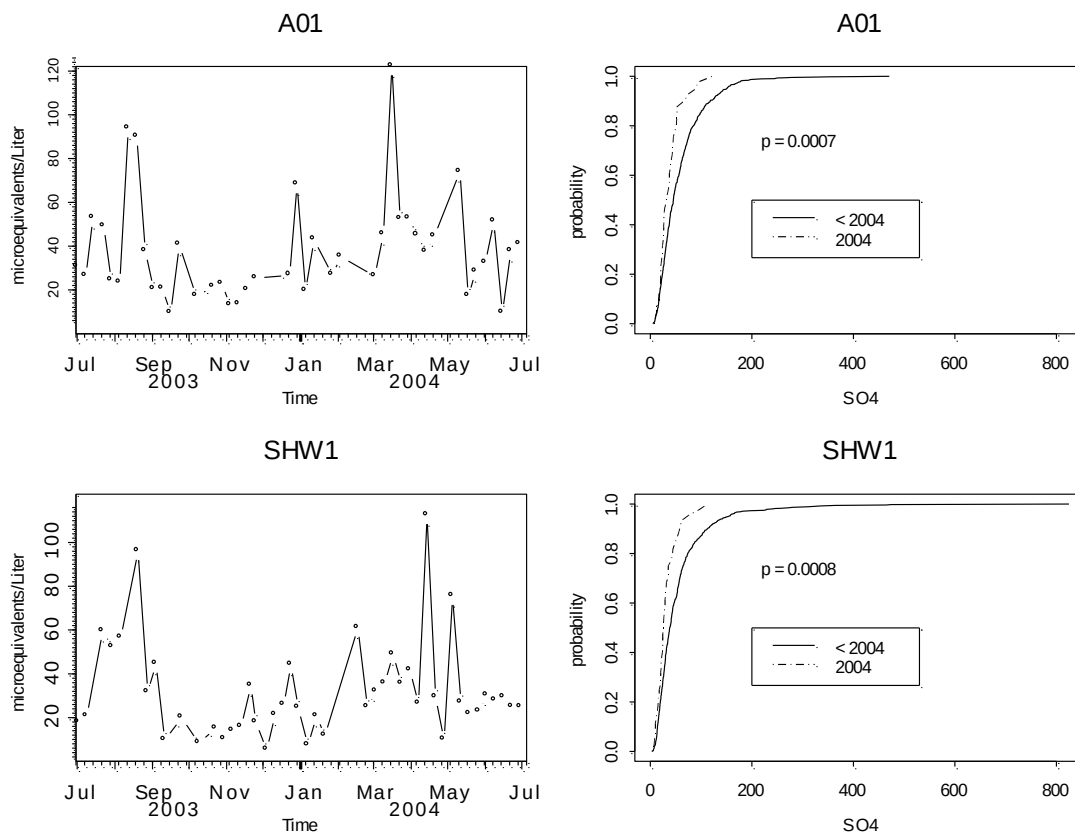
- AO1 is located adjacent the White Oak Run watershed, data collection period = 1979-present
- SHW1 is located in the North Fork of Dry Run watershed, data collection period = 1986-present
- p value = 2-tailed probability (based on the Kolmogorov-Smirnov statistic) that the current year's distribution of concentration values is the same as the distribution of all previous years' concentration values

Figure 8b: Precipitation composition; 2004 time series and comparison of cumulative frequency distributions for sum of base cations for 2004 and prior record



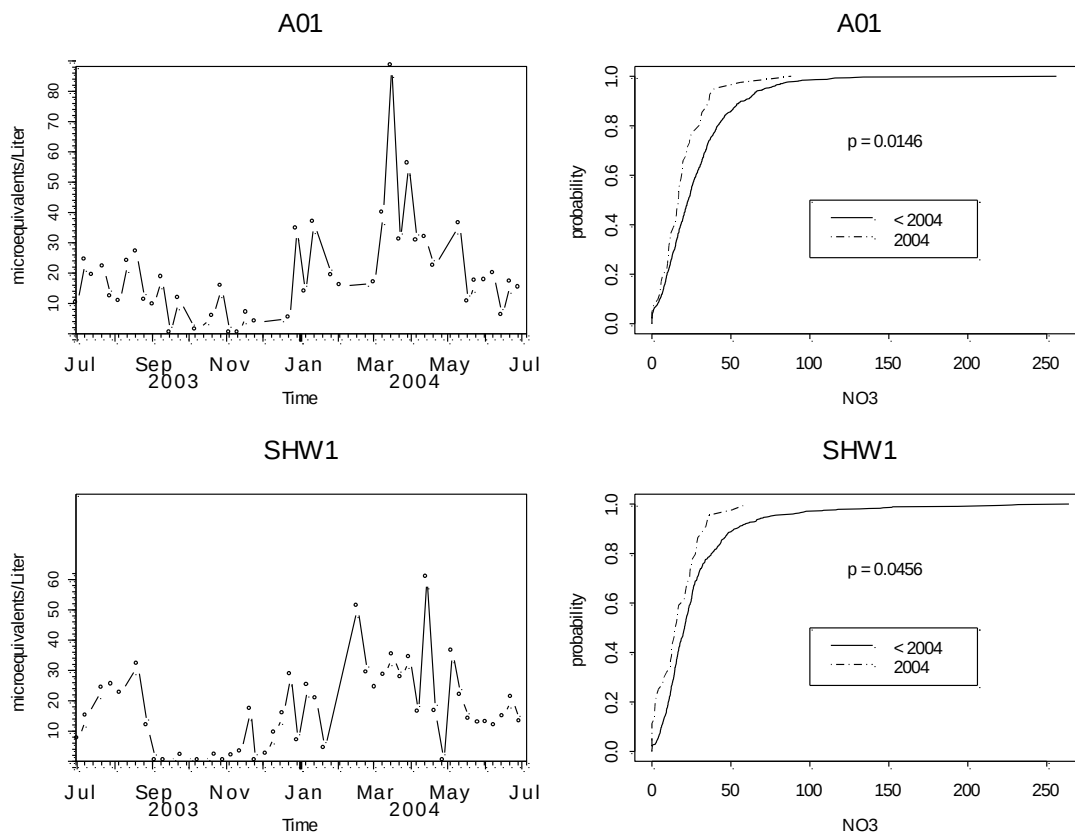
- AO1 is located adjacent the White Oak Run watershed, data collection period = 1979-present
- SHW1 is located in the North Fork of Dry Run watershed, data collection period = 1986-present
- sum of base cations =  $(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+})$
- p value = 2-tailed probability (based on the Kolmogorov-Smirnov statistic) that the current year's distribution of concentration values is the same as the distribution of all previous years' concentration values

Figure 8c: Precipitation composition; 2004 time series and comparison of cumulative frequency distributions for  $\text{SO}_4^{2-}$  for 2004 and prior record



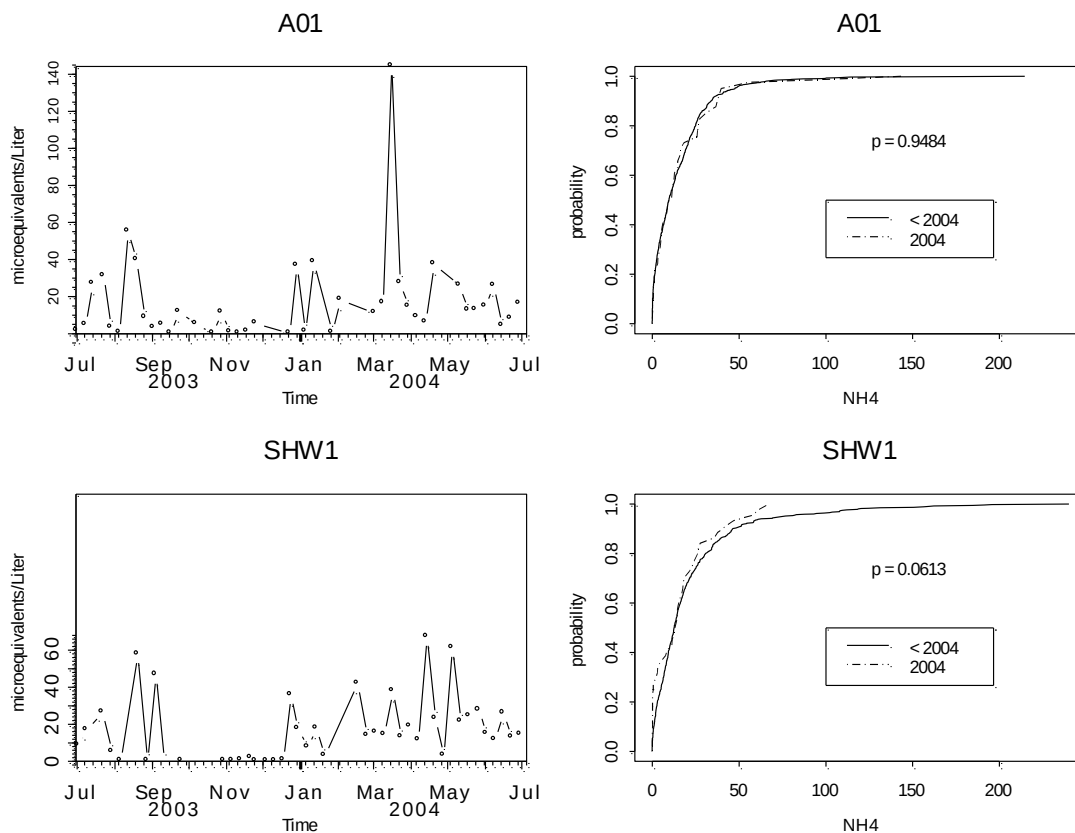
- AO1 is located adjacent the White Oak Run watershed, data collection period = 1979-present
- SHW1 is located in the North Fork of Dry Run watershed, data collection period = 1986-present
- p value = 2-tailed probability (based on the Kolmogorov-Smirnov statistic) that the current year's distribution of concentration values is the same as the distribution of all previous years' concentration values

Figure 8d: Precipitation composition; 2004 time series and comparison of cumulative frequency distributions for  $\text{NO}_3^-$  for 2004 and prior record



- AO1 is located adjacent the White Oak Run watershed, data collection period = 1979-present
- SHW1 is located in the North Fork of Dry Run watershed, data collection period = 1986-present
- p value = 2-tailed probability (based on the Kolmogorov-Smirnov statistic) that the current year's distribution of concentration values is the same as the distribution of all previous years' concentration values

Figure 8e: Precipitation composition; 2004 time series and comparison of cumulative frequency distributions for  $\text{NH}_4^+$  for 2004 and prior record



- AO1 is located adjacent the White Oak Run watershed, data collection period = 1979-present
- SHW1 is located in the North Fork of Dry Run watershed, data collection period = 1986-present
- p value = 2-tailed probability (based on the Kolmogorov-Smirnov statistic) that the current year's distribution of concentration values is the same as the distribution of all previous years' concentration values

## Appendices

### I. Publications

*The following publications for 2004 include data and analysis results obtained through the SWAS program. Some of these publications may have also been listed in previous reports.*

- Eshleman, K.N., D.A. Fiscus, N.M. Castro, J.R. Webb, and A.T. Herlihy. 2004. Regionalization of disturbance-induced nitrogen leakage from mid-Appalachian forests using a linear systems model. *Hydrological Processes*, 18: 2713-2725.
- Kahl, J.S., J. Stoddard, R. Haeuber, S. Paulsen, R. Birnbaum, F. Deviney, D. DeWalle, C. Driscoll, A. Herlihy, J. Kellogg, P. Murdoch, K. Roy, W. Sharpe, S. Urquhart, R. Webb, and K. Webster, 2004. Response of surface water chemistry to changes in acidic deposition: implications for future amendments to Clean Air Act. *Environmental Science and Technology*, 38: 473-496.  
([http://swas.evsc.virginia.edu/Assests/Docs/121504feature\\_kahl.pdf](http://swas.evsc.virginia.edu/Assests/Docs/121504feature_kahl.pdf))
- Sullivan, T.J., B.J. Cosby, A.T. Herlihy, J.R. Webb, A.J. Bulger, K.U. Snyder, P. Brewer, E.H. Gilbert, D. Moore. 2004. Regional Model Projections of Future Effects of Sulfur and Nitrogen Deposition on Streams in the Southern Appalachian Mountains. *Water Resources Research* Vol. 40, No. 2, W02101. doi:10.1029/2003WR001998.
- Rice, K.C., J.G. Chant, G.M. Hornberger, and J.R. Webb. 2004. Interpretation of concentration-discharge patterns in acid-neutralizing capacity during stormflow in three small, forested catchments in Shenandoah National Park, Virginia. *Water Resources Research*, 40, No. 5, W05301, doi:10.1029/2003WR002709.
- Rice, K.C., F.A. Deviney, G.M. Hornberger, and J.R. Webb. Predicting the Vulnerability of Streams to Episodic Acidification in Shenandoah National Park, Virginia. U.S. Geological Survey, Professional Paper, in review.
- Webb, J.R., B.J. Cosby, F.A. Deviney, Jr., J.N. Galloway, S.W. Maben, and A.J. Bulger. 2004. Are brook trout streams in western Virginia and Shenandoah National Park recovering from acidification?, *Environmental Science and Technology*, 38: 4091-496.  
(<http://swas.evsc.virginia.edu/Assests//Docs/Recovery-Question.pdf>)
- Webb, R. 2004. Twenty-Five Years of Watershed Research and Monitoring: Shenandoah Watershed Study Overview. National Park Service brochure.  
(<http://swas.evsc.virginia.edu/Assests/Docs/Twenty-Five-Years-Of-Watershed-Study.pdf>)
- Webb, R. 2004. Effects of Acidic Deposition on Aquatic Resources in the Central Appalachian Mountains: A Shenandoah Watershed Study Report.  
(<http://swas.evsc.virginia.edu/Assests/Docs/Effects.pdf>)

## II. Presentations

*The following presentations for 2004 include data and analysis results obtained through the SWAS program. Some of these presentations may have also been listed in previous reports.*

Webb, J.R. Effects of Acidic Deposition in the Forested Mountain Watersheds of the Central and Southern Appalachian Mountains. Atlantic Science and Conservation Strategies Workshop (The Nature Conservancy), Point Clear, Alabama, 2004.

Webb, J.R., B.J. Cosby, F.A. Deviney, Jr., and J.N. Galloway. Evidence for Recovery From Streamwater Acidification in Shenandoah National Park, Virginia. Annual meeting of the Virginia Chapter of the American Fisheries Society, Lexington, Virginia, 2004.

Webb, J.R., B.J. Cosby, F.A. Deviney, Jr., J.N. Galloway, S.W. Maben, and A.J. Bulger.. Are brook trout streams in western Virginia and Shenandoah National Park recovering from acidification? Virginia Mountain Streams Symposium, Charlottesville, Virginia. 2004

## III. Outreach

### The Virginia Mountain Stream Symposium

The Shenandoah Watershed Study celebrated its 25th anniversary in the fall of 2004 by hosting the Virginia Mountain Streams Symposium.

The Symposium focused on the challenges facing mountain streams due to changes within their watersheds (e.g., logging, fire, insect defoliation) and due to external stressors (ozone, acid rain, climate change).

The Symposium included a poster session and program information displays in the morning for both the scientific community and the interested public. In the afternoon there were presentations reflecting the perspectives of scientific, state, federal, industrial and not-for-profit stakeholders concerned with Virginia's mountain streams. Approximately two hundred people attended.

Funding and other support for the symposium was provided by the National Park Service, Trout Unlimited, Canaan Valley Institute, Southern Environmental Law Center, Dominion Resources, and the Environmental Protection Agency.

A description of the Symposium, including a listing of presentation, photographs, and a summary of findings is available on the SWAS website: <http://swas.evsc.virginia.edu>.

### The SWAS-VTSSS Website

The program website has been rebuilt (see <http://swas.evsc.virginia.edu>). The new site provides more information about the SWAS program in general than did the previous site, including

access to many reports, documents, and presentations. SWAS laboratory methods are posted and maps of study sites are provided.

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