

**SHENANDOAH NATIONAL PARK
SHENANDOAH WATERSHED STUDY (SWAS)
2005 Report**



James R. Webb, Frank A. Deviney, Jr., Suzanne Maben
Department of Environmental Sciences
University of Virginia

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Cover photo: bioassay research on Meadow Run, a SWAS program study stream

Shenandoah Watershed Study (SWAS)

2005 Report

1. EXECUTIVE SUMMARY	5
2. SIGNIFICANT FINDINGS.....	6
3. RECOMMENDATIONS FOR SHEN MANAGEMENT AND SWAS PROGRAM.....	6
4. INTRODUCTION/BACKGROUND	7
5. OBJECTIVES.....	8
6. STUDY AREA DESCRIPTION	8
7. METHODS.....	9
8. FINDINGS AND DISCUSSION.....	9
9. CURRENT RECOMMENDATIONS	11
10. CITATIONS	13
TABLES AND FIGURES	15
Table 1: SWAS study watersheds.....	16
Table 2: Difference between calendar-year 2005 and pre-2005 mean concentrations	17
Figure 1: Distribution of SWAS study watersheds in relation to major bedrock classes in SHEN	19
Figure 2: Schematic of SWAS watershed monitoring framework, indicating stratification by bedrock class and sampling frequency for study watersheds	20
Figure 3: Number of stream water samples collected.....	21
Figure 4: Discharge for 1992 – 2005 calendar years for Paine Run, Piney River, and Staunton River.....	22
Figure 5: Discharge for 2004 and 2005 calendar years and comparison of cumulative frequency distributions for discharge in 2005 and in all pre-2005 years.	23
Figure 6a: ANC concentrations for SWAS study streams by calendar year.....	25
Figure 6b: pH concentrations for SWAS study streams by calendar year..	27
Figure 6c: Sum of base cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$) values for SWAS study streams by calendar year.	29
Figure 6d: Sulfate concentrations for SWAS study streams by calendar year.....	31
Figure 6e: Nitrate concentrations for SWAS study streams by calendar year.	33
Figure 7a: Time-series plots of ANC for SWAS study streams..	37
Figure 7b: Time-series plots of pH for SWAS study streams.....	37
Figure 7c: Time-series plots of base cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$) for SWAS study streams.	39
Figure 7d: Time-series plots of sulfate concentrations for SWAS study streams.....	41
Figure 7e: Time-series plots of nitrate concentrations for SWAS study streams	43

I. PUBLICATIONS AND PRESENTATIONS.....	47
III. OUTREACH	47

Shenandoah Watershed Study (SWAS)

2005 Report

Start and End Dates: ongoing (1979 – present)

Report Period: 01/01/05 – 12/31/05

Principal Investigator(s): James N. Galloway, Bernard J. Cosby

Projects Coordinator: James R. Webb

Database Manager: Frank A. Deviney, Jr.

Laboratory Manager: Suzanne W. Maben

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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 26-year period, 1979-2005, 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 the SHEN 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 establishes a calendar year basis for data reporting and interpretation. The previous reporting schedule provided data and data interpretation for the July through June period. The previous transitional report provided data and interpretation for 07/01/04 – 12/31/04, completing the 2004 calendar year. This report and future reports will provide data and interpretation for complete calendar years.

We plan a 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 data obtained in the period, 01/01/05 – 12/31/05, including comparisons with previous years in the SWAS program record.

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. Some of this work has been initiated. We again 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. We have also proceeded to adopt the relatively new NPSTORET data management system developed by the National Park Service for management of water resources data in national parks.

2. Significant Findings

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

- Differences in stream water quality parameters between 2005 and previous years were consistent with continuing stream acidification and recovery from the effects of forest defoliation associated with the gypsy moth.
- In 2005 the acidity levels of 10 of the 14 SWAS study streams were higher than in previous years. Consistent with observations for streams associated with forested watersheds in the surrounding mountain region, there is no consistent pattern of recovery from acidification in streams in SHEN.
- In 2005 mean nitrate concentrations in the 14 SWAS study streams were lower compared to mean concentrations prior to 2005. The higher nitrate levels in earlier years can be attributed to severe forest defoliation in the early 1990s by gypsy moth larva.
- In 2005 mean sulfate concentrations in nine of the 14 SWAS study streams were lower compared to mean concentrations prior to 2005. This mixed response occurred in a context of decreasing deposition of sulfate in precipitation.
- In 2005 mean concentrations of base cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+}$) in eight of the 14 SWAS study streams were higher compared to mean concentrations prior to 2005. This mixed response occurs in a context of possible long-term base cation depletion in some SHEN watershed soils.

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, and seepage areas that are not presently sampled as part of SWAS or other components of the SHEN Long-Term Ecological Monitoring program. [Note: research has been initiated in response to this recommendation.]
- Further investigate the fate and transport of atmospherically deposited mercury in SHEN surface waters. [Note: research has been initiated in response to this recommendation.]

- Investigate the relationship between episodic discharge-related extremes in SHEN stream water quality and the status of aquatic biota.
- Establish a long-term monitoring program to track change in the availability of base-cations (e.g., calcium and magnesium ions) in SHEN soils.

4. Introduction/Background

Over the 26-year period, 1979-2005, 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, climate 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.

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 the 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 the three major bedrock classes in SHEN 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 the 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 the stream miles and land area in SHEN.

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.. 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 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, 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 lower number of samples collected in recent years compared with the early 1990s is due to less-frequent sampling during high-discharge conditions. The number of grab samples has been generally constant. The high number of ISCO samples collected in 2003 was due to unusually high discharge.

Discharge

Figure 4 compares total annual discharge amounts (given as runoff) for the three more intensively studied SWAS study streams with continuous discharge gauging. As indicated, annual runoff for 2003 was the highest in the period of record (1992 – 2005).

Figure 5 provides time series plots of discharge in 2004 and 2005 for the five SWAS study streams with continuous discharge gauging, as well as cumulative frequency distributions comparing discharge in 2005 with prior years. The time series plots show more high-flow events in 2004 than in 2005, but show a period of high runoff in the fourth quarter of 2005. As evidenced by comparison of the cumulative frequency distributions, the distribution of runoff in 2005 was not significantly different than in previous years.

Acid-Base Status of Stream Water

Figure 6 provides plots of major acid-base constituent concentrations for the fourteen SWAS study streams by calendar year, indicating weekly and quarterly grab sample values and median values by year. Figure 7 provides time-series plots of major acid-base constituent concentrations for the fourteen SWAS study streams. As evidenced in Figure 7, the concentrations of these constituents change on both seasonal and shorter-term time-scales

Change that occurs over longer-time scales is indicated in Table 2, which lists differences in mean values of the major acid-base constituents for all 14 of the primary SWAS study watersheds between (1) calendar-year 2005 and (2) pre-2005 (1988 – 2004). Data were collected for all 14 study sites beginning in 1988.

Figure 8 summarizes the differences in mean values indicated in Table 2.

The differences in mean values between 2005 and pre-2005 are indicative of long-term change associated with acidic deposition and forest defoliation.

The comparison of ANC means shows that ten of the 14 study streams were more acidic in 2005 than during the prior data collection period. ANC is an integrator of the factors that contribute to the acid-base status of surface waters, and decreasing ANC is consistent with continuing acidification of both stream water and watershed soils.

The comparison of nitrate concentration means shows that mean nitrate concentrations were lower in all 14 of the study stream in 2005 than in the previous years. This is consistent with the previously observed decrease in nitrate concentrations following the transient increase associated with the gypsy moth infestation and forest defoliation in the early 1990s.

Explanations for the differences observed in the other parameters included in Table 2 and Figure 8 are less obvious.

The mean sulfate concentrations were lower in nine of the 14 streams, but higher in the other five. Given reductions in sulfur emissions and deposition, sulfate concentrations in surface waters are declining in some regions. However, as discussed in previous reports and suggested by the current comparison, sulfate concentrations in southeastern surface waters are not consistently declining. This has been attributed to the effect of sulfur retention in soils. Although

sulfate concentrations are declining in some SHEN stream waters, sulfate concentrations are increasing in others. Although a single year's change does not provide a strong basis for interpretation, the comparison between the 2005 means and the means of previous years is consistent with the results of long-term trend analysis provided with past reports. More perspective on watershed response to reductions in sulfur emissions will be provided when long-term trend analysis is repeated.

The mean for the sum of base cation concentrations was higher in eight of the 14 streams. This is a mixed result, suggesting that soils in some areas of SHEN are losing base cations, while others are not. The base cations, including calcium, magnesium, and potassium ion, are mainly derived from watershed soils, and depletion of base cations in watershed soils is a primary aspect of ecosystem harm associated with both acidic deposition and forest disturbance. Again, a single year's change does not provide a strong basis for interpretation.

The mean pH values for all of the study streams were higher in 2005 than the mean for the previous years. The explanation for this is unclear, given the positive correlation generally observed between ANC and pH. This result may be distorted given the problem of comparing means of log values. This result may also be indicative of problems associated with summary analysis of acid-base status based on means. Although means tests are commonly applied to examine regional changes in surface water composition, these comparisons suggest that analysis based on mean concentrations fails to effectively capture the dynamics of acid-base status in these systems.

Episodic Acidification

Figure 9 compares ANC distributions for routine weekly grab samples and high-runoff samples collected with automated ISCO samplers (1992 – 2005). The ISCO samplers collect samples at 2-hour intervals during periods of discharge exceeding the 95th flow-duration percentile (determined separately for cold and warm seasons). The median values (50% probability) for routine grab samples and ISCO samples are indicated. The difference in median ANC concentrations for the 1992 – 2005 period was 5 $\mu\text{eq/L}$ for Paine Run, 9 $\mu\text{eq/L}$ for Staunton River, and 26 $\mu\text{eq/L}$ for Piney River. As observed previously, ANC values are lower during high-discharge conditions. The extreme values that occur during high-runoff conditions have been associated with fish recruitment failure (mortality of eggs and lava) in previous studies. In 2005 there was only one notable high-runoff event (see Figure 5).

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. The WRSR 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.

In response to this recommendation, a project has been initiated to examine headwater reaches and springs and seeps in the park. This project is entitled *Biological significance of headwater streams and springs in Shenandoah National Park* (Snyder et al., 2007). The project involves collection of water composition and benthic macroinvertebrate data for a representative sample of headwaters and springs throughout SHEN. The project is a collaborative effort conducted by the U.S. Geological Survey and the University of Virginia.

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

This is a continuing recommendation.

Base cations in some SHEN watershed soils are evidently decreasing as a result of prolonged exposure to acidic deposition and other disturbance (e.g., forest defoliation). 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. Soil sampling conducted at 79 sites within these watersheds in 2000 could serve as a baseline and foundation for a long-term soil monitoring program (Welsch, 2001).

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

This is a continuing recommendation.

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) has been completed (Snyder et al, 2006). The findings indicate associations between Hg levels in brook trout and both bedrock type and elevation. Another study has been completed as a graduate thesis project investigate longitudinal and temporal variation of Hg in SHEN stream waters and sediments (Moore, 2006). A project is currently underway by University of Virginia researchers to examine Hg fluxes at the Big Meadows wetland in SHEN. Results of this work are not yet available.

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.

This is a continuing recommendation.

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. 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 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 (Rice et al., 2005; Deviney et al., 2006). 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.

10. Citations

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Tables and Figures

Table 1: SWAS study watersheds

Site	Stream Name	Streamwater Sampling Frequency	ELEV (ft)	AREA (km ²)	UTM Coordinates		Percent Bedrock Coverage		
							SILI ¹	GRAN ²	BASA ³
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

¹ SILI = siliciclastic (Harper, Antietam, and Weverton Formations)

² GRAN = granitic (Pedlar and Old Rag Formations)

³ BASA = basaltic (Catoctin Formation)

Table 2: Difference and confidence interval between calendar-year 2005 and pre-2005 mean concentrations (grab samples only)

StationID	AnalyticalGroup	LowerCL	Difference Between Means (pre-2005 minus 2005)	UpperCL
DR01	ANC_ALL	-3.024315	1.454368	5.933051
DR01	NITRATE_ALL	-0.471549	0.666280	1.804110
DR01	PH_ALL	-0.061860	-0.013558	0.034744
DR01	SBC_ALL	-1.092597	3.898658	8.889912
DR01	SULFATE_ALL	-0.778290	2.386469	5.551227
NFDR	ANC_ALL	-3.135737	5.647234	14.430206
NFDR	NITRATE_ALL	5.317462	10.300141	15.282820
NFDR	PH_ALL	-0.059737	-0.006427	0.046883
NFDR	SBC_ALL	3.381716	12.140349	20.898982
NFDR	SULFATE_ALL	-2.937971	-0.315646	2.306679
PAIN	ANC_ALL	-1.558322	0.037009	1.632340
PAIN	NITRATE_ALL	1.275464	3.880954	6.486444
PAIN	PH_ALL	-0.121304	-0.054971	0.011362
PAIN	SBC_ALL	2.672544	5.202903	7.733261
PAIN	SULFATE_ALL	0.091317	1.705213	3.319109
PINE	ANC_ALL	-32.783885	-12.695982	7.391921
PINE	NITRATE_ALL	4.125365	8.137495	12.149624
PINE	PH_ALL	-0.137953	-0.090250	-0.042547
PINE	SBC_ALL	-24.700859	-9.192502	6.315855
PINE	SULFATE_ALL	-2.000796	1.218333	4.437461
STAN	ANC_ALL	-5.202958	0.124199	5.451356
STAN	NITRATE_ALL	0.257979	1.146853	2.035728
STAN	PH_ALL	-0.163715	-0.088492	-0.013270
STAN	SBC_ALL	-4.862067	-0.542321	3.777425
STAN	SULFATE_ALL	-4.558563	-2.969717	-1.380871
VT36	ANC_ALL	-4.442514	-0.449019	3.544475
VT36	NITRATE_ALL	-2.949171	0.867973	4.685116
VT36	PH_ALL	-0.253244	-0.073493	0.106257
VT36	SBC_ALL	-6.610213	2.588351	11.786915
VT36	SULFATE_ALL	-11.573421	-0.232978	11.107464
VT51	ANC_ALL	-101.839230	0.713314	103.265857
VT51	NITRATE_ALL	-8.124331	5.690757	19.505845
VT51	PH_ALL	-0.427637	-0.182639	0.062360
VT51	SBC_ALL	-86.529148	-0.248805	86.031537
VT51	SULFATE_ALL	-13.036001	5.342735	23.721471
VT53	ANC_ALL	-7.518766	1.360656	10.240079
VT53	NITRATE_ALL	-4.324338	0.275722	4.875782
VT53	PH_ALL	-0.291024	-0.101806	0.087413
VT53	SBC_ALL	-6.605033	2.384121	11.373275
VT53	SULFATE_ALL	-10.666532	2.834669	16.335871
VT58	ANC_ALL	-23.202775	4.810667	32.824110
VT58	NITRATE_ALL	-2.188432	2.704183	7.596798
VT58	PH_ALL	-0.529577	-0.274930	-0.020283
VT58	SBC_ALL	-19.172040	3.515152	26.202343
VT58	SULFATE_ALL	-4.825336	2.366220	9.557776
VT61	ANC_ALL	-94.868514	-8.453640	77.961234
VT61	NITRATE_ALL	-11.027889	6.365206	23.758302
VT61	PH_ALL	-0.506904	-0.225563	0.055777
VT61	SBC_ALL	-69.249788	-10.438796	48.372197
VT61	SULFATE_ALL	-16.384379	1.223106	18.830592

VT62	ANC_ALL	-26.474961	1.830243	30.135447
VT62	NITRATE_ALL	-2.695410	1.649988	5.995386
VT62	PH_ALL	-0.500201	-0.237782	0.024638
VT62	SBC_ALL	-27.566231	-5.487949	16.590333
VT62	SULFATE_ALL	-6.996827	1.352830	9.702487
VT66	ANC_ALL	-36.575488	3.897042	44.369572
VT66	NITRATE_ALL	-9.161382	6.538868	22.239118
VT66	PH_ALL	-0.387383	-0.179930	0.027524
VT66	SBC_ALL	-37.156454	-3.924737	29.306980
VT66	SULFATE_ALL	-10.203705	-2.269007	5.665692
VT75	ANC_ALL	-38.396235	3.201282	44.798800
VT75	NITRATE_ALL	-7.189536	3.308112	13.805760
VT75	PH_ALL	-0.405401	-0.224280	-0.043158
VT75	SBC_ALL	-39.896335	-1.958600	35.979135
VT75	SULFATE_ALL	-10.256446	-1.468984	7.318477
WOR1	ANC_ALL	-7.466657	-2.312323	2.842011
WOR1	NITRATE_ALL	-0.137623	3.994645	8.126914
WOR1	PH_ALL	-0.092963	-0.031817	0.029330
WOR1	SBC_ALL	-10.784109	-3.403638	3.976834
WOR1	SULFATE_ALL	-3.289254	-0.726502	1.836251

- Differences indicated in highlighted text are significant at $p = 0.05$

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

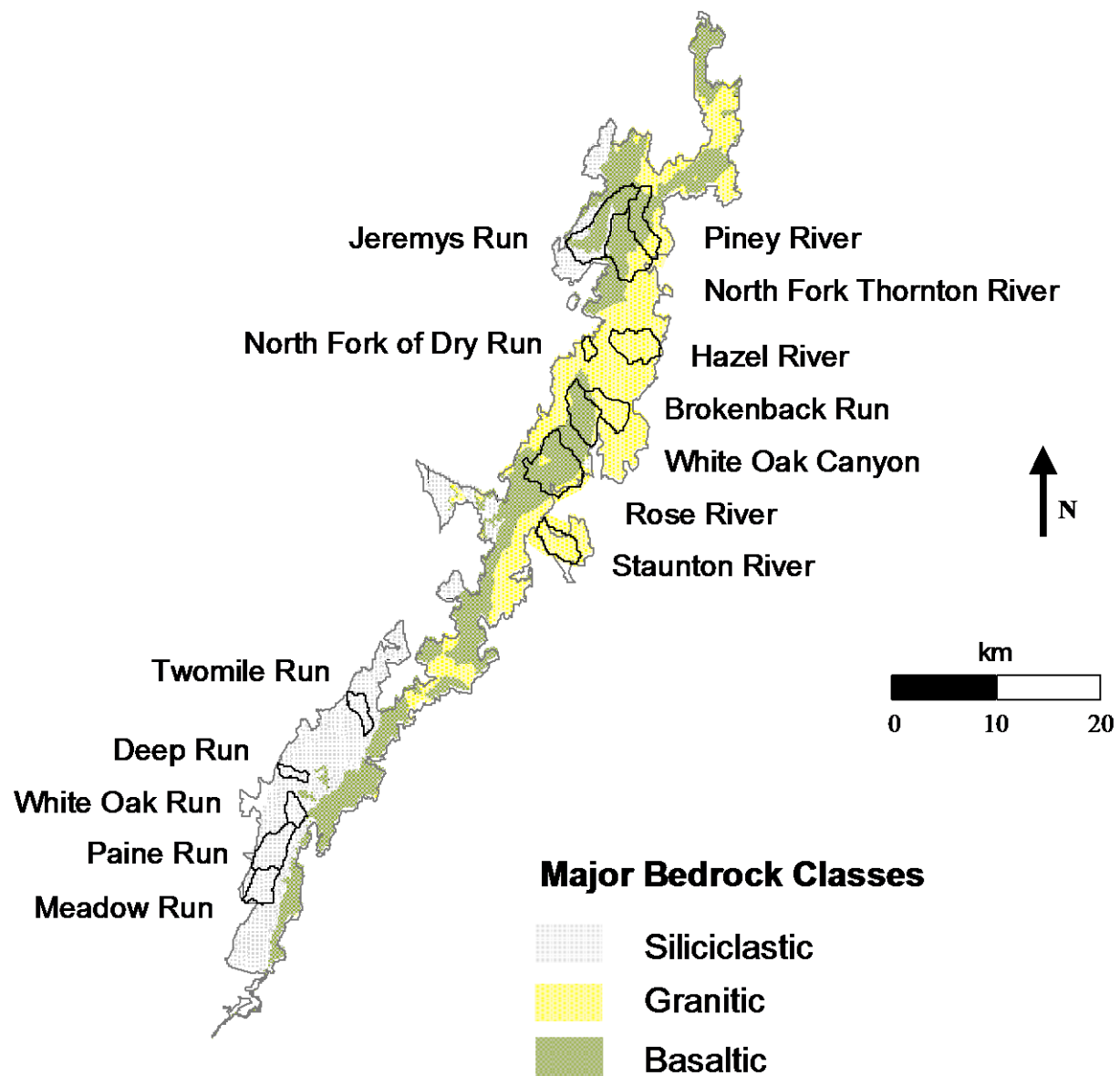
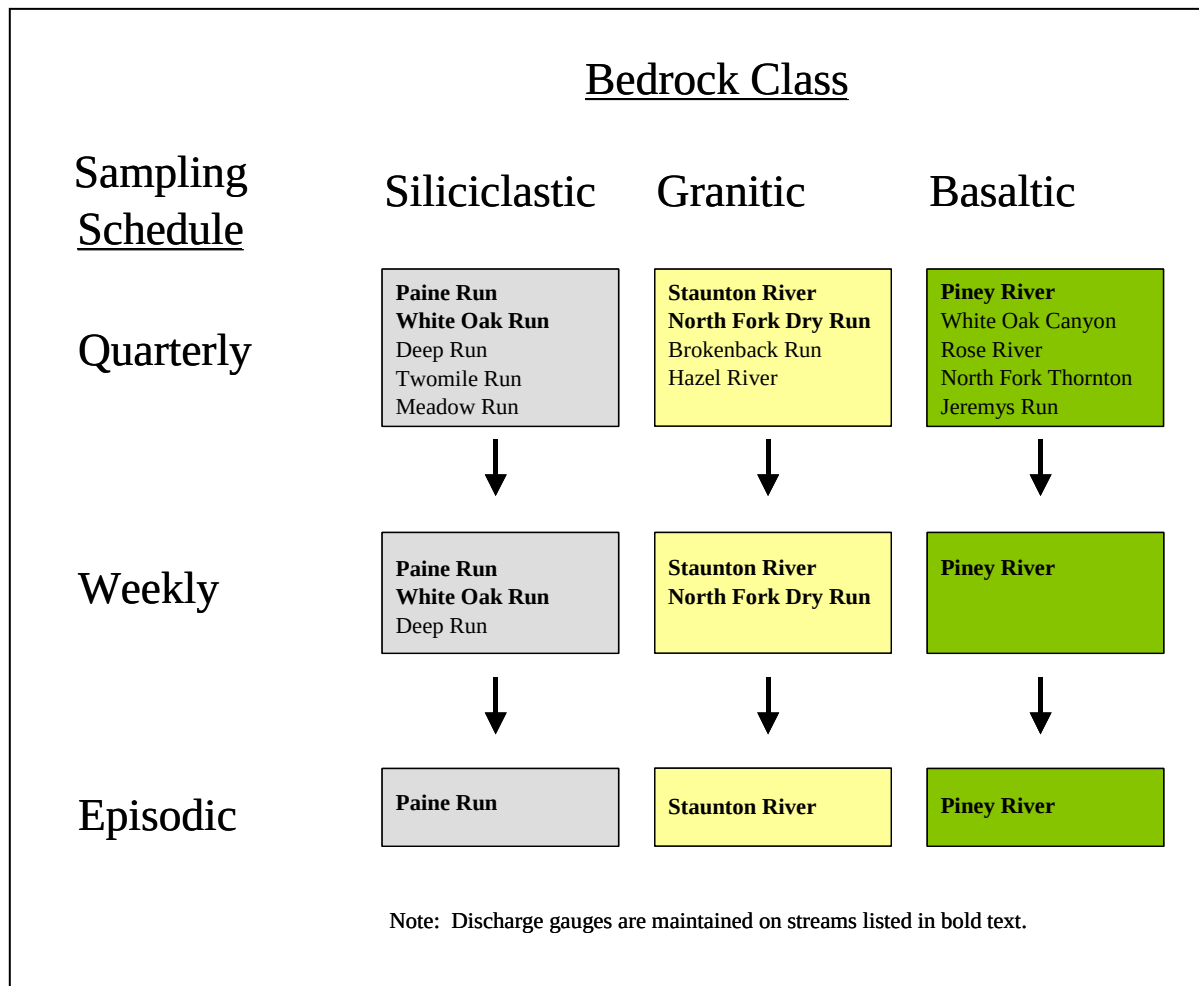
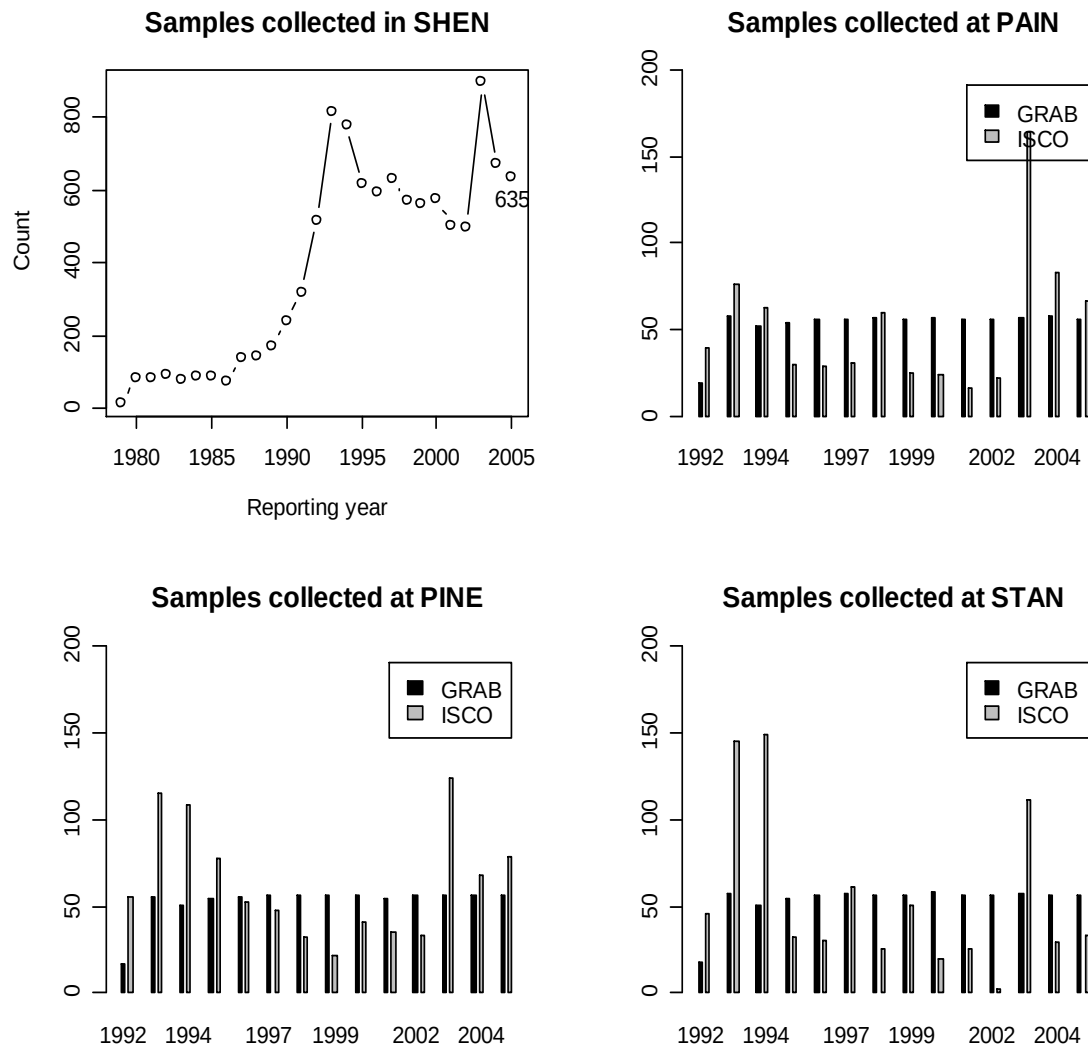


Figure 2: Schematic of SWAS watershed monitoring framework, indicating stratification by bedrock class and sampling frequency for study watersheds



- Episodic sampling is conducted at 2-hour intervals during periods of discharge exceeding the 95th 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 4: Discharge for 1992 – 2005 calendar years for Paine Run, Piney River, and Staunton River. Continuous discharge gauging was initiated on these three streams in 1992.

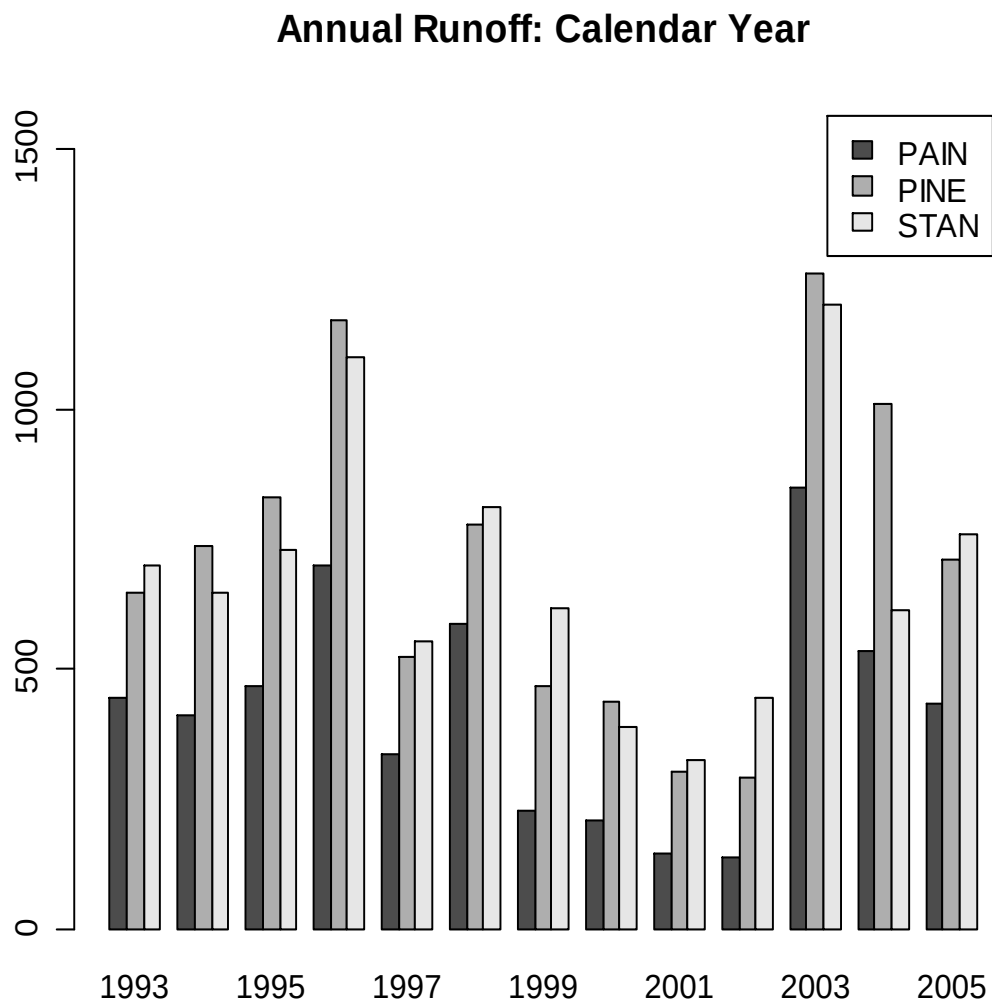
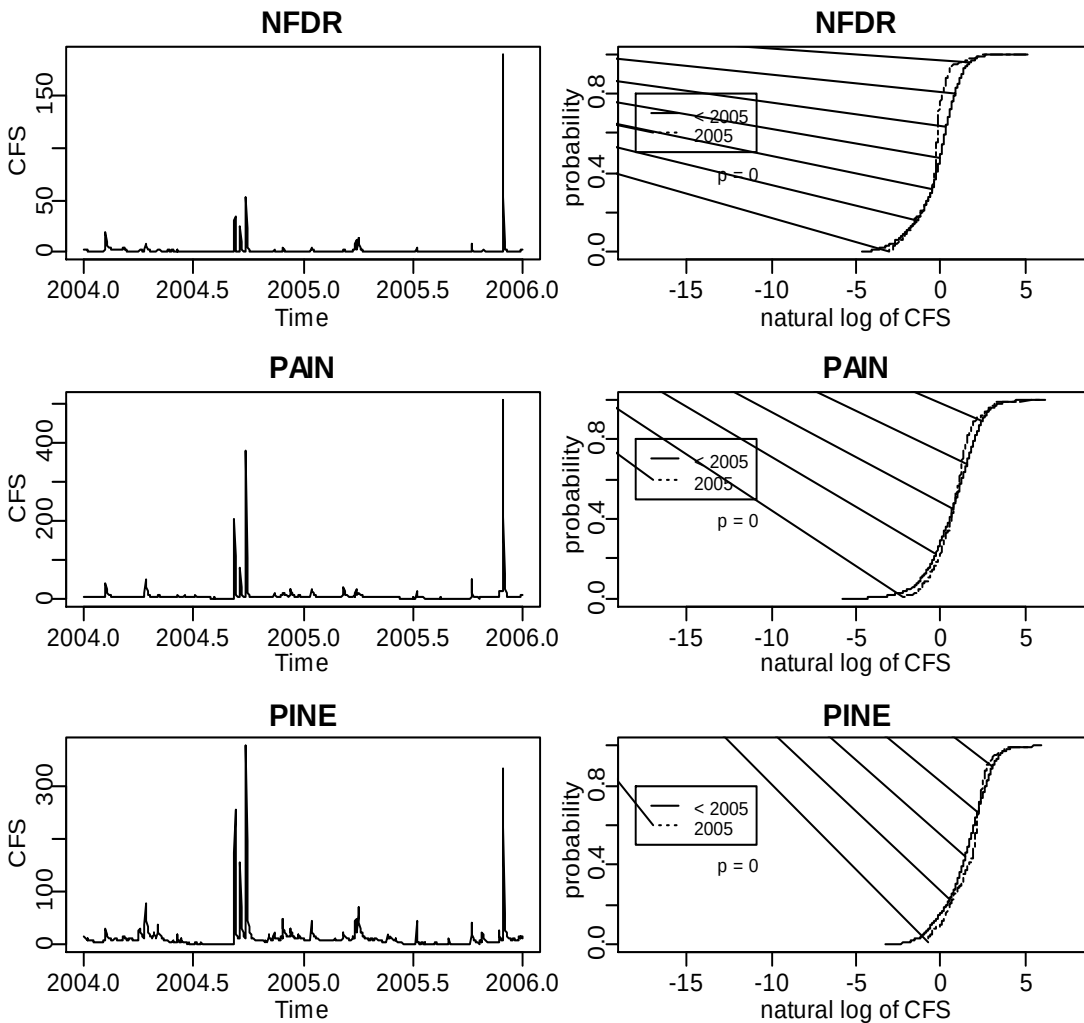
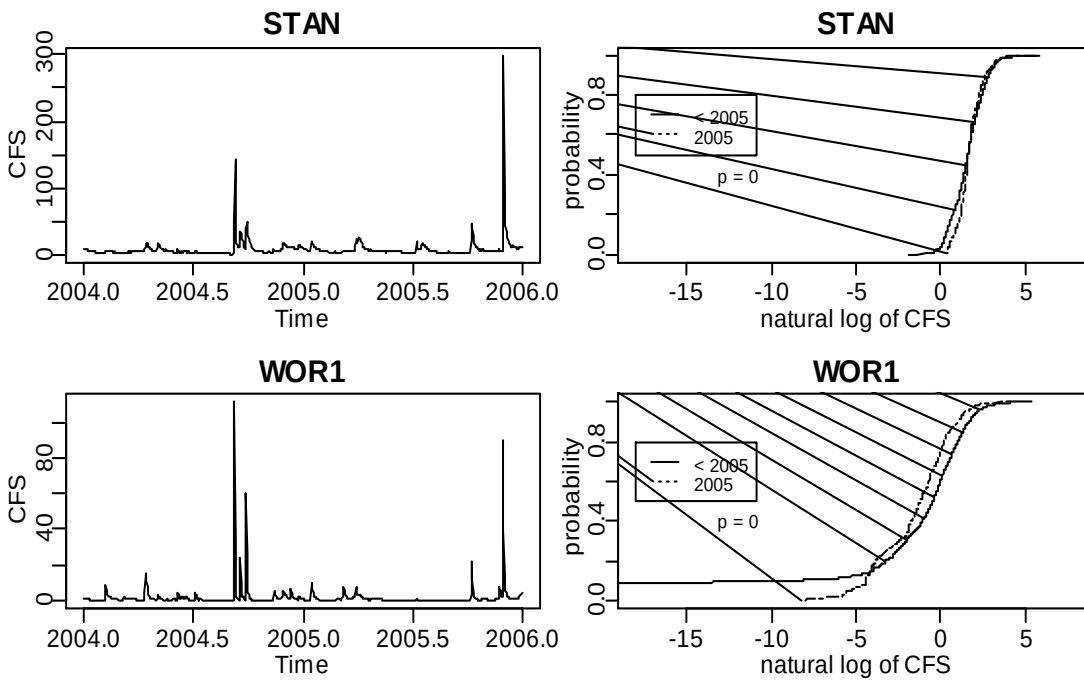


Figure 5: Discharge for 2004 and 2005 calendar years and comparison of cumulative frequency distributions for discharge in 2005 and in all pre-2005 years.



- 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 indicated previous years' discharge values

Figure 5 (continued): Discharge for 2004 and 2005 calendar years and comparison of cumulative frequency distributions for discharge in 2005 and in pre-2005 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 indicated previous years' discharge values

Figure 6a: ANC concentrations for SWAS study streams by calendar year. The points represent weekly or quarterly grab sample. The line connects median values for each year.

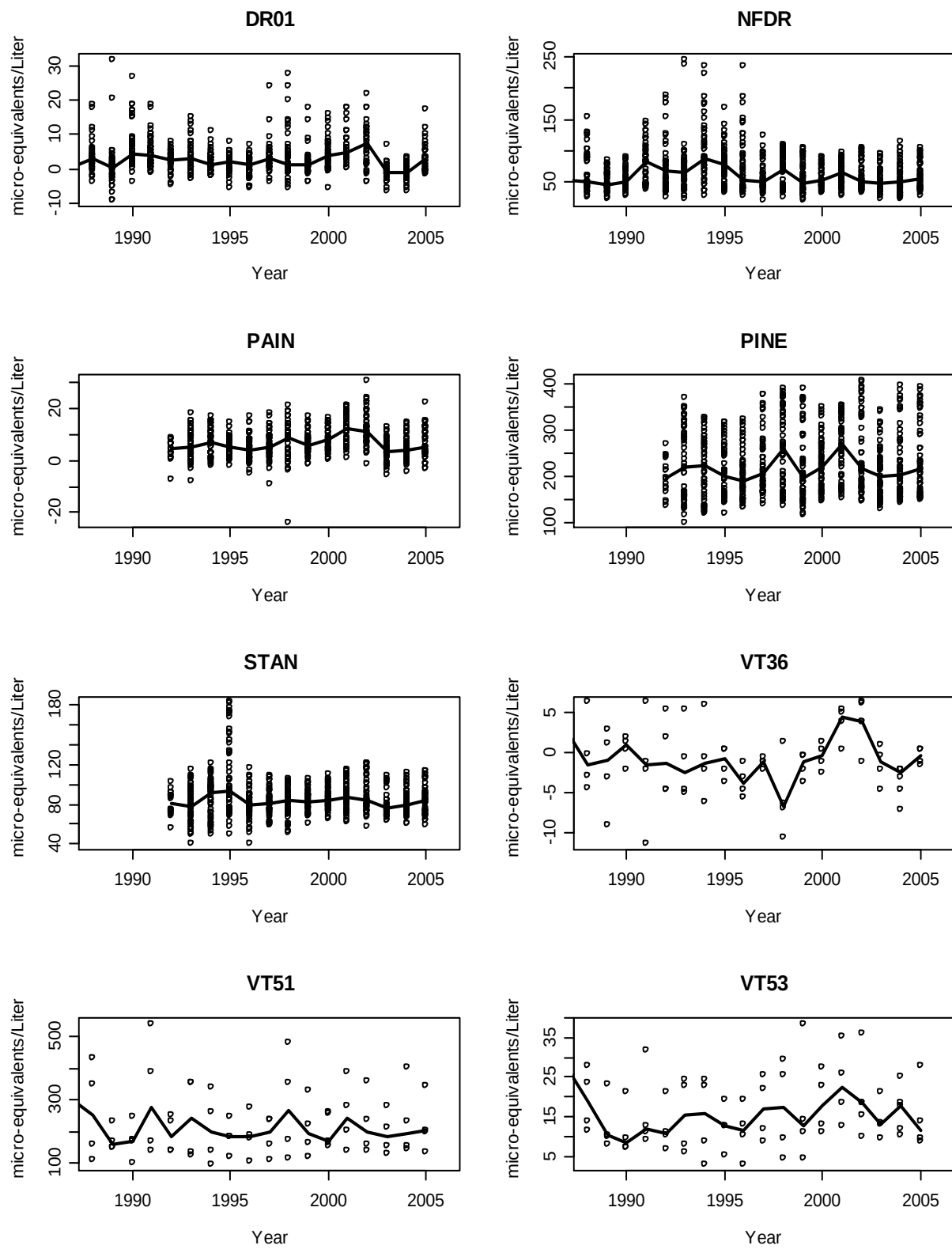


Figure 6a (continued): ANC concentrations for SWAS study streams by calendar year. The points represent weekly or quarterly grab sample. The line connects median values for each year.

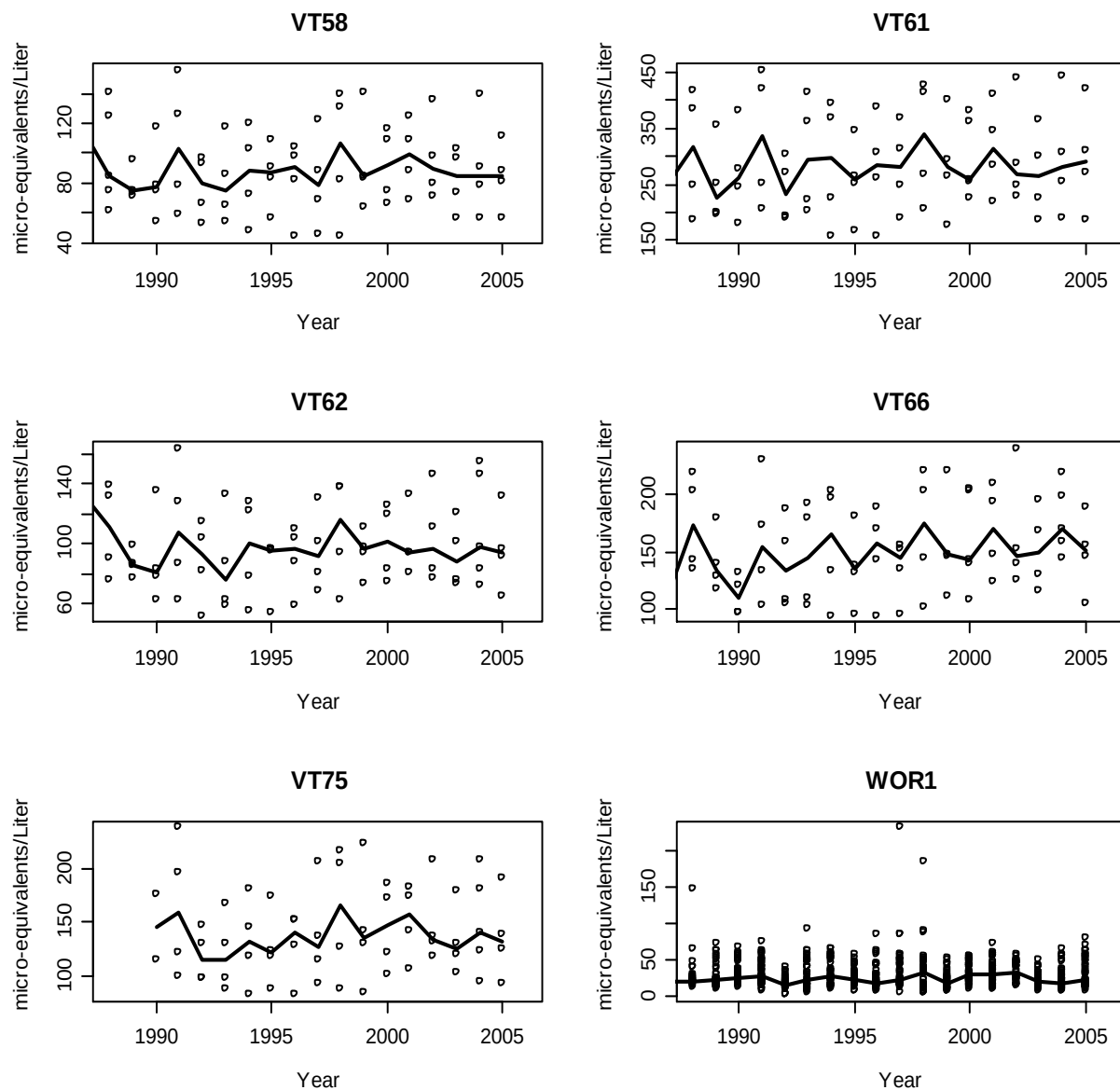


Figure 6b: pH concentrations for SWAS study streams by calendar year. The points represent weekly or quarterly grab sample. The line connects median values for each year.

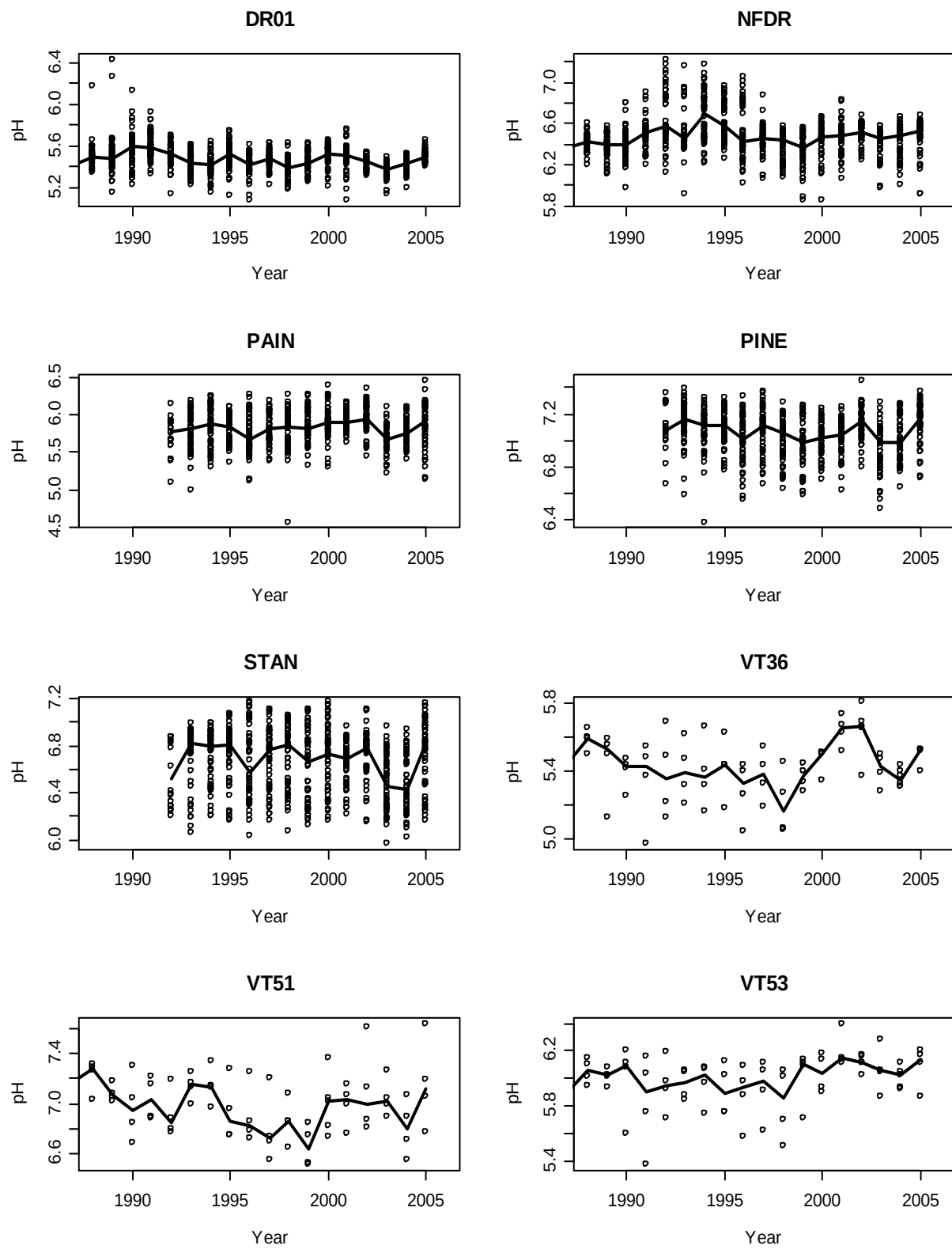


Figure 6b (continued): pH values for SWAS study streams by calendar year. The points represent weekly or quarterly grab sample. The line connects median values for each year.

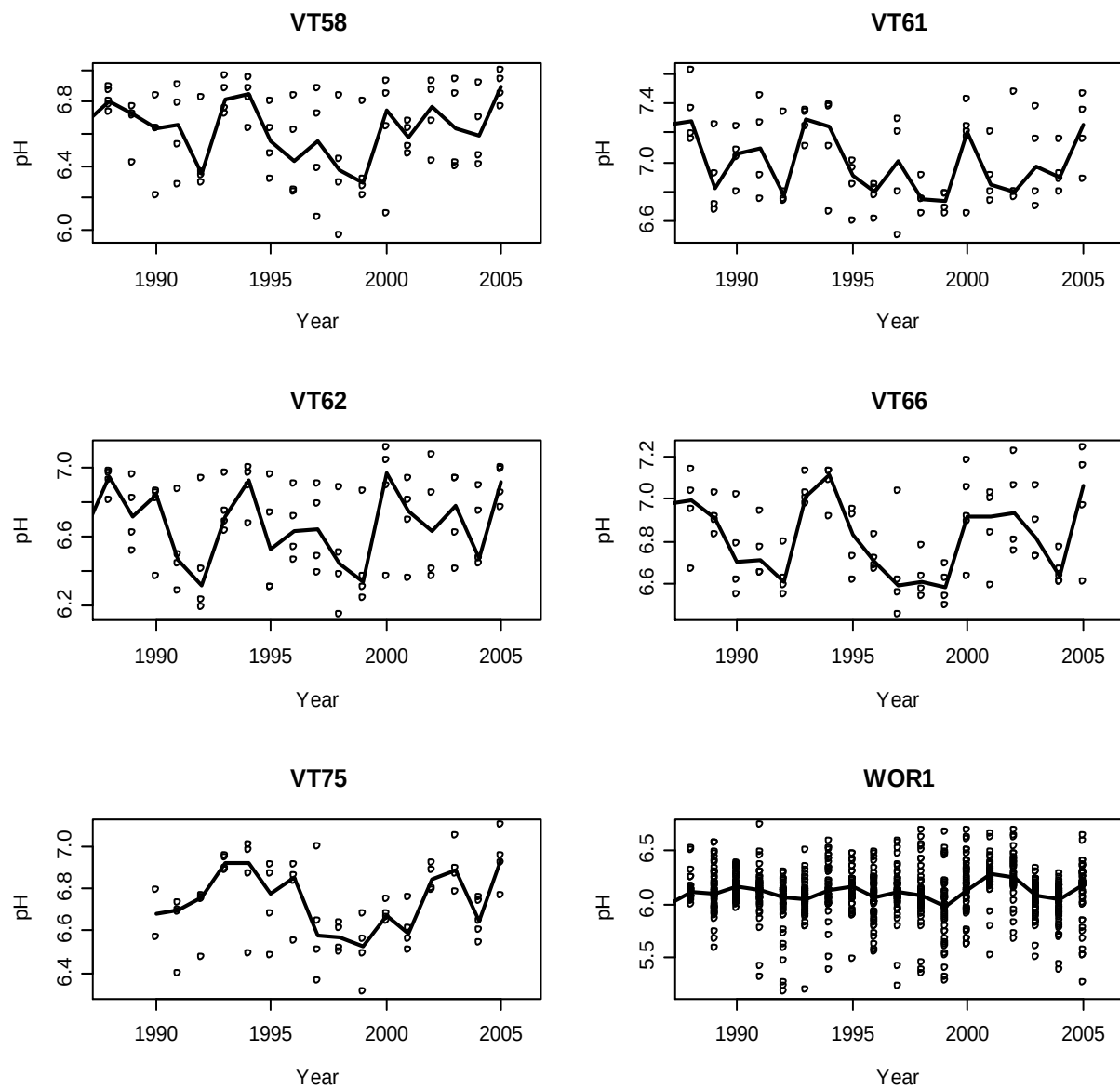


Figure 6c: Sum of base cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+}$) values for SWAS study streams by calendar year. The points represent weekly or quarterly grab sample. The line connects median values for each year.

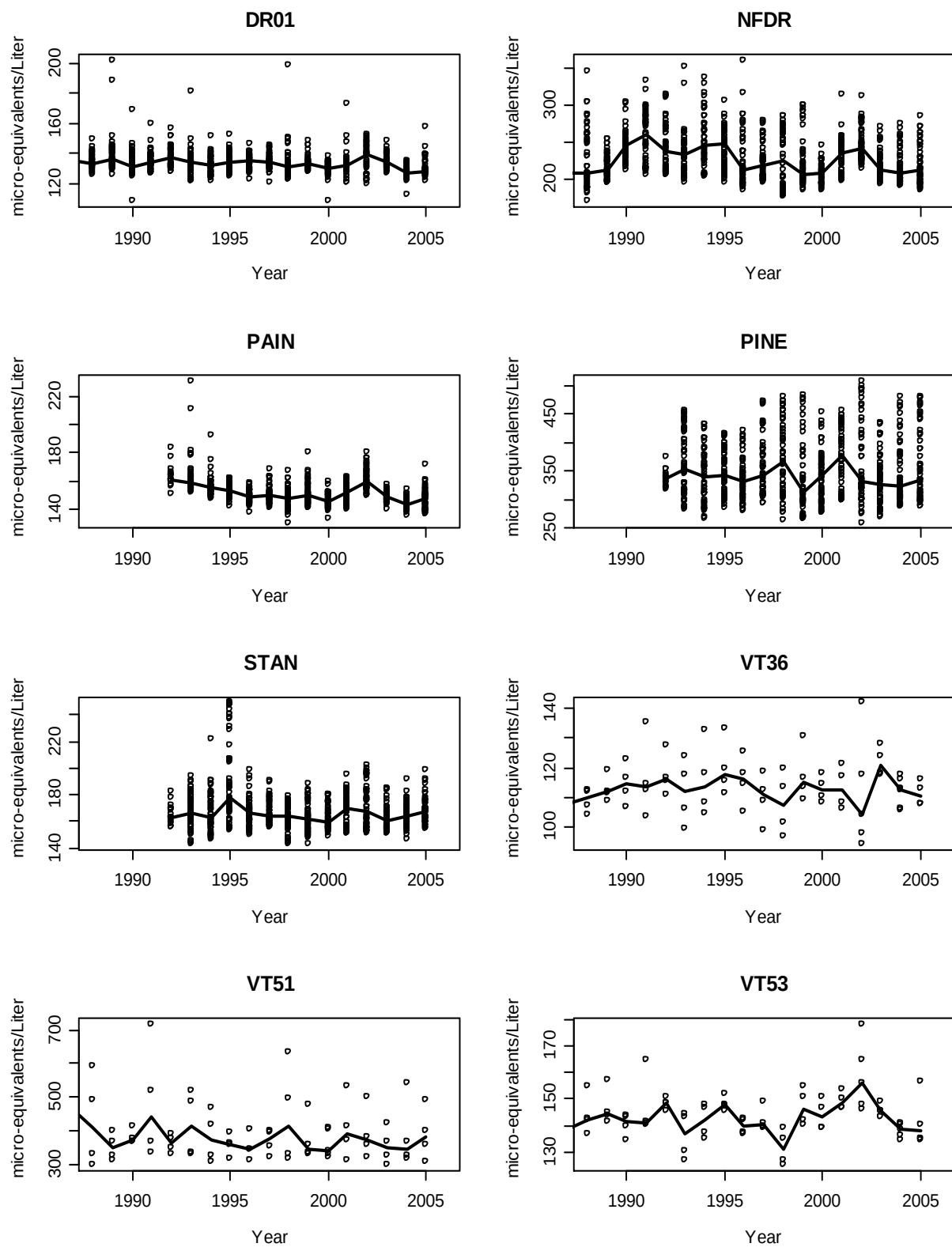


Figure 6c (continued): Sum of base cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+}$) for SWAS study streams by calendar year. The points represent weekly or quarterly grab sample. The line connects median values for each year.

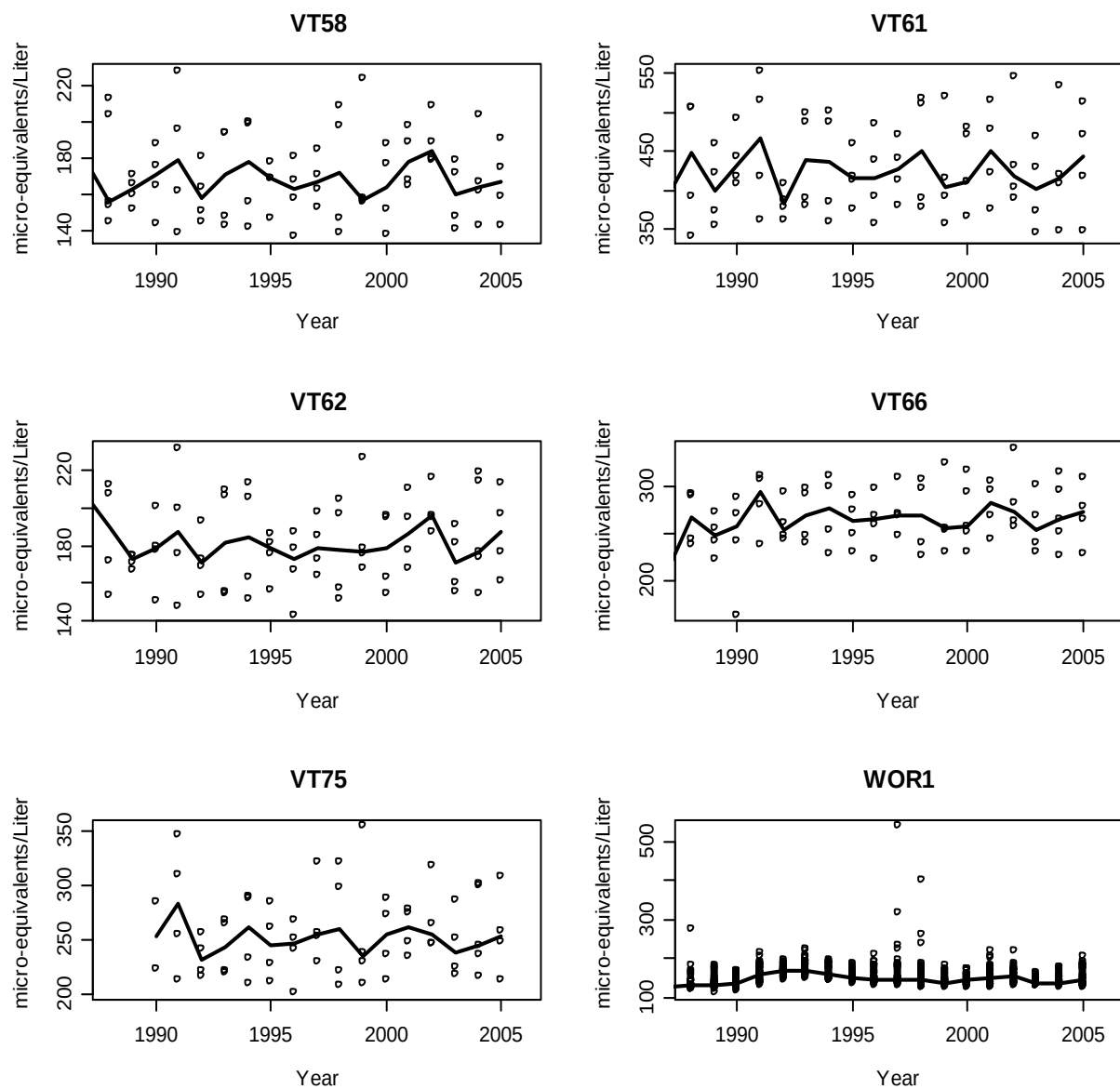


Figure 6d: Sulfate concentrations for SWAS study streams by calendar year. The points represent weekly or quarterly grab sample. The line connects median values for each year.

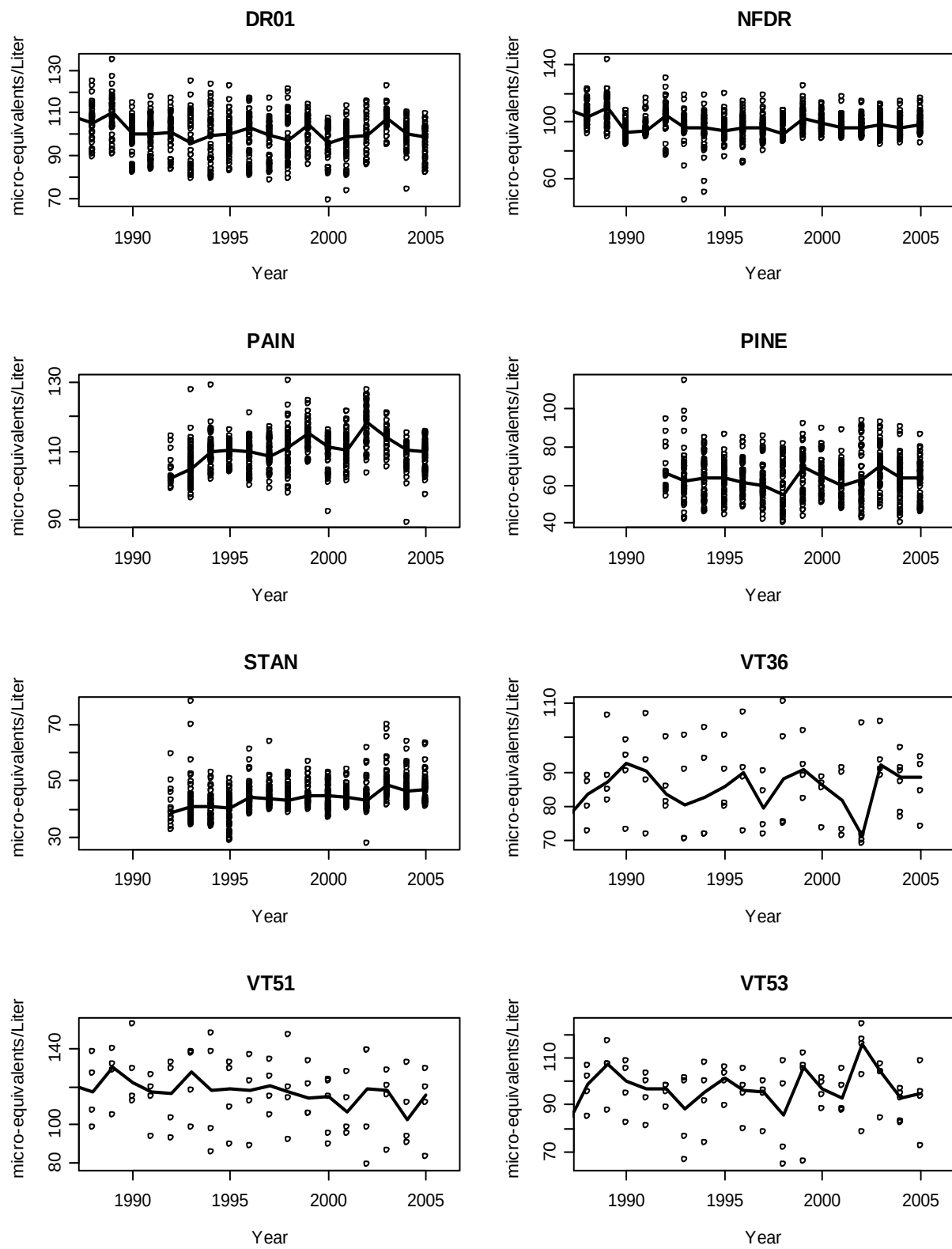


Figure 6d (continued): Sulfate concentrations for SWAS study streams by calendar year. The points represent weekly or quarterly grab sample. The line connects median values for each year.

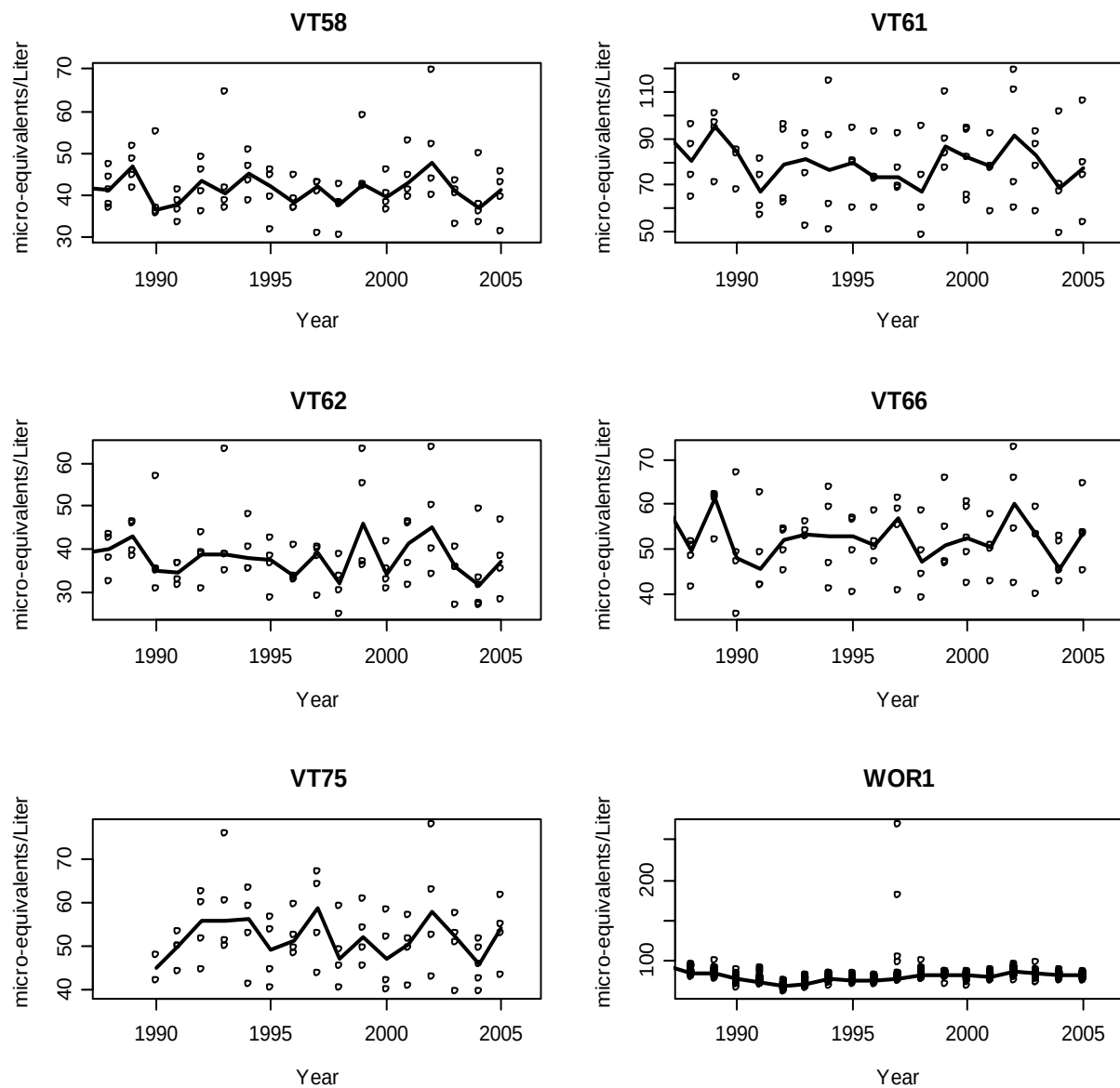


Figure 6e: Nitrate concentrations for SWAS study streams by calendar year. The points represent weekly or quarterly grab sample. The line connects median values for each year.

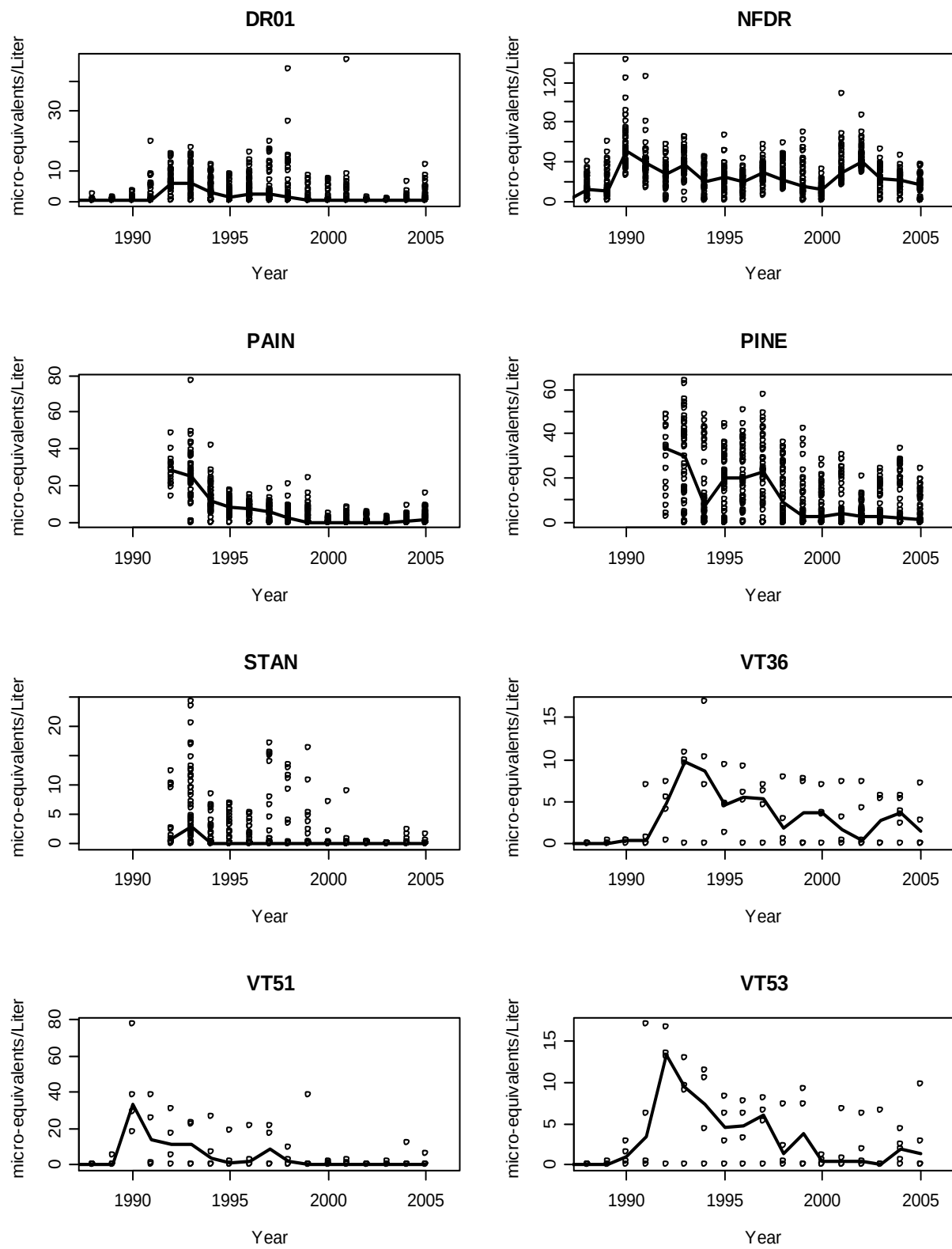


Figure 6e (continued): Nitrate concentrations for SWAS study streams by calendar year. The points represent weekly or quarterly grab sample. The line connects median values for each year.

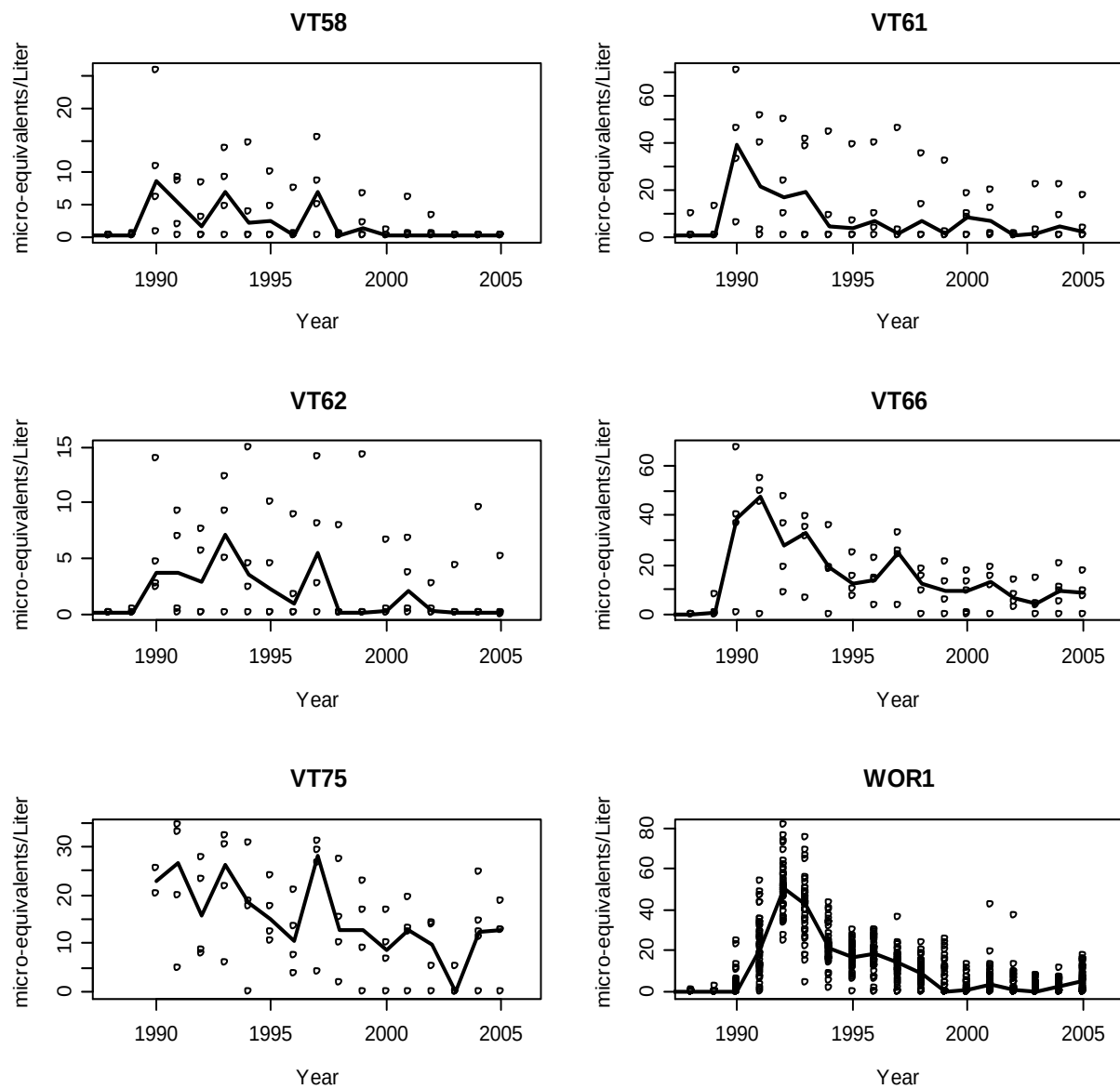


Figure 7a: Time-series plots of ANC concentrations for SWAS study streams. The points represent quarterly, weekly, and episodic (ISCO) samples.

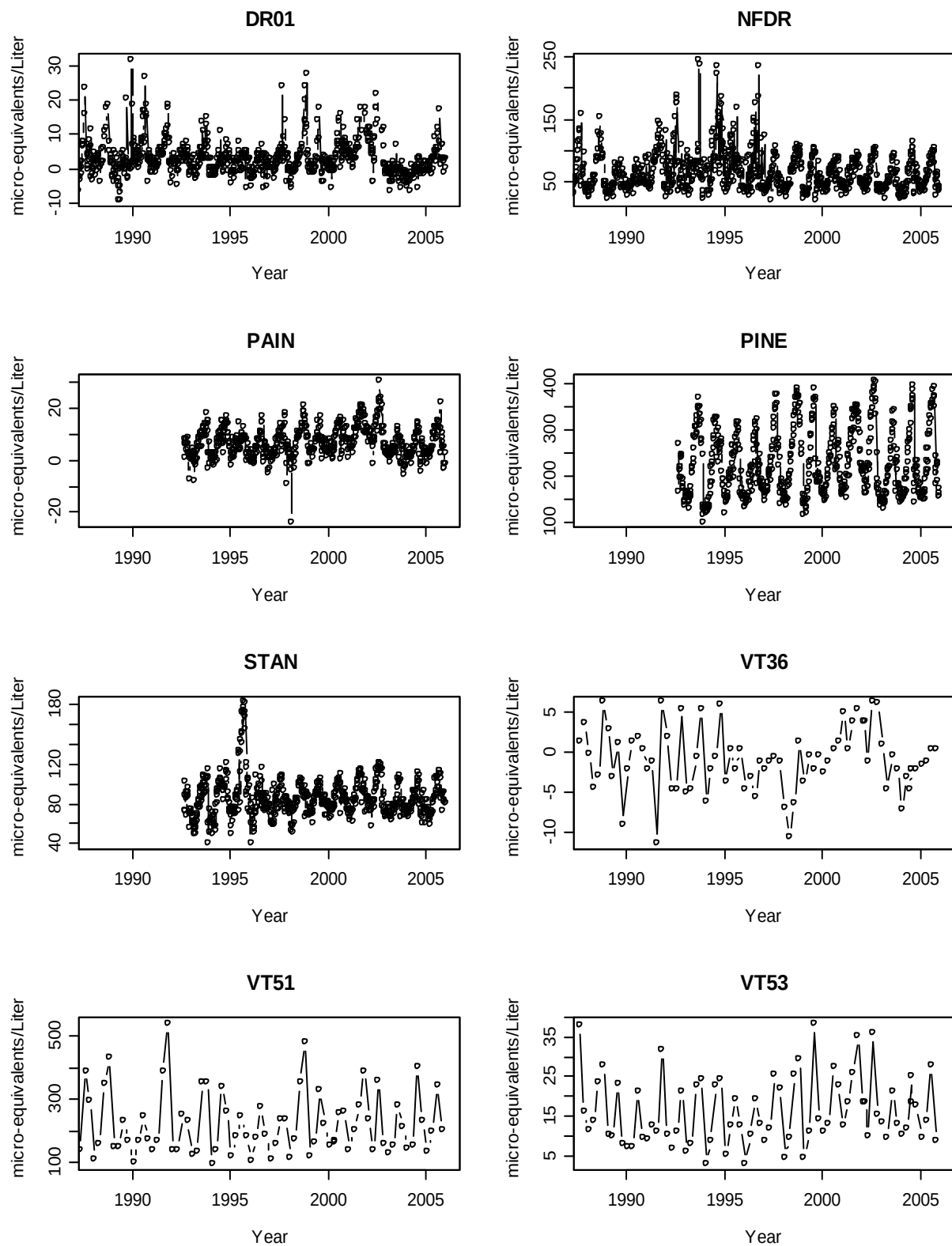


Figure 7a (continued): Time-series plots of ANC concentrations for SWAS study streams. The points represent quarterly, weekly, and episodic (ISCO) samples.

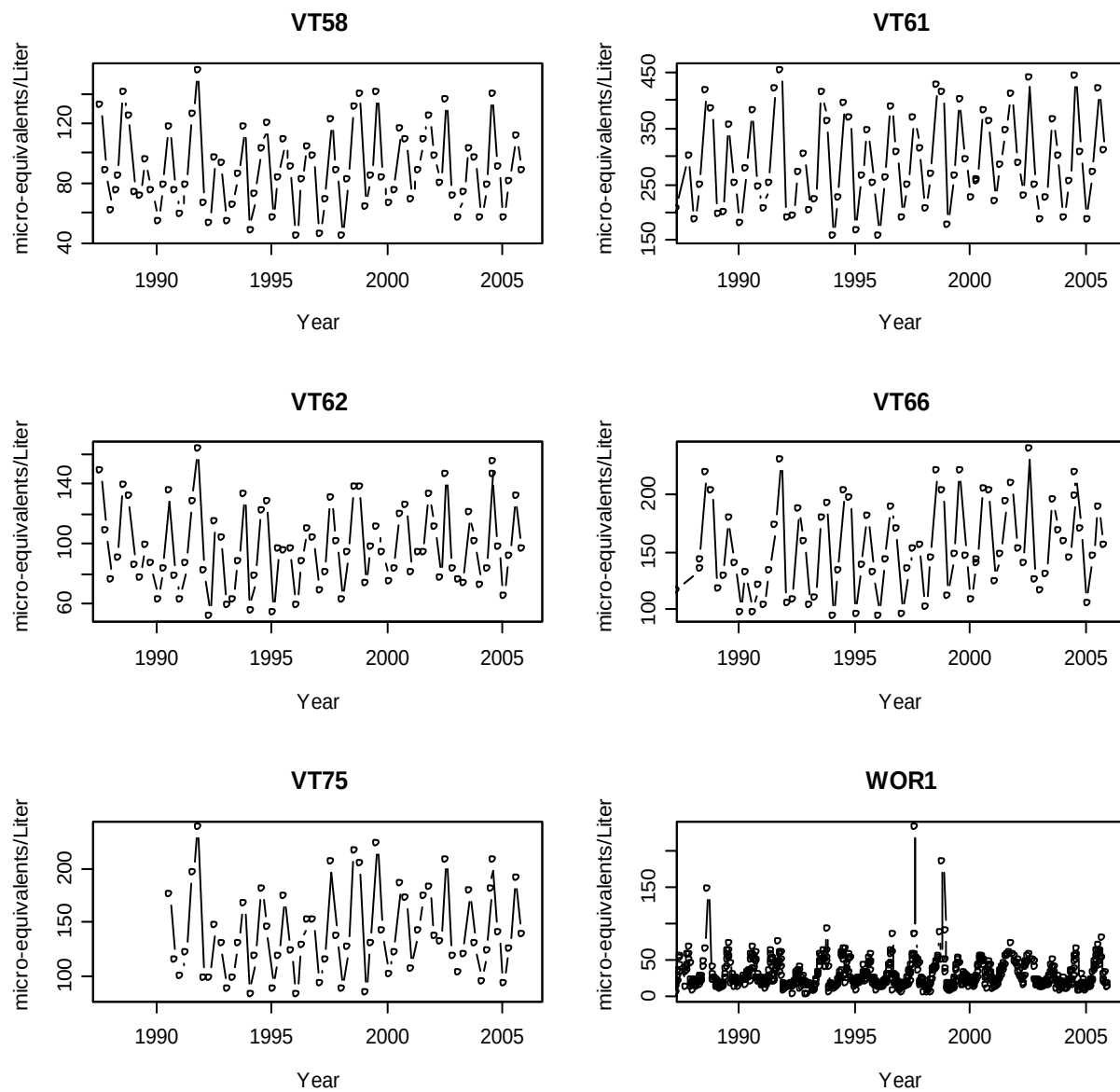


Figure 7b: Time-series plots of pH for SWAS study streams. The points represent quarterly, weekly, and episodic (ISCO) samples.

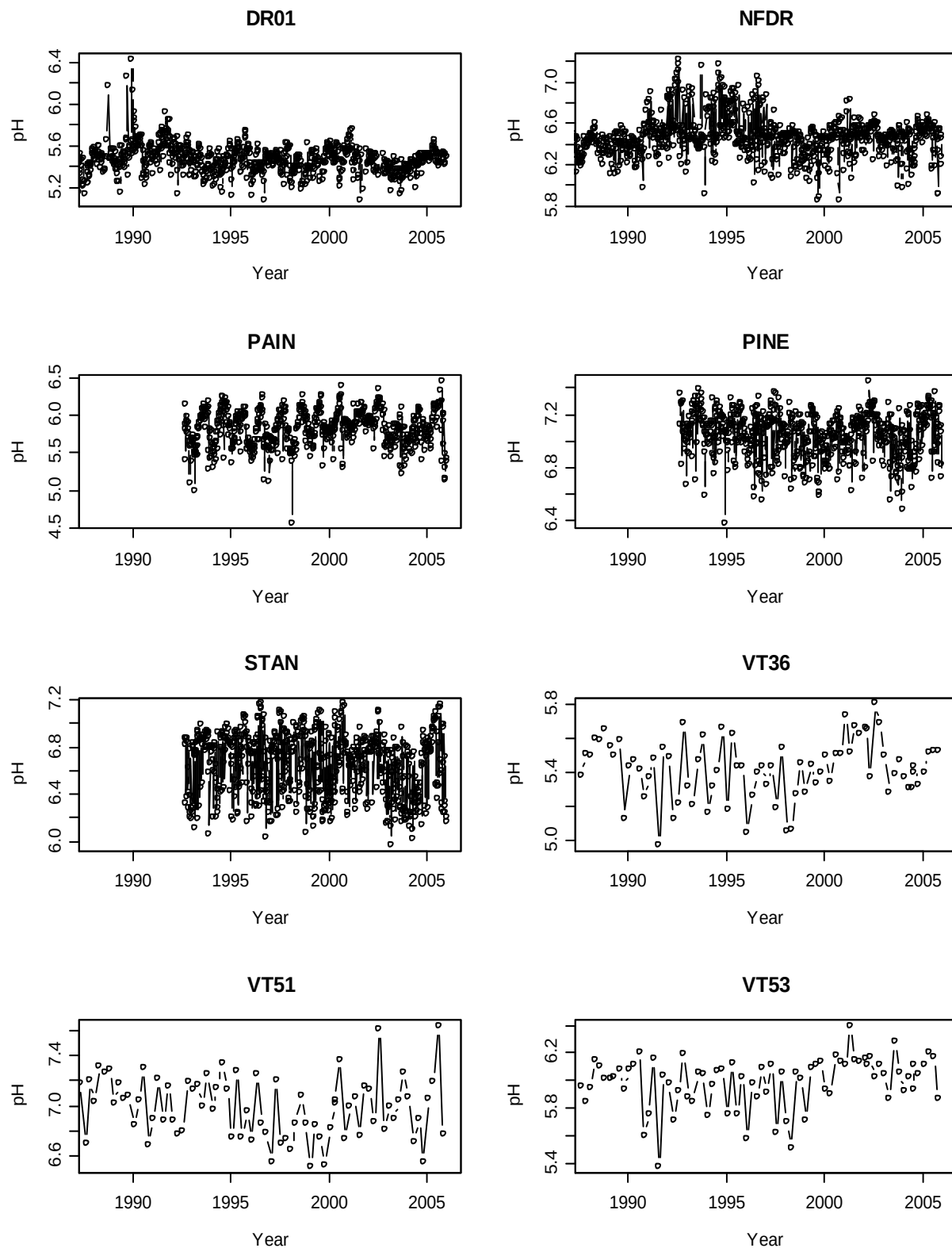


Figure 7b (continued): Time-series plots of pH for SWAS study streams. The points represent quarterly, weekly, and episodic (ISCO) samples.

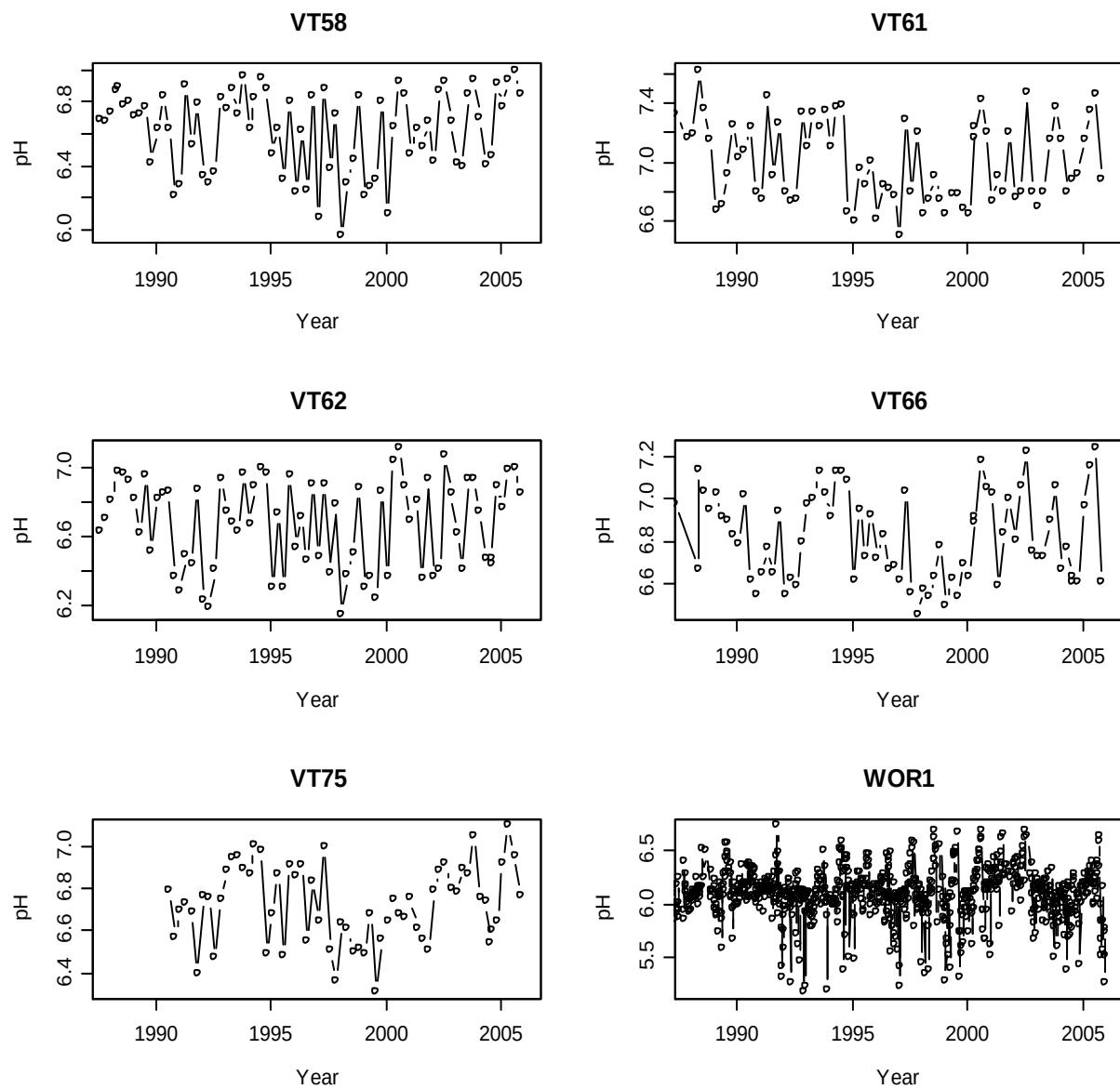


Figure 7c: Time-series plots of base cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+}$) for SWAS study streams. The points represent quarterly, weekly, and episodic (ISCO) samples.

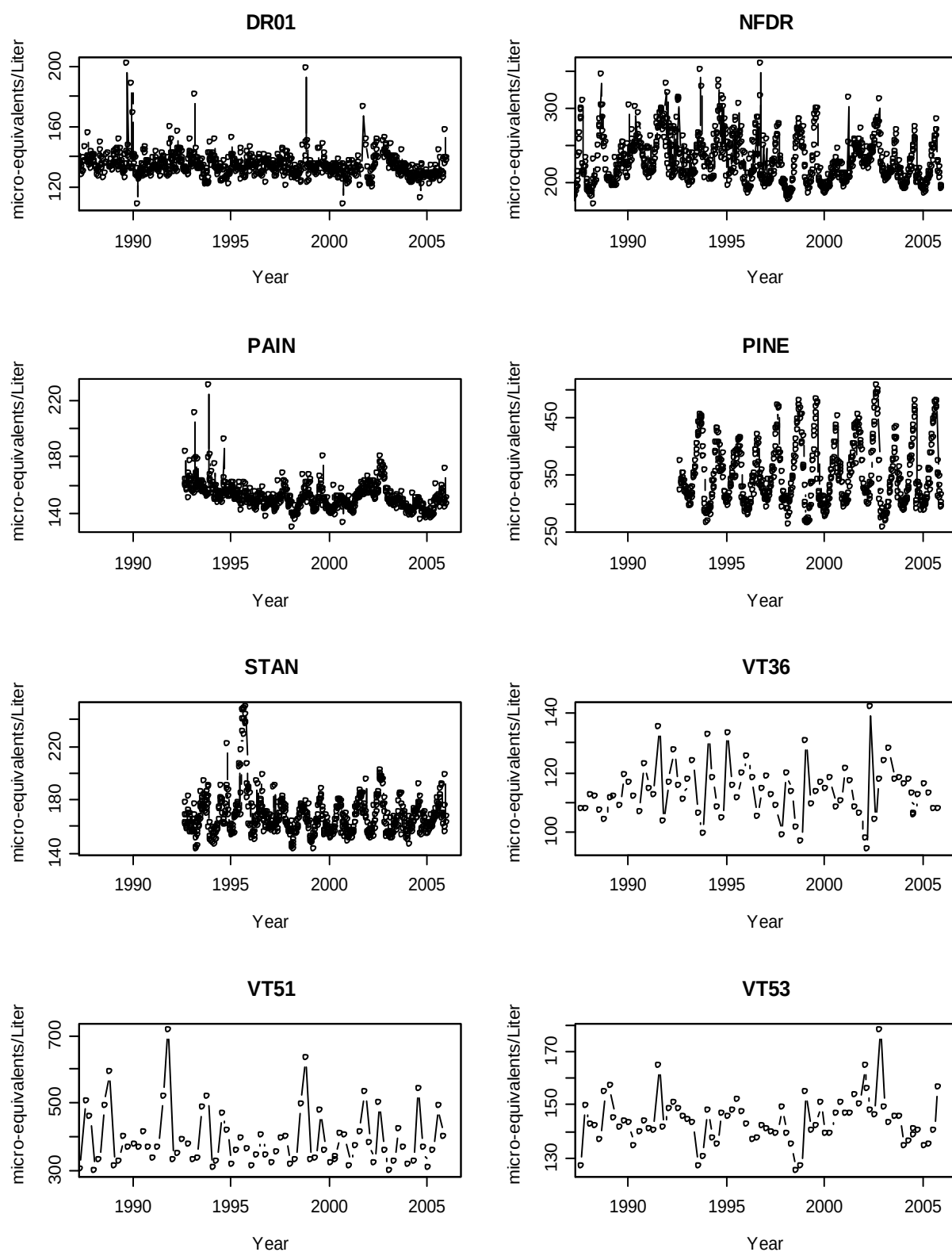


Figure 7c (continued): Time-series plots of base cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+}$) for SWAS study streams. The points represent quarterly, weekly, and episodic (ISCO) samples.

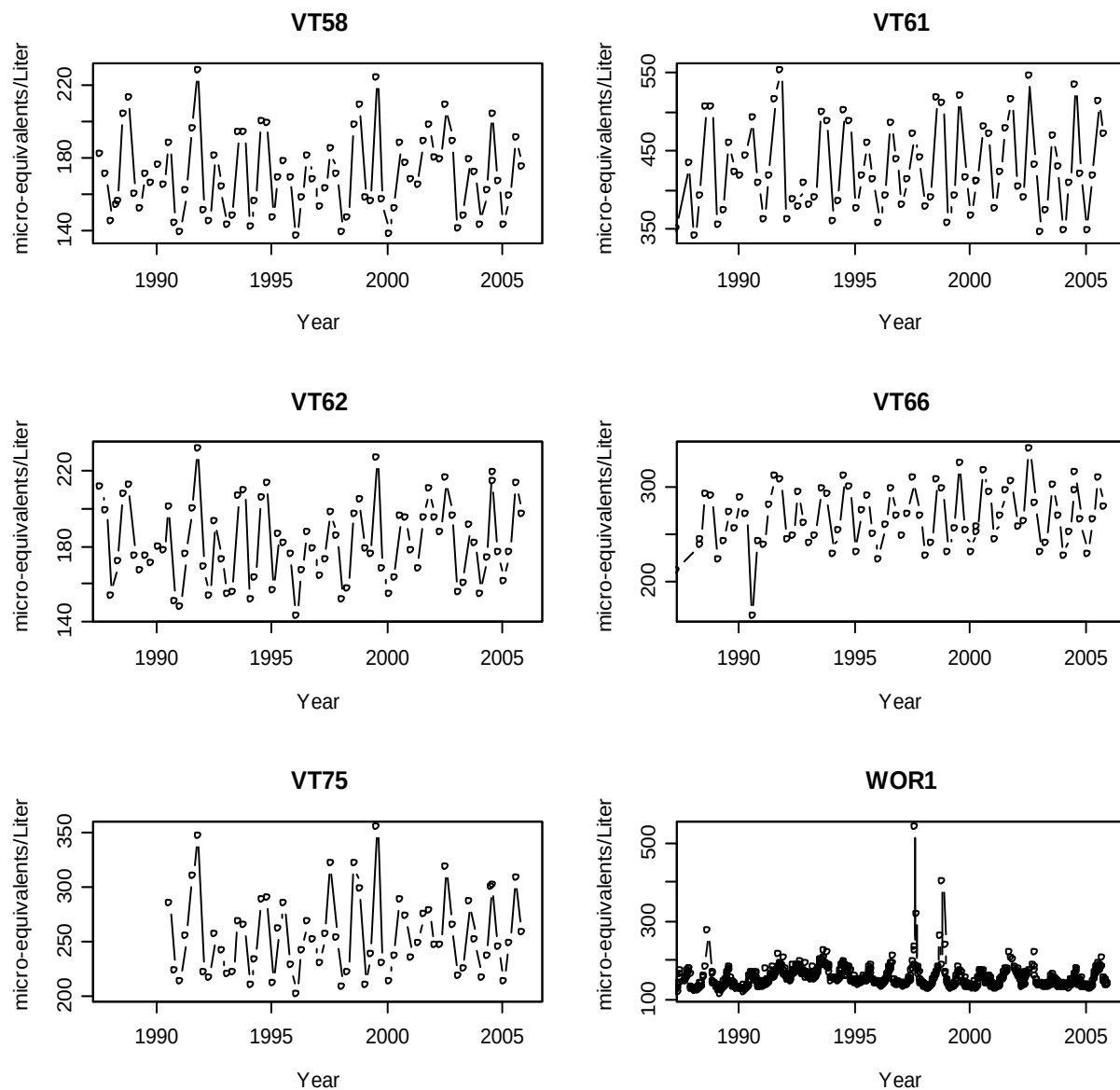


Figure 7d: Time-series plots of sulfate concentrations for SWAS study streams. The points represent quarterly, weekly, and episodic (ISCO) samples.

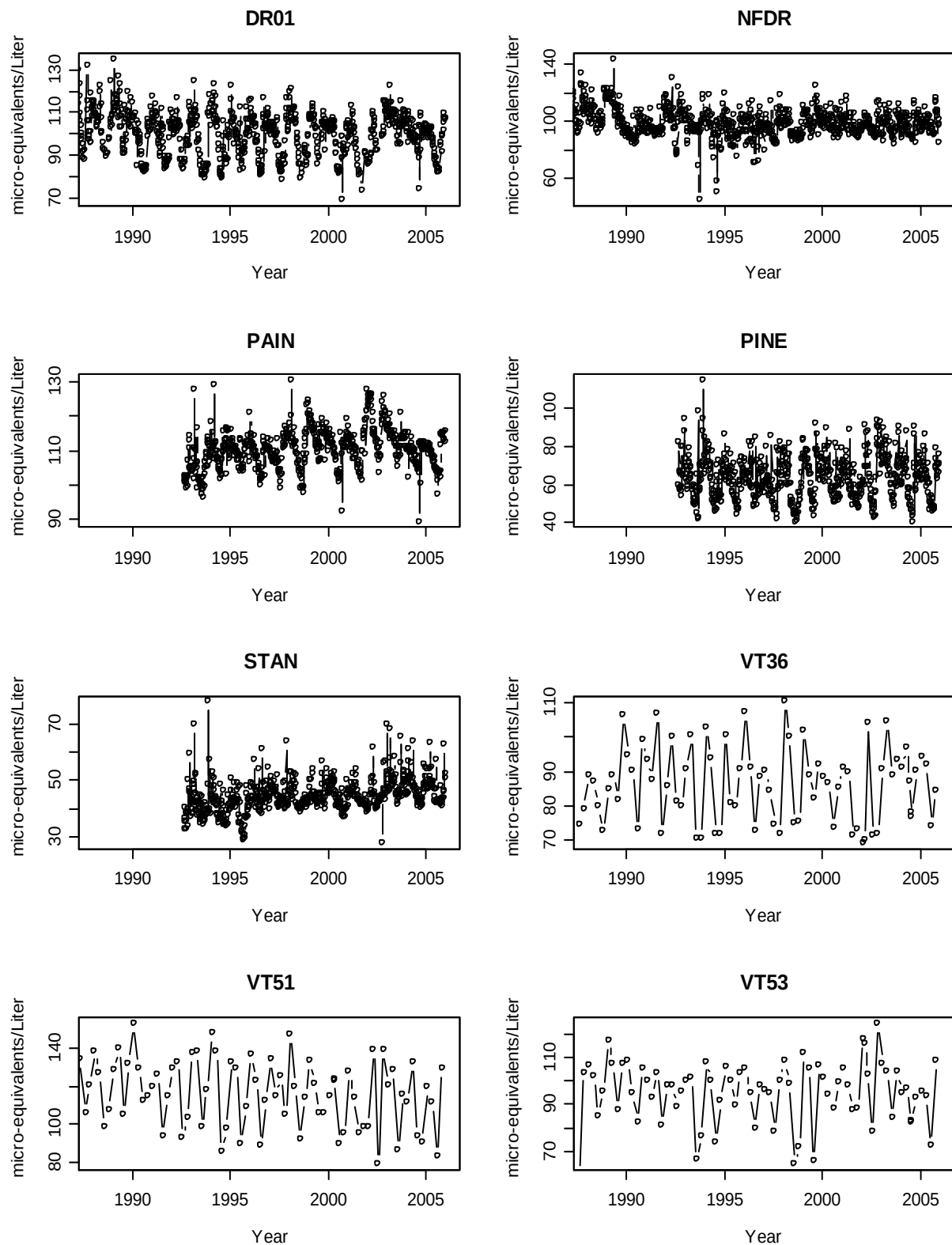


Figure 7d (continued): Time-series plots of sulfate concentrations for SWAS study streams. The points represent quarterly, weekly, and episodic (ISCO) samples.

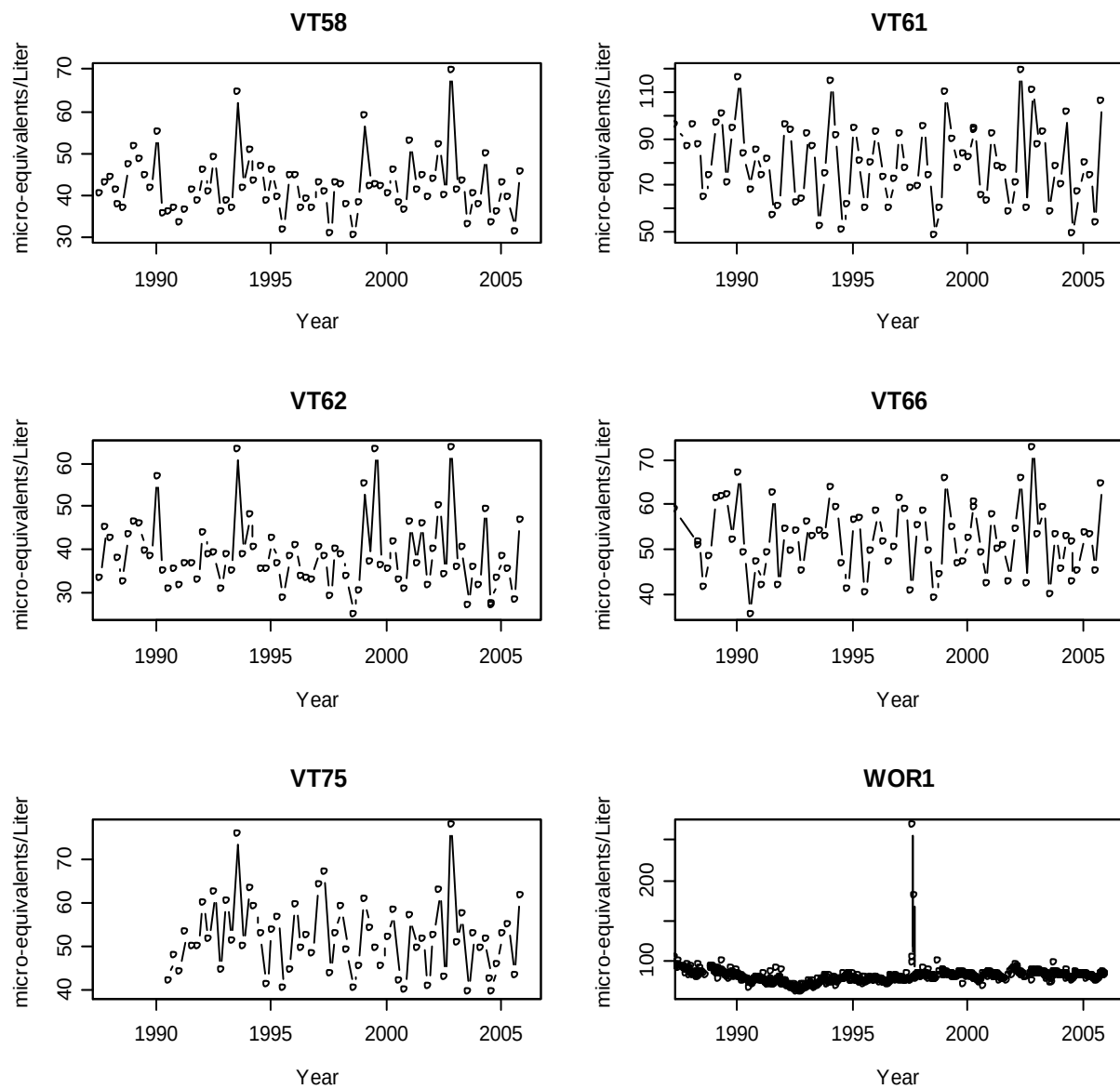


Figure 7e: Time-series plots of nitrate concentrations for SWAS study streams. The points represent quarterly, weekly, and episodic (ISCO) samples.

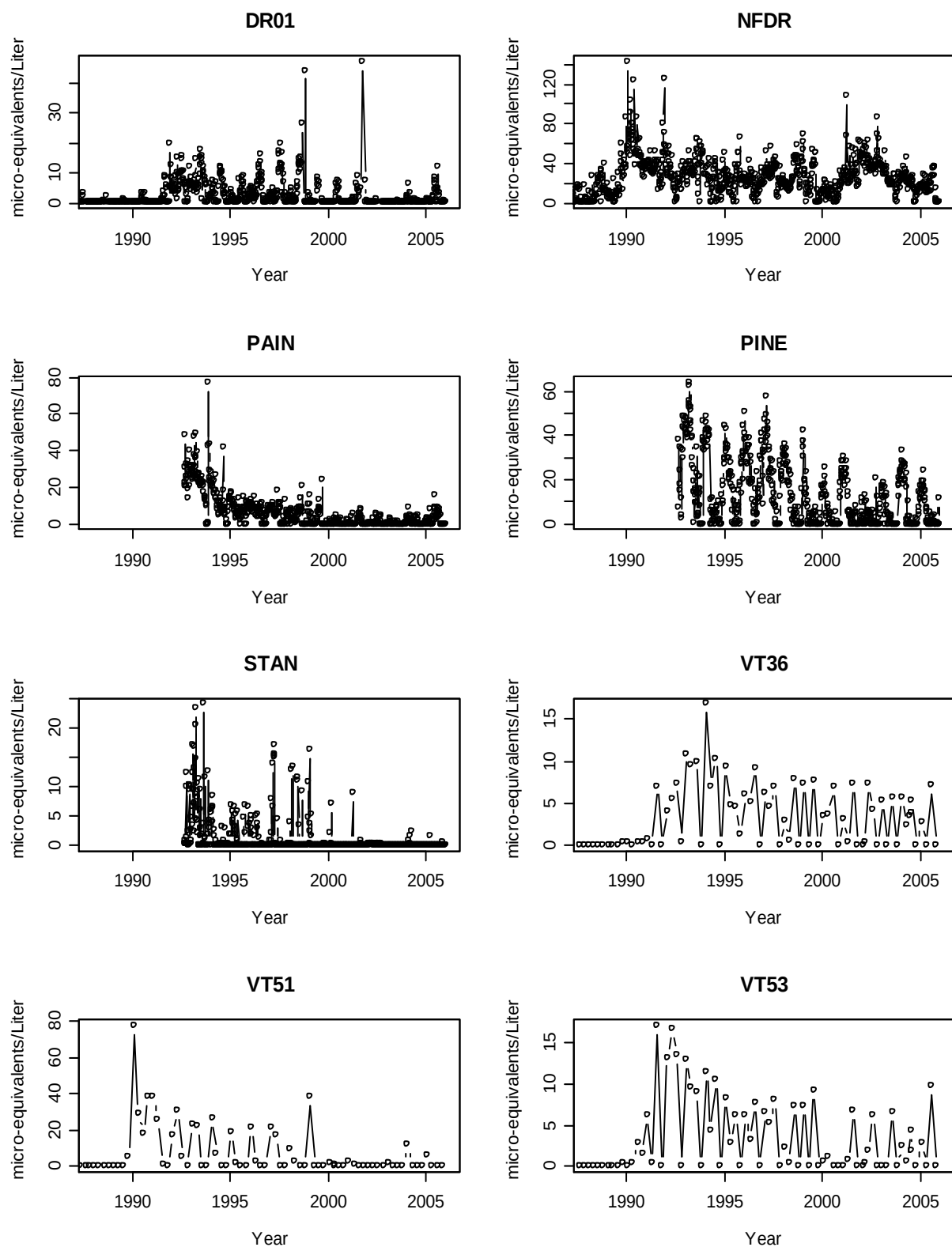
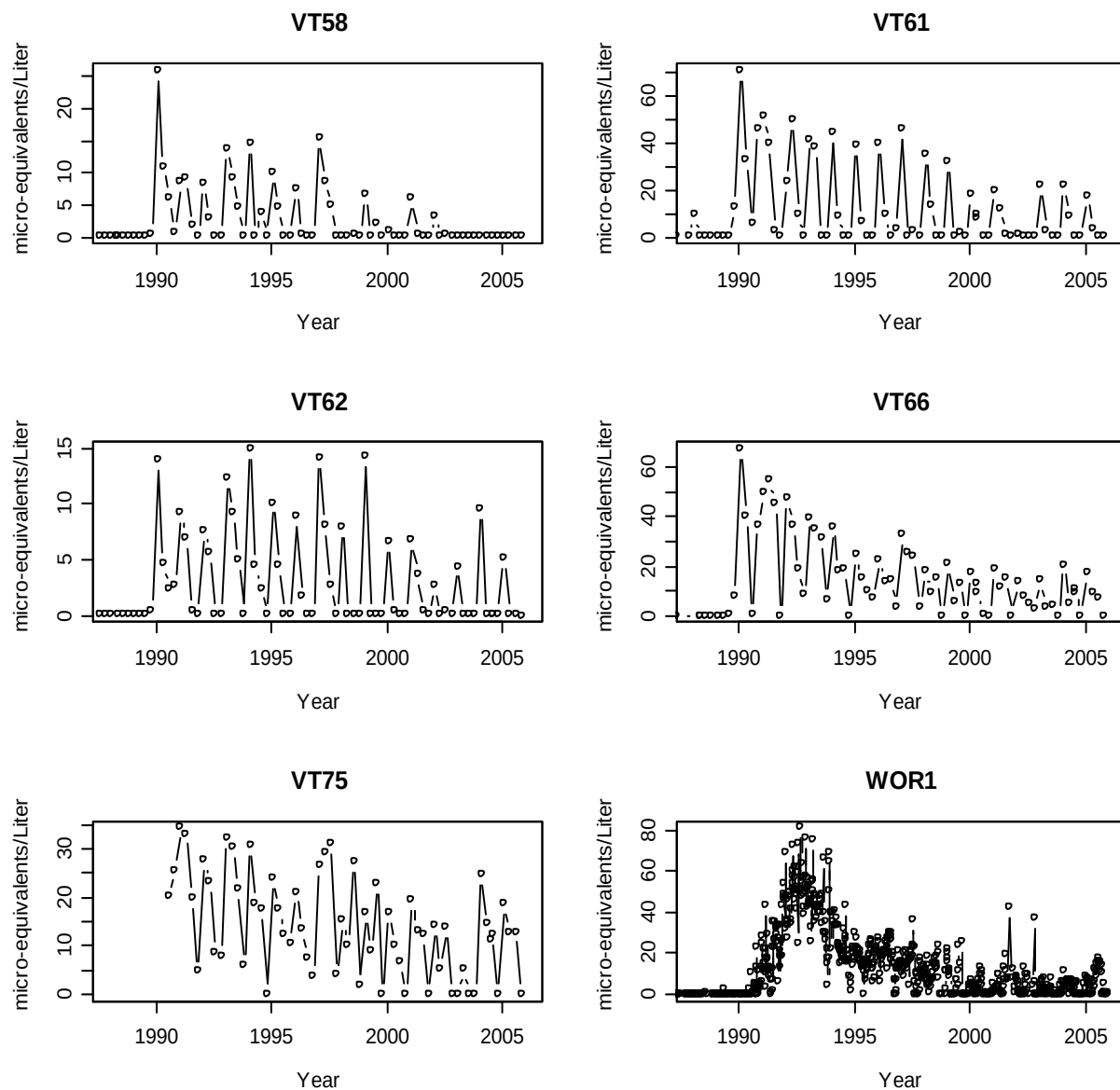


Figure 7e (continued): Time-series plots of nitrate concentrations for SWAS study streams. The points represent quarterly, weekly, and episodic (ISCO) samples.



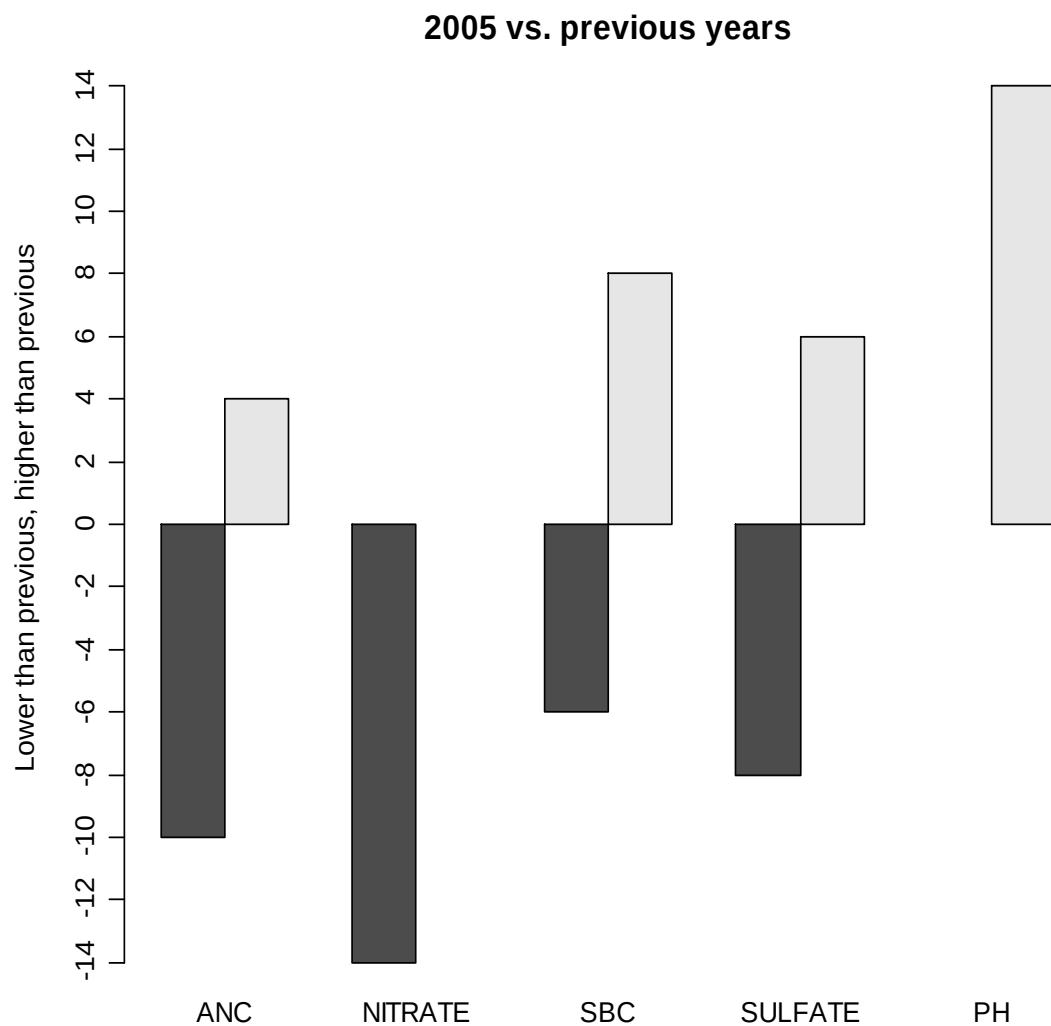


Figure 8: Comparison of current and previous years' data: summary of differences in mean values of major acid-base constituents. Solid bars indicate the number of sites for which the current year mean values were lower than for previous years. Light bars indicate the number of sites for which the current year mean values were greater than for previous years.

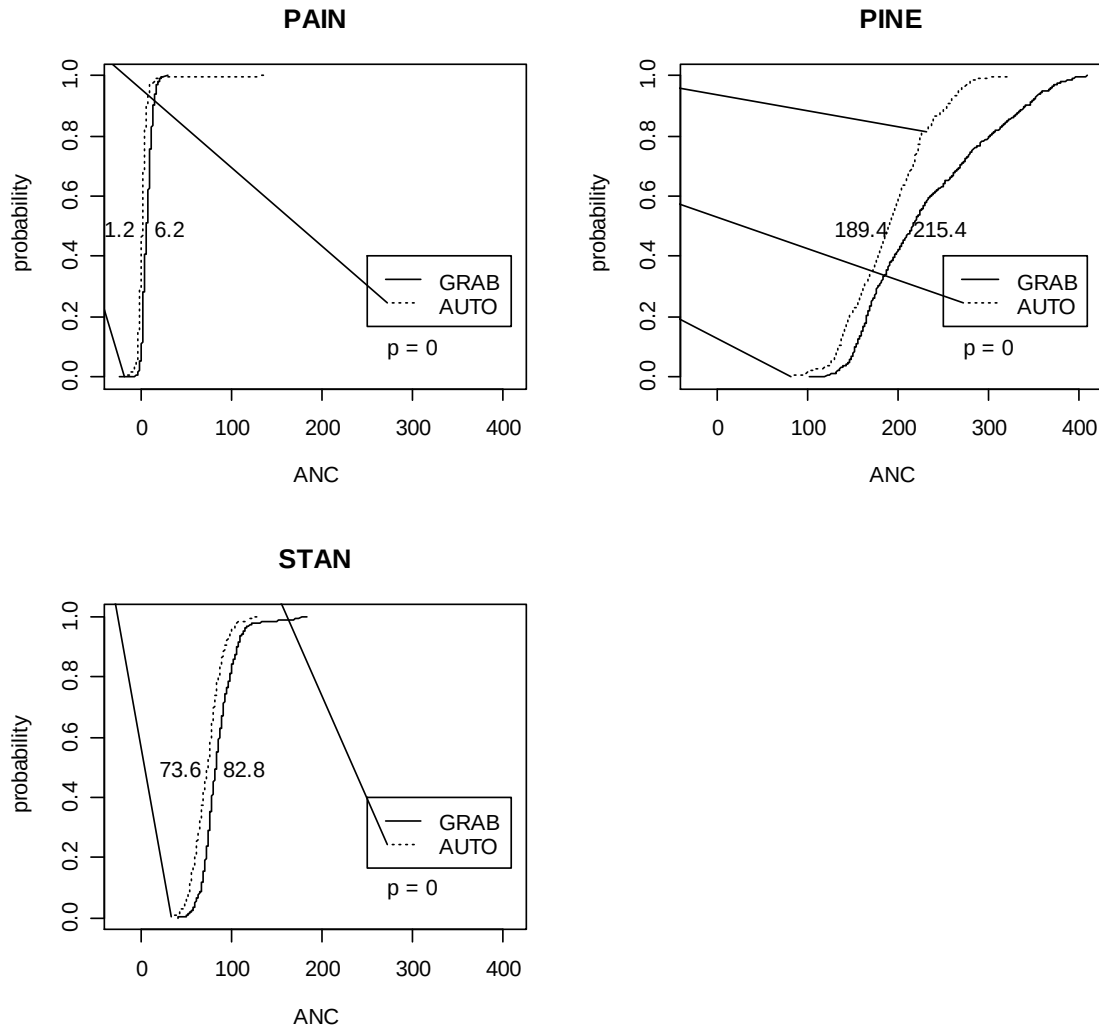


Figure 9: Comparison of ANC distributions for routine weekly grab samples and high-runoff samples collected with automated ISCO samplers (1992 – 2005). The ISCO samplers collect samples at 2-hour intervals during periods of discharge exceeding the 95th flow-duration percentile (determined separately for cold and warm seasons). The median values (50% probability) for routine grab samples and ISCO samples are indicated.

APPENDICES

I. Publications and Presentations

The following publication and presentation update for 2005 include data and analysis results obtained through the SWAS program.

Krawzcel, J.K. Assessing the lethal and sublethal effects of stream acidification on five fish species in Shenandoah National Park. Masters Thesis, University of Virginia. 2004.

Chanat, J.G. Hydrologic Mechanisms Underlying Episodic Concentration-Discharge Relationships in Headwater Catchments. Ph.D. Dissertationm University of Virginia. 2004.

Webb, J.R. Identification of Native Brook Trout Streams That Are Impaired by Acidification, Report to Virginia Water Resources Research Center, Virginia Tech. 2005.

Webb, J.R. Identification of Native Brook Trout Streams That Are Impaired by Acidification. National Water Research Symposium: Balancing Water Law andScience, Virginia Water Resources Research Center, Virginia Tech, Blacksburg, Virginia. 2005.

III. Outreach

Meetings were held with staff of both The Nature Conservancy and the Canaan Valley Institute to discuss the SWAS and VTSSS programs and the possibility of expanding the geographic focus of the coordinated research and monitoring effort.

A project was initiated with The Nature Conservancy to examine potential acidic deposition vulnerabilities for areas included in The Nature Conservancy's Ecological Portfolio, including SWAS study watershed in the Shenandoah National Park.

SWAS staff, Rick Webb and Frank Deviney, participated in planning meetings for the Mid-Atlantic Regional Observatory (MAREO) of the proposed NEON ecological research and observatory network. The potential inclusion of the SWAS program and related Shenandoah National Park locations as a part of the MAREO network was promoted.

A proposal was submitted to the National Science Foundation to obtain laboratory equipment for the SWAS program.

An article, Researchers, Environment Win Big in Pollution Cases, was published in Inside UVA. The article described Clean Air Act cases brought by the U.S. Environmental Protection Agency against Midwestern utilities responsible for air pollution emissions. Testimony in the cases relied substantially on data collected by the SWAS program for Shenandoah National Park (see <http://swas.evsc.virginia.edu/Assests/Docs/environment.pdf>)

