CHAPTER 6

TEMPORAL TRENDS AND INTERRELATIONSHIPS OF AEROSOL CONCENTRATIONS

The IMPROVE aerosol monitoring network, established in March 1988, initially consisted of 36 sites instrumented with aerosol sampling modules A through D [Sisler *et al*., 1993]. Many of the IMPROVE sites are successors to sites where aerosol monitoring with stacked filter units (SFU) was carried out as early as 1979 [Sisler and Malm, 1989]. The IMPROVE module A is identical in many aspects to the second stage of the SFU sampler. Both methods measured $PM_{2.5}$ samples of ambient aerosol on Teflon filters and were subjected to the same assay techniques (see Table 2.1). In this discussion, three measured values will be examined in some detail: gravimetric fine mass (FM), sulfur as measured by Proton Induced X-ray Emission (PIXE), and absorption (b_{abs}) measured by the Laser Integrating Plate Method (LIPM) [Eldred *et al*., 1988, Cahill *et al*., 1986]. Assuming an absorption efficiency of 10 m^2/gm, b_{abs} is expressed as a mass in ng/m^3.

The IMPROVE sites that can be paired with antecedent SFU sites have an almost unbroken record of sulfur and fine mass (and other elements measured by PIXE) from as early as 1979 and b_{abs} from 1983. Table 6.1 lists the sites and time periods that IMPROVE or SFU samplers were operated. These data provide an excellent opportunity to look for evidence of long-term trends in aerosol concentrations.

Two distinct temporal trends are considered here: seasonal, and long-term trends of statistical measures such as maxima, minima, percentiles, and standard deviations. For the sake of completeness, Appendix 1 has time lines of FM, sulfur, and b_{abs} for every IMPROVE/SFU site. Presented here for discussion are data that demonstrate identifiable trends and differences between sites.

6.1 Protocol Induced Trends of Sulfur Concentrations and b_{abs}

Two significant changes in sampling protocol have occurred since sampling began in 1979. In June 1986, the SFU sampling schedule was changed from two 72-hour duration samples per week, with start times alternating between midnight and noon, to two 24-hour samples per week, with both start times at midnight. The IMPROVE network has maintained the new schedule. In March 1988, the IMPROVE network succeeded the SFU network. There was a three month hiatus from December 1987 through February 1988 when almost no samples were obtained while equipment was changed.

Table 6.1 Sites and time periods for IMPROVE and SFU.

Acronym	Full Name	SFU Start	SFU End	IMPROVE Start	IMPROVE End
ACAD	Acadia NP	9/21/85	11/28/87	3/01/88	Present
ARCH	Arches NP	9/28/79	11/28/87	3/01/88	5/92
BAND	Bandelier NM	10/02/82	2/09/85	3/01/88	Present
BIBE	Big Bend NP	7/27/82	11/28/87	3/01/88	Present
BRCA	Bryce Canyon NP	9/21/79	12/02/87	3/01/88	Present
BRLA	Brooklyn Lake	3/01/91	7/31/93	7/31/93	Present
CANY	Canyonlands NP	9/21/79	11/28/87	3/01/88	Present
CHIR	Chiricahua NM	6/8/82	5/31/86	3/01/88	Present
CRLA	Crater Lake NP	10/12/82	11/28/87	3/01/88	Present
CRMO	Craters of the Moon	7/17/82	3/29/86	5/12/92	Present
DENA	Denali NP &	9/10/86	11/25/87	3/01/88	Present
DEVA	Death Valley NP	6/01/82	3/29/86	10/18/93	Present
GLAC	Glacier NP	9/28/82	12/5/87	3/01/88	Present
GICL	Gila NF	10/1/79	8/31/81	3/28/94	Present
GRBA	Great Basin NP	10/12/82	3/29/86	5/00/88	Present
GRCA	Grand Canyon NP	8/03/79	11/28/87	3/01/88	Present
GRSA	Great Sand Dunes	9/15/80	8/31/81	5/04/88	Present
GRSM	Great Smoky Mtns	1/31/84	11/28/87	3/01/88	Present
GUMO	Guadalupe Mtns NP	2/19/83	12/02/87	3/01/88	Present
LAVO	Lassen Volcanic NP	6/29/82	5/29/84	3/01/88	Present
MEVE	Mesa Verde NP	10/30/82	12/05/87	3/01/88	Present
MORA	Mount Rainier NP	7/23/83	12/16/87	3/01/88	Present
PEFO	Petrified Forest NP	7/30/79	11/25/87	3/01/88	Present
ROMO	Rocky Mountain NP	9/21/79	12/02/87	9/15/90	Present
SAGU	Saguaro NM	7/2/85	8/31/88	3/1/88	Present
SALM	Salmon NF	9/01/90	11/13/93	11/09/93	Present
SHEN	Shenandoah NP	7/13/82	11/28/87	3/01/88	Present
TONT	Tonto NM	8/3/79	11/29/83	3/01/88	Present
VOYA	Voyageurs NP	7/13/85	Present	3/01/88	Present
YELL	Yellowstone NP	9/29/79	12/05/87	3/01/88	Present
YOSE	Yosemite NP	9/25/82	10/28/87	3/01/88	Present

NP = National Park
NM = National Monument
NF = National Forest

Both changes in protocol are relatively close to each other in time. Therefore, it is difficult to separate the effects of one change from the other using the data. Since there are no monitoring sites where SFU samplers and IMPROVE samplers were operated side by side, any changes due to protocol must be hunted for in the data. The purpose of this chapter is not to put this issue to rest by exhaustive statistical analysis but rather to alert the reader to the possibility. However, since the changes in protocol affect all sampling sites, the affects should be systematic across the network.

Two changes in the data that are most probable are a smoothing effect due to the change in the sampling duration and a bias in elemental concentrations, absorption and fine mass due to the change from SFU samplers to IMPROVE samplers. One would expect a smoothing effect for data collected over 72 hours compared to data collected over 24 hours. Smoothing of the data would show a tighter distribution about the mean resulting in a smaller standard deviation and less extreme maximum and minimum values. Bias in the data, resulting from switching the equipment from SFU samplers to IMPROVE samplers, comes from the actual sampling methodology. For example, the SFU fine mass ($PM_{2.5}$) is a sequential filter that sites behind a filter that collects coarse material, while the IMPROVE module A filter has a cyclone inlet that is calibrated to 2.5 microns. Any discrepancy in cutpoint efficiency and derivative, as a function of aerodynamic radius between the two samplers, could generate a bias in seasonal mean values. If there is a long-term trend in the data, this bias could either enhance the trend or mask it.

It appears, based on a cursory inspection of the data as presented here, that a systematic effect associated with changes in protocols is not evident for fine mass and sulfur concentrations. Most clearly identifiable changes in the data can be explained by other physical causes. One such notable change occurred at Mount Rainier where the sampling site was moved from a high altitude to a low altitude location. Other explanations are related to changes in emissions. In general, the expected changes due to smoothing did not materialize, instead the changes in data behavior appear random and slight at best. No systematic bias in the data between SFU samplers and IMPROVE samplers was noted, suggesting that any bias at one particular site must be due to circumstances unique to that site such as equipment calibration, or characteristics of the ambient aerosol and meteorology that would affect sampler performance, or actual location/orientation of the equipment.

In the case of absorption, Figure 6.1 shows time lines for b_{abs} for five sites that demonstrate a clear change before and after the IMPROVE network was initialized. The sites included are Acadia, Glacier, Great Smoky Mountains, Mount Rainier, and Shenandoah National Parks. It is clear by inspection of Figure 6.1 that a significant change occurred after March 1988. Almost all sites for all seasons show significant increases in b_{abs} between sampling regimes with the IMPROVE values being larger than the SFU. As with sulfur, it should be noted that increases of b_{abs} at Mount Rainier are likely related to changing of the sampler location. Reasons for the changes at the other sites are not known and it should be noted that these five sites are exceptions as most sites show little if any change by inspection.

6.2 Seasonal Trends of Sulfur

Sulfur concentrations often have a readily identifiable seasonal trend [Day *et al*., 1996, Malm *et al*., 1994; Sisler *et al*., 1993; Sisler and Malm, 1989; Trijonis and Yuan 1987; Flocchini *et al*., 1981]. These trends have been related to a number of factors including meteorology, photochemistry, and long-range transport with sulfur concentrations being the highest during the summer and lowest during the winter.

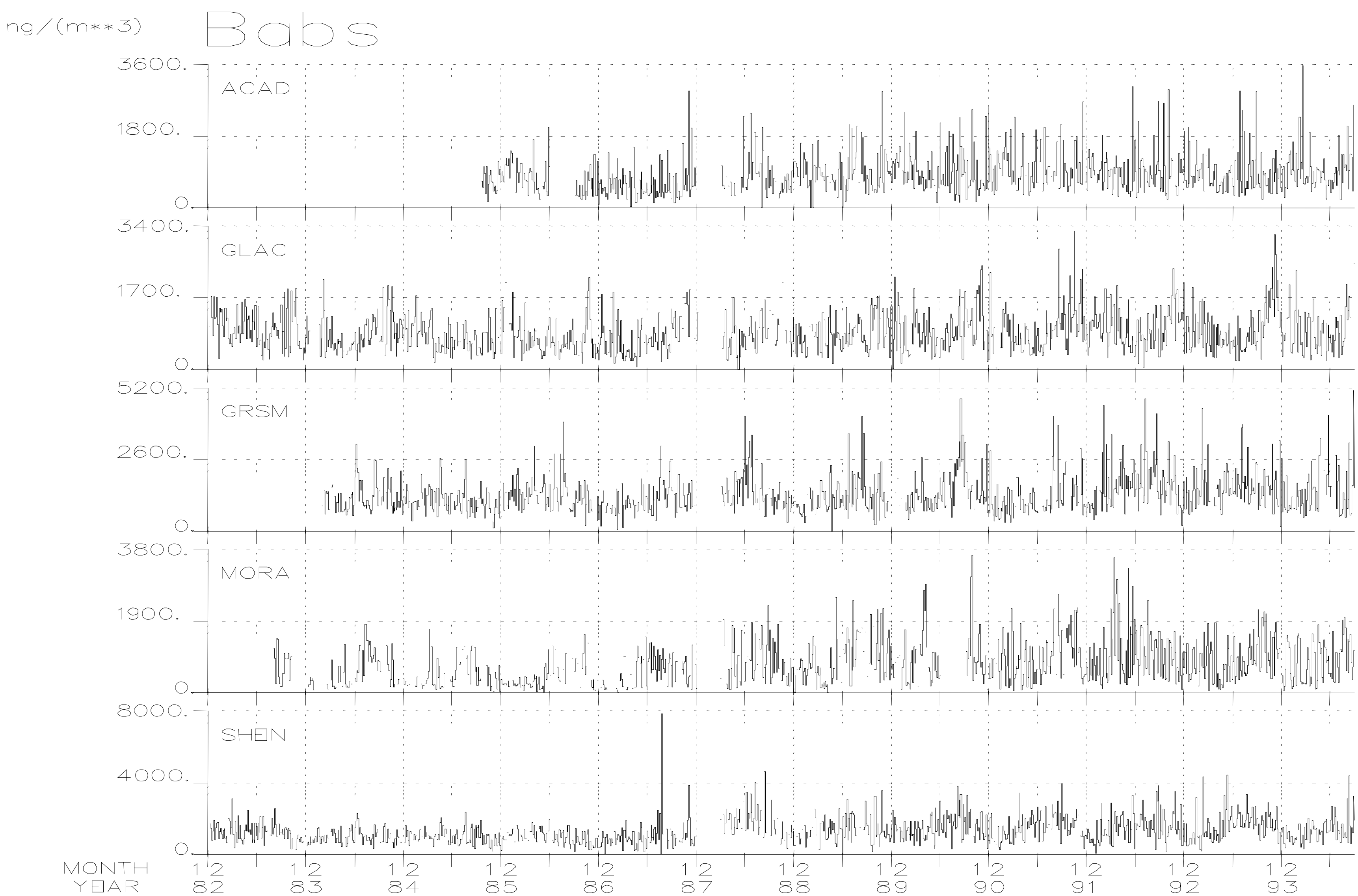

Figure 6.1 Time line of absorption (b_{abs}) at five sites that demonstrate a clear change before and after the IMPROVE network was initiated.

Figure 6.2 shows the time lines of sulfur at seven sites: Shenandoah, Great Smoky Mountains, Yosemite, Rocky Mountain, Canyonlands, Yellowstone, and Glacier National Parks. Table 6.2 has seasonal statistics for these sites. At two sites, Yellowstone and Glacier, one extreme value was discarded from the time lines presented in Figure 6.2. This value, 1364 ng/m^3 at Yellowstone on May 31, 1989 is a factor of 10 higher than the mean and 200% higher than the next highest value. Similarly, one value of 1326 ng/m^3 at Glacier on June 2, 1993, was discarded.

These sites demonstrate a range in amplitude of seasonal variation. The two sites with the highest sulfur concentrations, Great Smoky Mountains and Shenandoah, are in the East. The maximum sulfur concentrations for these sites, 8700 and 6900 ng/m^3 at Shenandoah and Great Smoky Mountains, respectively, occurred during the summer.

At Shenandoah, Great Smoky Mountains, Yosemite, and Rocky Mountain National Parks, sulfur concentrations have clear seasonal patterns. The pattern is less clear at Canyonlands, while at Yellowstone and Glacier a seasonal pattern is not apparent. These seven sites represent the range of seasonal variability of sulfur in the data set.

It is notable that even at sites with strong seasonal trends there are some sampling periods that have zero or near zero concentrations in any season.

Yosemite is interesting as the maximum sulfur is only about 1400 ng/m^3, yet a seasonal pattern is clearly evident from the minimums, which are much greater during the summer months. At Rocky Mountain, the seasonality is much weaker than at Yosemite as evidenced by the variability in time that yearly maximum values occur. However, it is clear from the minimum values that a seasonal trend exists with higher minimums occurring during the summer.

The three remaining sites shown in Figure 6.2, Canyonlands, Yellowstone, and Glacier have much lower sulfur concentrations. None of these sites exhibit obvious seasonal trends as displayed by the other sites. Their maximum values are quite a bit less than the other sites and about equal to each other.

6.3 Seasonal Trends of Absorption (b_{abs})

Absorption, like sulfur, has a strong seasonal trend at many sites with highest concentrations usually occurring during the summer and early autumn months. Figure 6.3 shows time lines of b_{abs} at six sites across the United States: Acadia, Glacier, Great Smoky Mountains, Rocky Mountain, and Yosemite National Parks, and Saguaro National Monument. This ensemble demonstrates the range of the strength of the seasonal signature that varies from none at Acadia and Saguaro, to moderate at Glacier and Great Smoky Mountains, to strong at Rocky Mountain and Yosemite.

Table 6.3 has seasonal statistics for absorption at these six sites. Acadia, a site with minimal seasonality, has a mean value that varies from 750 ng/m^3 in the spring to 950 ng/m^3 in the winter. Acadia's maximum concentrations are similar between seasons at about 3000 ng/m^3, except during the winter when the maximum value of 3562 ng/m^3 was obtained.

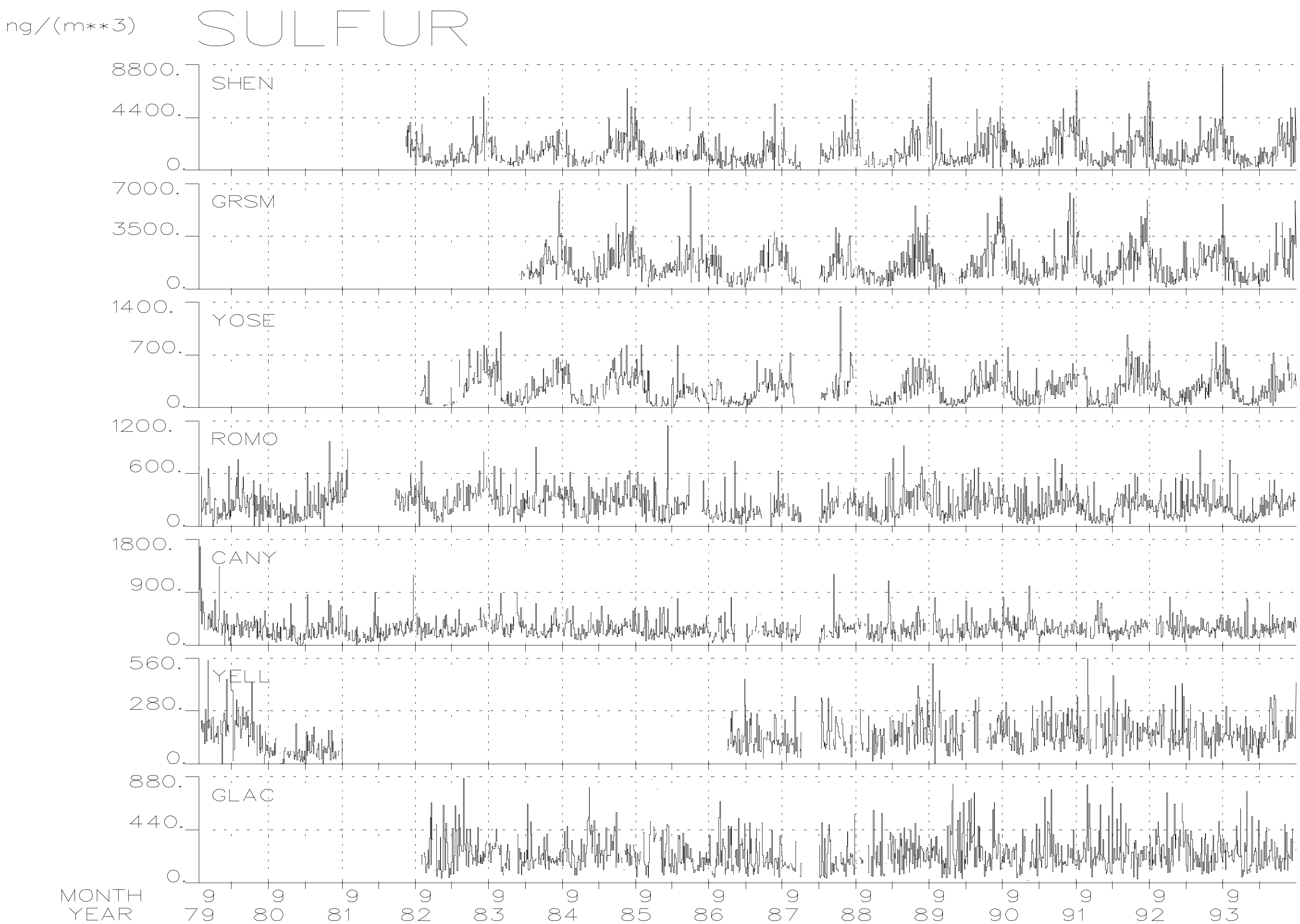

Figure 6.2 Time lines of sulfur concentration at seven sites that demonstrate a range of seasonal behavior with the strongest seasonality at the top and the weakest at the bottom.

Table 6.2. Seasonal statistics (in ng/m^3) for particulate sulfate at seven sites.

Site	N	Mean	Std Dev	Minimum	Maximum
SPRING					
SHEN	299	1415	809	131	5199
GRSM	267	1508	838	175	6789
YOSE	284	261	156	11	964
ROMO	354	270	140	0	921
CANY	374	257	127	36	1202
YELL	220	177	120	0	1365
GLAC	308	257	146	36	866
SUMMER					
SHEN	304	2495	1286	11	8665
GRSM	267	2407	1250	393	6928
YOSE	283	374	178	55	1339
ROMO	354	319	130	0	963
CANY	374	306	130	66	1206
YELL	237	148	73	0	432
GLAC	301	216	96	26	669
AUTUMN					
SHEN	283	1413	1059	15	7722
GRSM	237	1374	892	27	5610
YOSE	259	260	182	16	1008
ROMO	348	236	148	0	877
CANY	343	282	175	0	1679
YELL	192	149	92	0	558
GLAC	274	231	132	39	862
WINTER					
SHEN	255	827	441	62	2588
GRSM	214	831	462	110	3152
YOSE	256	86	69	12	525
ROMO	327	168	143	14	1146
CANY	329	280	194	0	1339
YELL	205	135	89	0	488
GLAC	261	259	181	13	1326

Saguaro shows even less variability in the mean with a low of 826 ng/m^3 in the spring to a high of 927 ng/m^3 in the winter.

Glacier and Great Smoky Mountains have relatively stable means with Glacier obtaining its low of 743 ng/m^3 during spring and its high of 1085 ng/m^3 in the autumn. Great Smoky Mountains obtains its lowest during the winter at 1156 ng/m^3 and highest in the summer with 1585 ng/m^3. The seasonality at Great Smoky Mountains and Glacier is more readily observed

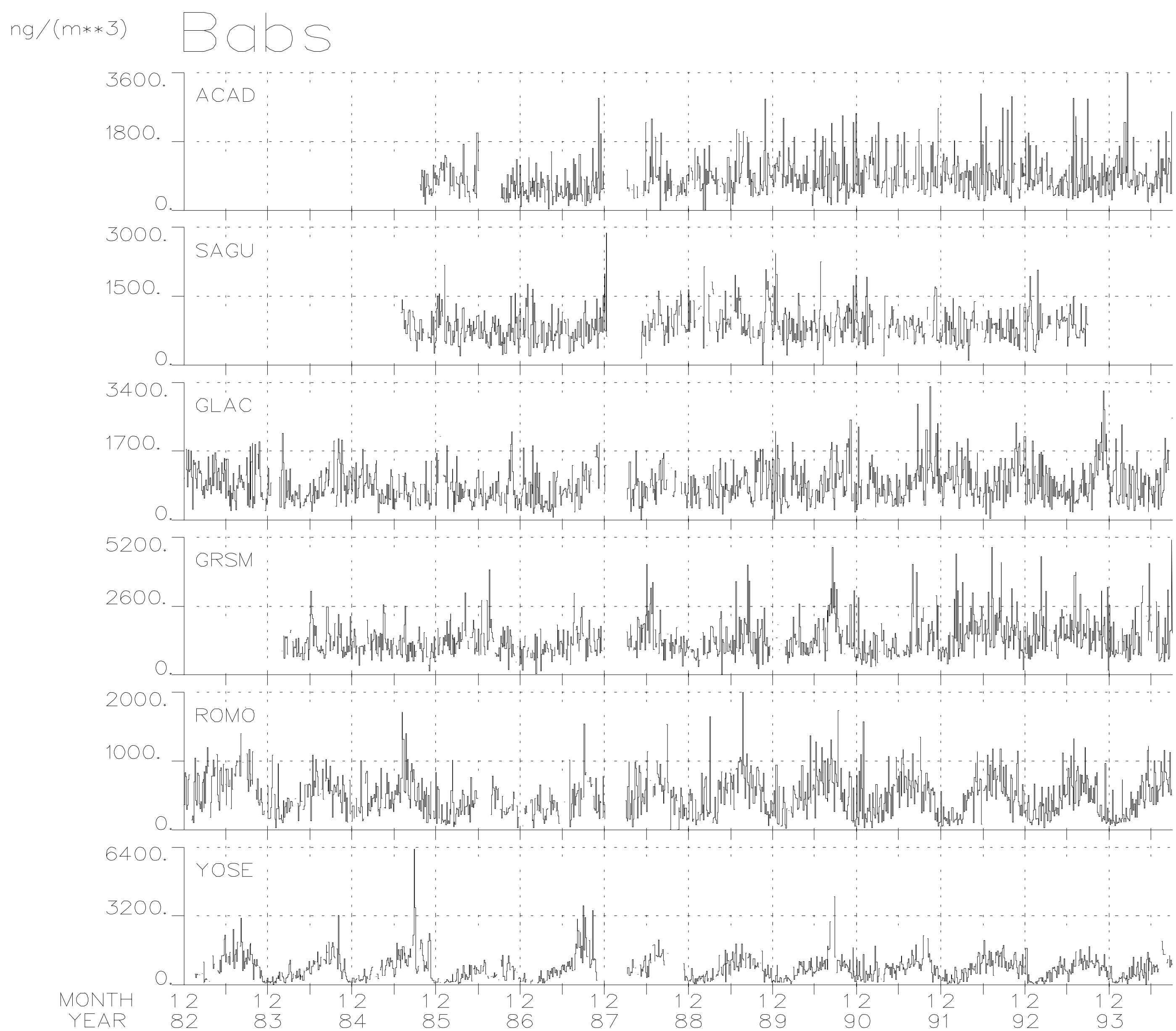

Figure 6.3 Time lines of absorption at six sites that demonstrate a range of seasonal behavior with the weakest seasonality at the top and the strongest at the bottom.

Table 6.3 Seasonal statistics for absorption (in ng/m^3) at six sites.

Site	N	Mean	Std Dev	Minimum	Maximum
SPRING					
ACAD	211	750	418	0	3041
SAGU	167	826	295	98	1799
GLAC	305	743	361	0	1994
GRSM	265	1332	567	0	4195
ROMO	290	480	255	36	1633
YOSE	282	661	357	0	2305
SUMMER					
ACAD	196	942	589	0	2932
SAGU	210	843	299	21	2239
GLAC	297	812	371	38	2852
GRSM	266	1585	887	391	5104
ROMO	272	713	281	37	1990
YOSE	278	1155	617	148	6295
AUTUMN					
ACAD	218	779	509	116	2963
SAGU	186	868	369	0	2087
GLAC	255	1085	571	152	3284
GRSM	235	1275	599	132	3292
ROMO	263	449	256	0	1729
YOSE	239	867	588	56	3655
WINTER					
ACAD	195	950	455	0	3563
SAGU	161	927	468	198	2883
GLAC	259	911	461	20	2347
GRSM	209	1156	627	51	4564
ROMO	262	308	245	23	1566
YOSE	242	300	264	0	1773

by the extreme values. The minimum for Great Smoky Mountains varies from 0 (below detection) to 381 ng/m^3 in the summer when the maximum of 5104 ng/m^3 is obtained as well. Glacier exhibits similar though not as extreme behavior where the largest minimum of 152 ng/m^3 and largest maximum of 3284 ng/m^3 are in the winter.

Yosemite and Rocky Mountain, which have the strongest seasonal variation, have means of 300 ng/m^3 and 308 ng/m^3 in the winter, and 1155 ng/m^3 and 713 ng/m^3 in the summer.

6.4 Long-Term Variability

Because of seasonal variability, long-term trends can more easily be explored by examining trends in seasonally-averaged data over a number of years. Seasonal statistics by year are graphically portrayed at each site for both fine mass concentrations, sulfur concentrations, and absorption. Appendix 2 has plots for every site and season. The box icon used for each season portrays the minimum, the mean minus one standard deviation, the 25th percentile, 50th percentile (median), mean, 75th percentile, mean plus one standard deviation, and maximum. The percentiles are connected by a solid line. Presented here are representative examples for sites that demonstrate trends and the lack of trends.

6.4.1 Bryce Canyon National Park

Bryce Canyon in the autumn (Figures 6.4a, 6.4b, 6.4c) is an example showing an apparent change in fine mass concentrations (Figure 6.4a). Excluding the fall of 1979, there appears to be a step increase in fine mass concentrations beginning in 1987. All percentiles, means, maxima and standard deviations increase noticeably after 1987. It is tempting to associate this with a bias caused by changing the equipment from an SFU sampler to an IMPROVE module A; however, the changeover did not occur until after the autumn of 1987 when the 75th percentile and mean are greater than all succeeding years.

Sulfur concentrations (Figure 6.4b) at Bryce Canyon show no apparent trend. The sulfur concentrations from year to year are variable with the median hovering around 250 ng/m^3. However, the highest median value occurs at the start of the data record in the winter of 1979 at about 400 ng/m^3, which exceeds the 75th percentile for all other years. This season has been analyzed by a number of researchers and has been associated with transport from the smelters in Arizona.

Absorption is somewhat greater than sulfur at around 400 ng/m^3 and displays a variable pattern between years. The first year of the absorption record is notable in that the 75th percentile is greater than the maxima for all subsequent years except 1993; similarly, the mean for 1983 at about 600 ng/m^3 is on par with the 75th percentile for all years after and including 1988.

6.4.2 Rocky Mountain National Park

Fine mass concentrations at Rocky Mountain National Park (Figure 6.5a) during winter, the season of best visibility, shows no trend for the 25th and 50th percentile, which vary around 900 ng/m^3 and 1500 ng/m^3, respectively. There is a most interesting block of years beginning in 1986 running through 1991 that demonstrate inflated variability marked by increased standard deviations caused by high maximum values and 75th percentiles driving the mean values up. Association of this behavior with the decrease in sampling time from 72 hours to 24 hours is at first tempting. This explanation seems doubtful noting the dramatic quieting that occurs after 1991 when the standard deviations, maximums, and 75th percentiles dropped sharply. Also, it is worth noting that the change in protocol did not occur until the summer of 1986 after the start of the period of inflation in the winter of 1986.

Sulfur concentrations (Figure 6.5b) have a fairly constant median level of sulfur during the winters of about 150 ng/m^3. The pattern of variability is mixed and the median sulfur concentration never moves in the same direction for more than two seasons.

A clear downward trend in absorption (Figure 6.5c) is readily seen. The median absorption in the winter of 1982-1983 is about 400 ng/m^3 then drops to about 125 ng/m^3 by the winter of

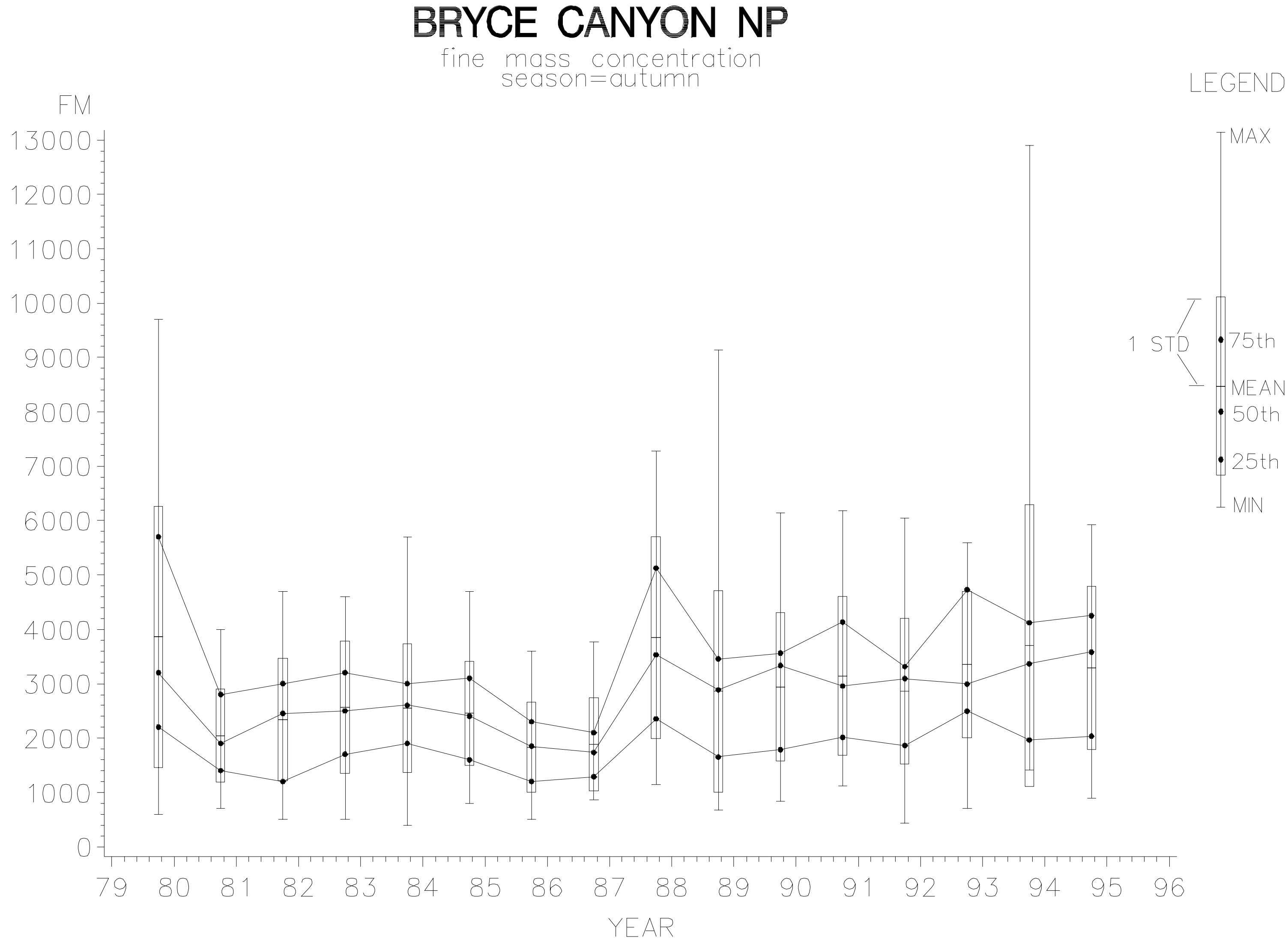

Figure 6.4a Monthly statistics for fine mass concentration (ng/m^3) at Bryce Canyon National Park in the autumn.

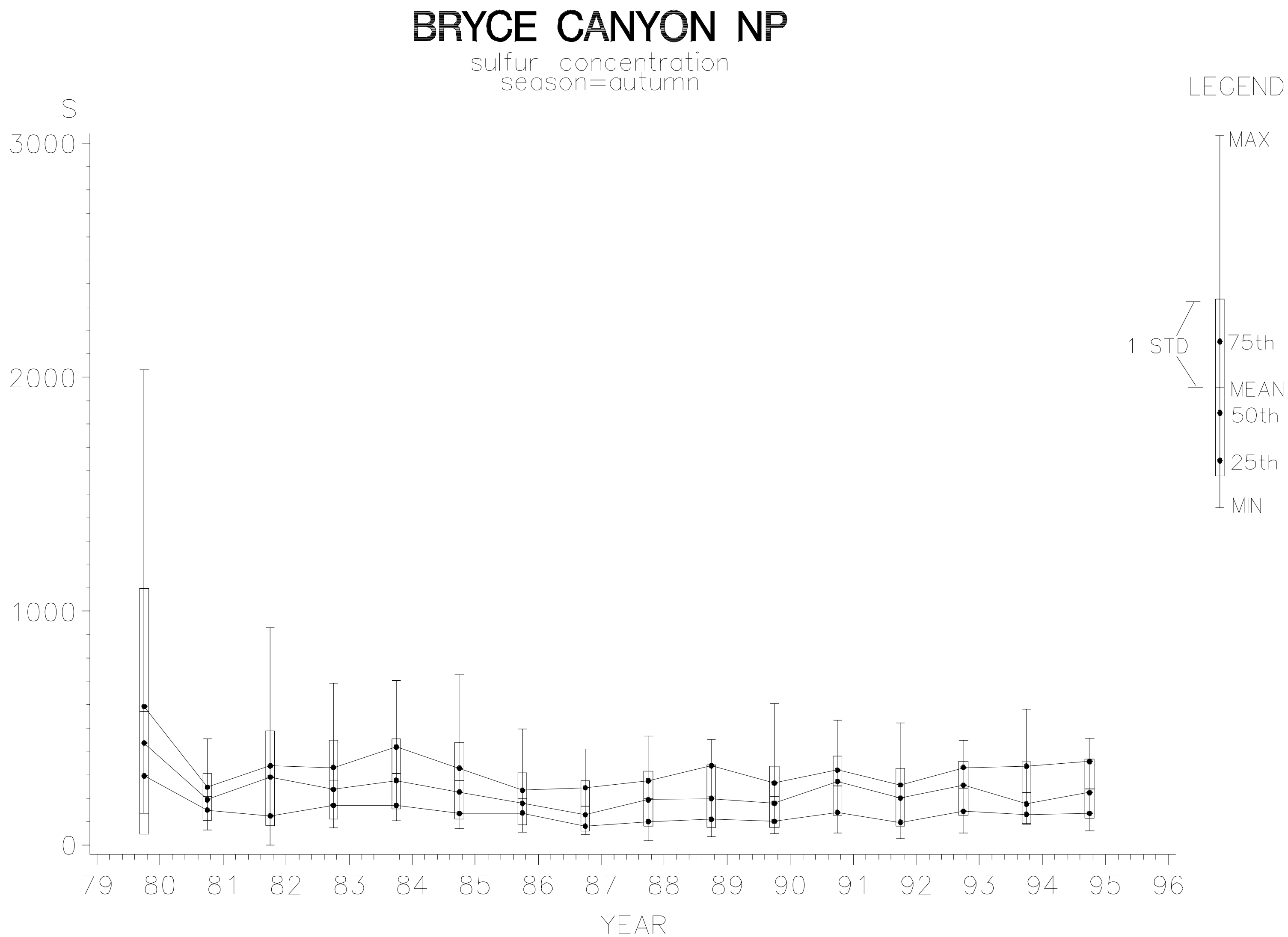

Figure 6.4b Monthly statistics for sulfur concentration (ng/m^3) at Bryce Canyon National Park in the autumn.

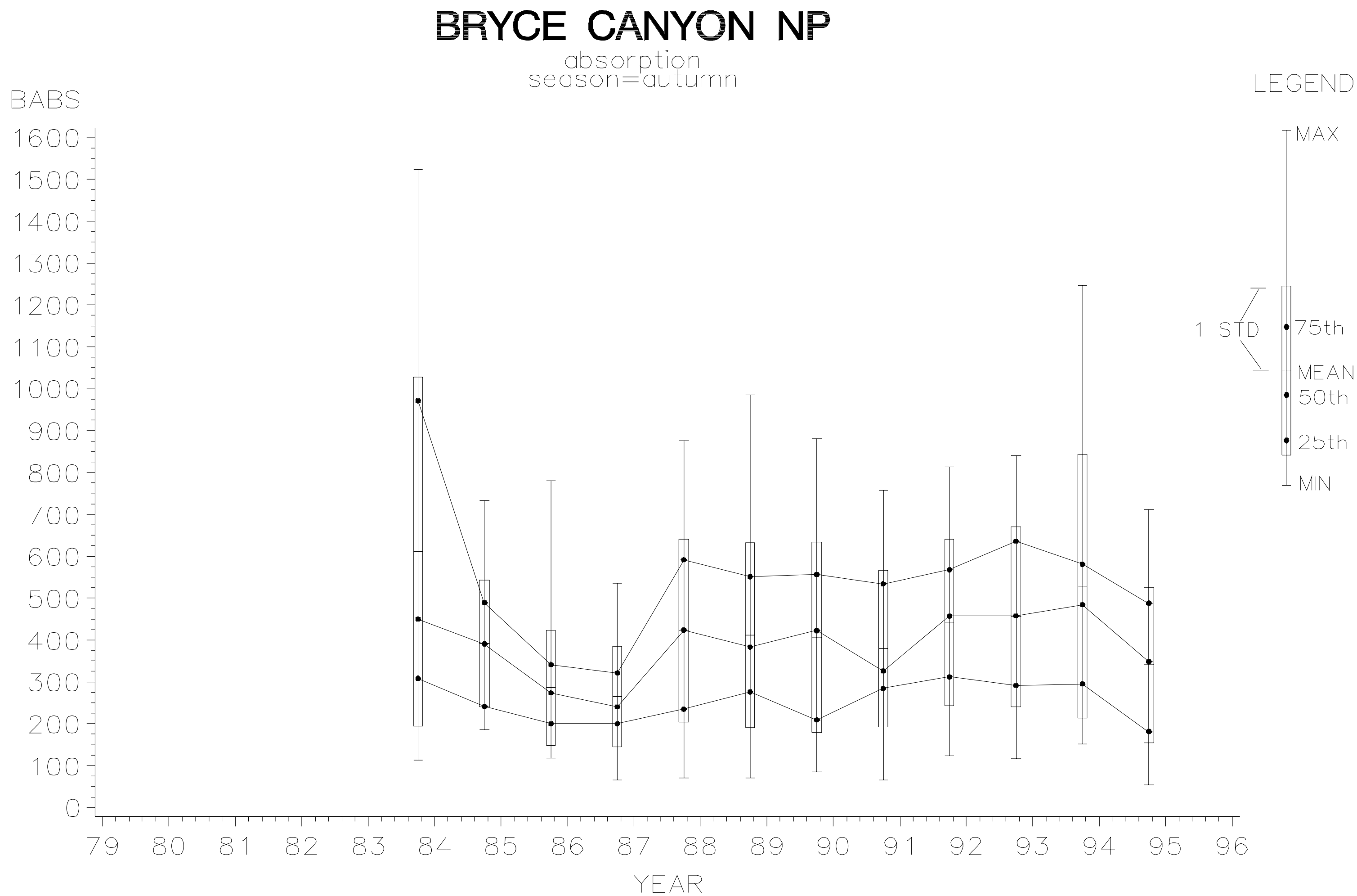

Figure 6.4c Monthly statistics for absorption (ng/m^3) at Bryce Canyon National Park in the autumn.

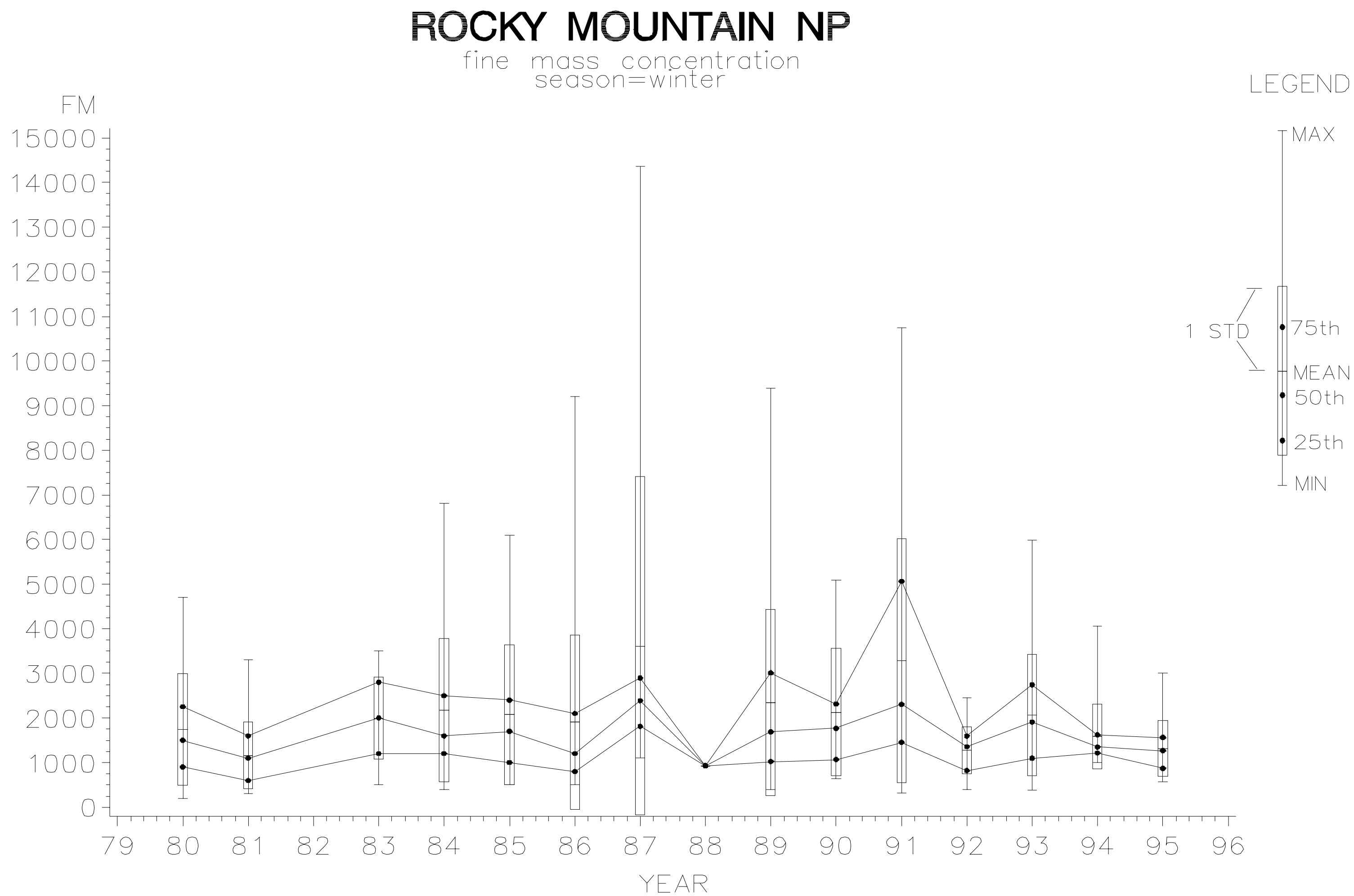

Figure 6.5a Monthly statistics for fine mass concentration (ng/m^3) at Rocky Mountain National Park in the winter.

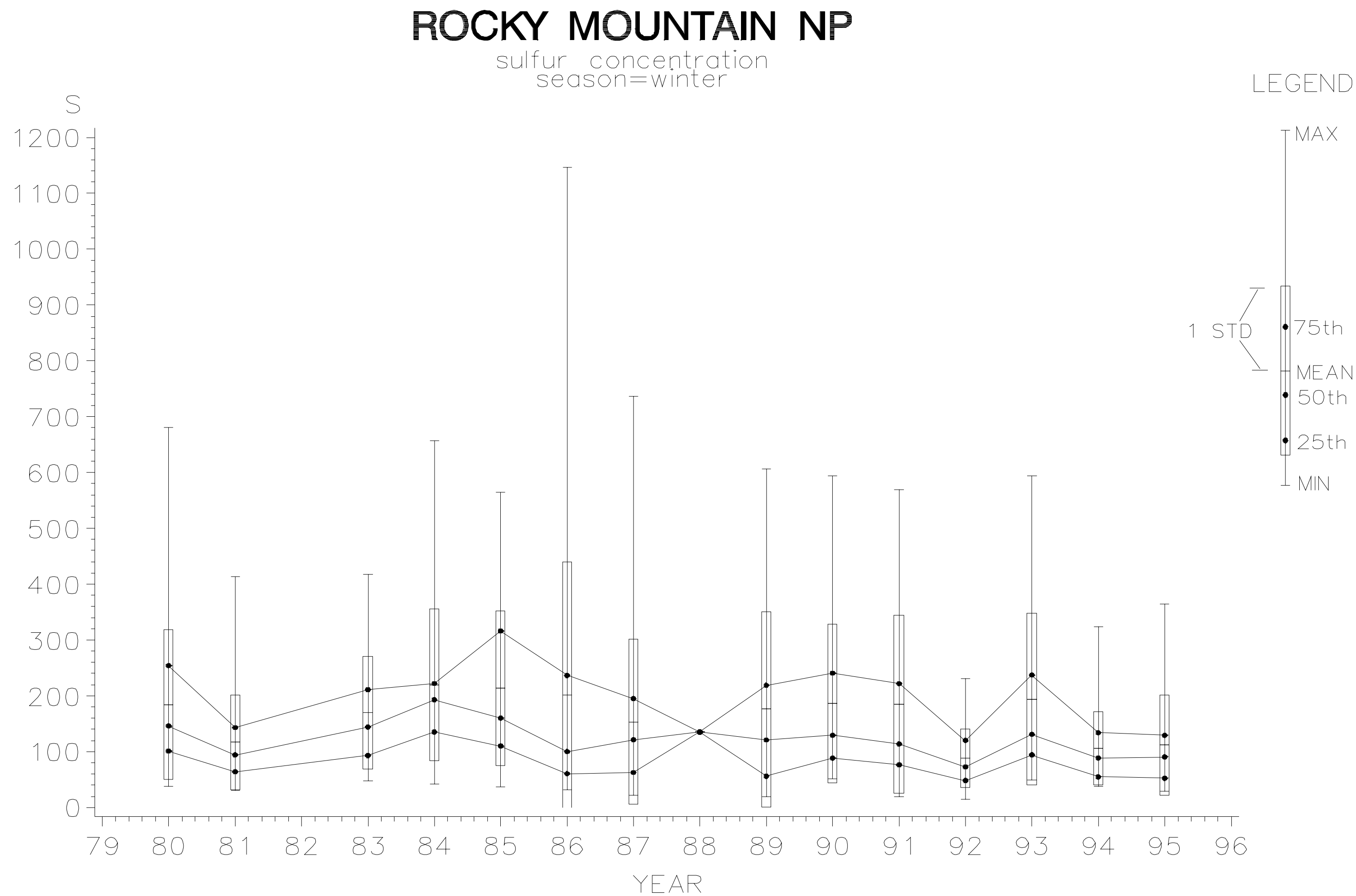

Figure 6.5b Monthly statistics for sulfur concentration (ng/m^3) at Rocky Mountain National Park in the winter.

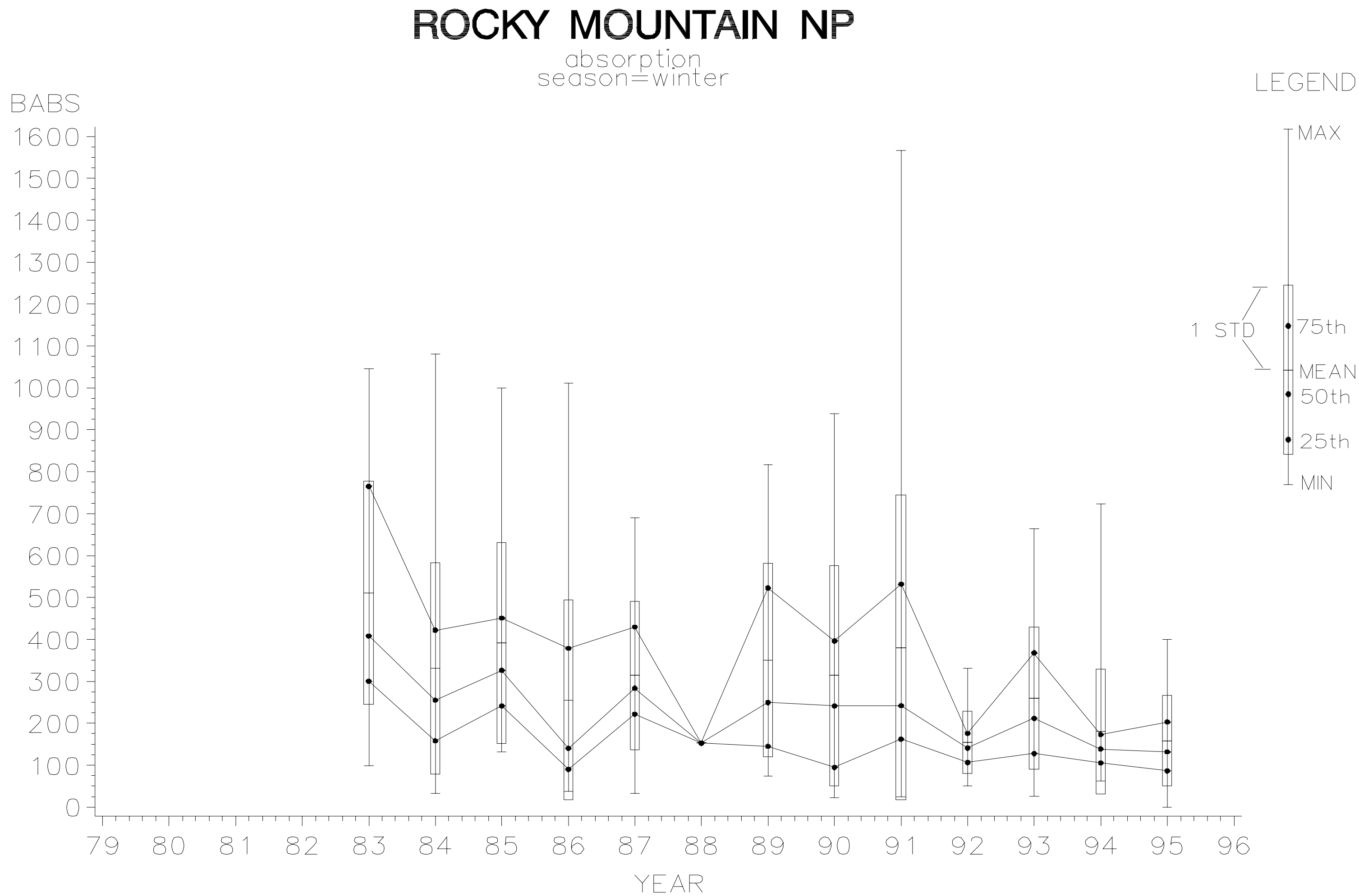

Figure 6.5c Monthly statistics for absorption (ng/m^3) at Rocky Mountain National Park in the winter.

1994-1995. Since 1991-1992 the median absorption has never exceeded 200 ng/m^3. The trend of the 75th percentile is even more impressive, the maximum occurs in the winter 1982-1983 at about 800 ng/m^3 then drops to less then 200 ng/m^3 in recent years.

6.4.3 Guadalupe Mountains National Park

Fine mass concentrations at Guadalupe Mountains (Figure 6.6a) in the autumn have been quite variable. Concentrations decreased steadily the first four years. The 75th percentile and 50th percentile decrease every year from 6500 ng/m^3 and 5200 ng/m^3, respectively in 1982 to 4200 ng/m^3 and 3500 ng/m^3, respectively, in 1986. The 25th percentile obtains its minimum as well in 1986 of 2000 ng/m^3. After 1986 there is a precipitous rise in the 50th and 75th percentile in 1990 to almost 6000 ng/m^3 and 9000 ng/m^3, respectively. Then a quick recovery to almost 1986 levels occurs by 1993 followed by an upturn in 1994.

Sulfur at Guadalupe Mountains in the autumn (Figure 6.b) does not display the gyrations of fine mass and appears to be trending downward. The median concentration is highest (650 ng/m^3) during autumn 1984, then drops to about 400 ng/m^3 the next year. After a slight increase in 1986 to 500 ng/m^3 the median sulfur never exceeds that level again and trends downward. The last four years show a steady decline of the median to 350 ng/m^3 in 1994.

Absorption, on the other hand (Figure 6.6c), while trending down at first, increases to a high of 700 ng/m^3 for the median in autumn 1990, then steadily declines. Similarly, the 75th percentile trends up to its maximum in 1988 at almost 1000 ng/m^3 then steadily declines to about 600 ng/m^3 in the autumn of 1994. The large increase in b_{abs}, coincident with the change from SFU to IMPROVE between 1987 and 1988, is suspicious and should be further investigated to confirm that the apparent trend is not a measurement artifact.

6.4.4 Crater Lake National Park

Fine mass concentrations at Crater Lake during the winters (Figure 6.7a) appear to have trended down slightly. During the first five winters the 75th percentile has trended down from 3400 ng/m^3 to 2500 ng/m^3. With the exception of the winter of 1990-1991, which shows a significant up tick in all measures (except the minimum), all winters after 1989 the 75th percentile is below 2000 ng/m^3 for five out of six winters.

On the other hand, during the winter, sulfur appears to be holding steady at around 60 ng/m^3 for the median (Figure 6.7b). The winters of 1984-85, 1985-86, and 1986-87 are interesting due the very large maximums with concentrations as much as a factor of 10 larger than the medians.

Crater Lake in the winter displays a strong absorption trend (Figure 6.7c). In the winter of 1982-83, the 75th percentile value was about 900 ng/m^3. During the next five out of six winters of record all percentiles decline with the 75th percentile obtaining a minimum of less than 400 ng/m^3 during the winter of 1989-90. The remaining winters, until the last, have a very steady 25th percentile at about 150 ng/m^3. The other percentiles are variable and obtain their global minimum during the winter of 1993-94. The last winter of 1994-95 shows a dramatic increase in all measures, with the 75th percentile exceeding 1400 ng/m^3.

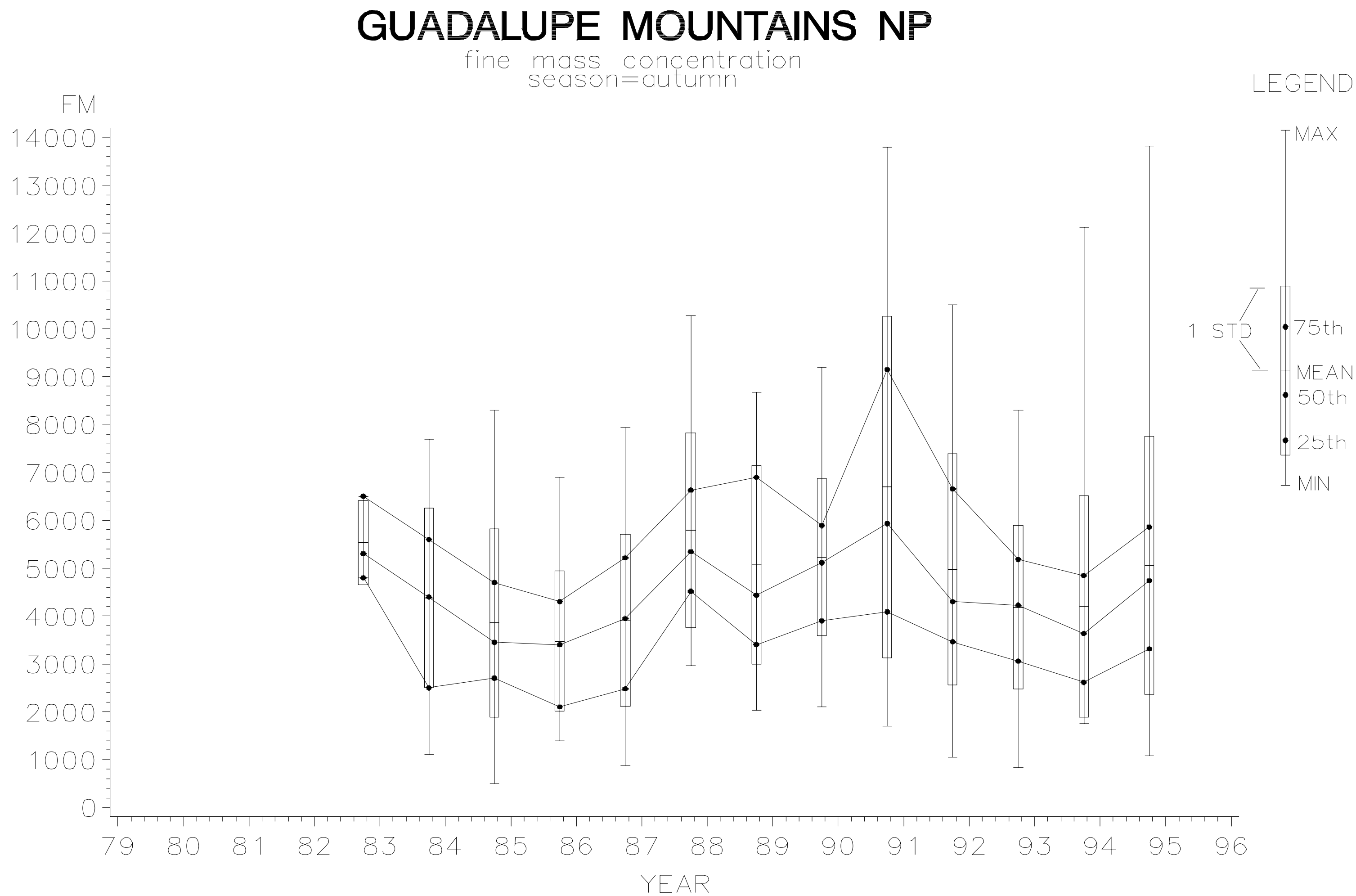

Figure 6.6a Monthly statistics for fine mass concentration (ng/m^3) at Guadalupe Mountains National Park in the autumn.

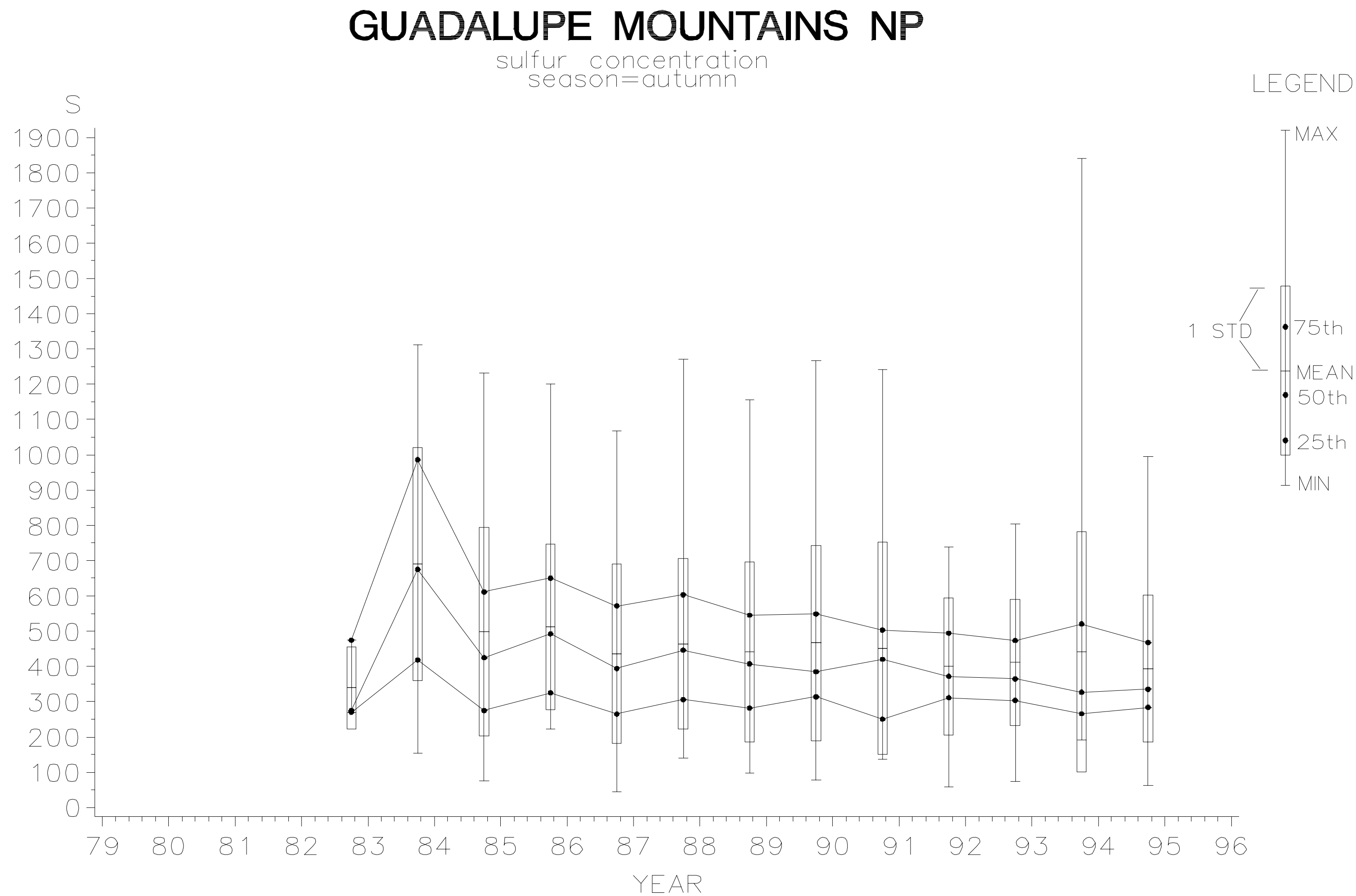

Figure 6.6b Monthly statistics for sulfur concentration (ng/m^3) at Guadalupe Mountains National Park in the autumn.

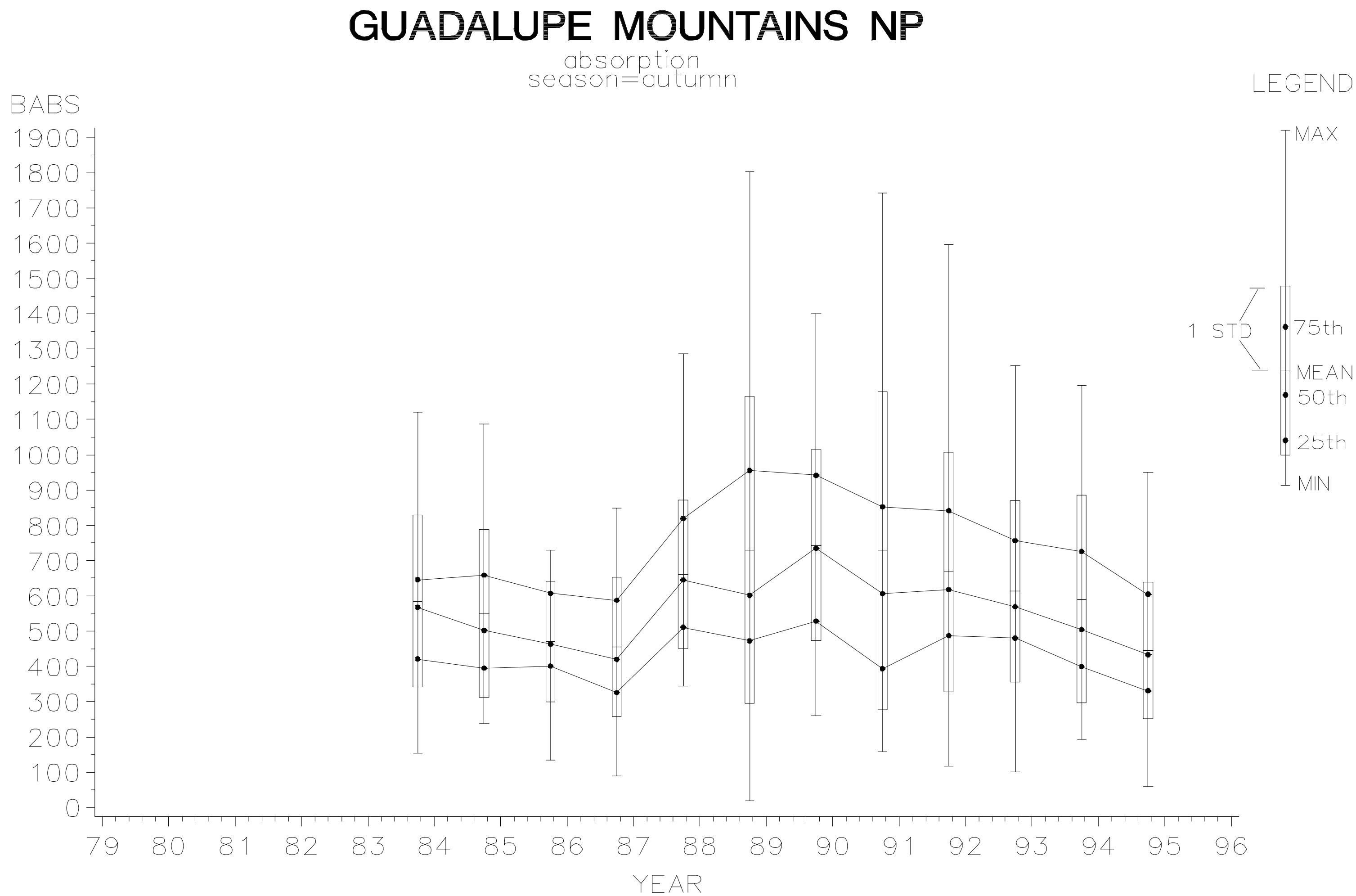

Figure 6.6c Monthly statistics for absorption (ng/m^3) at Guadalupe Mountains National Park in the autumn.

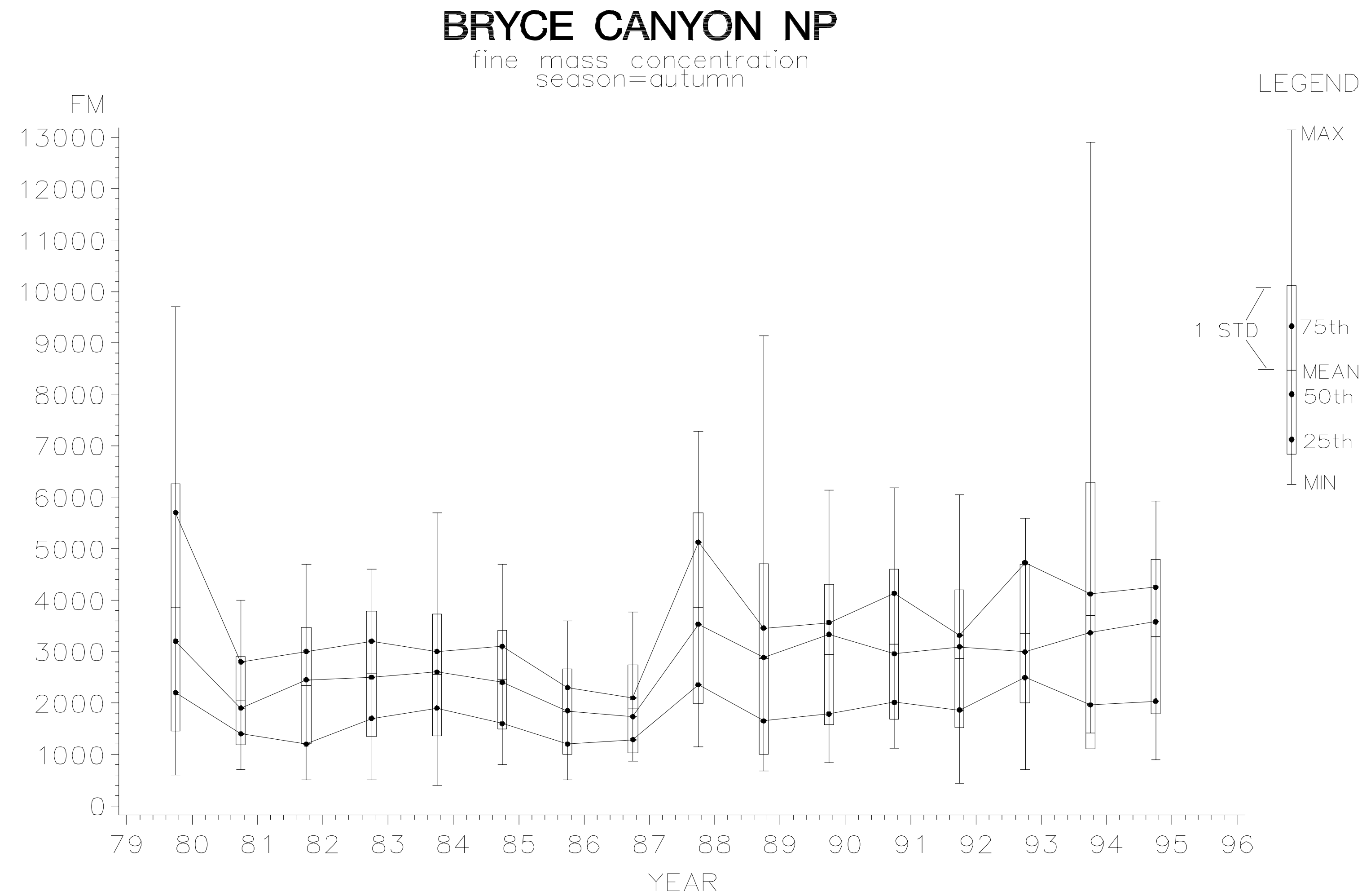

Figure 6.7a Monthly statistics for fine mass concentration (ng/m^3) at Crater Lake National Park in the winter.

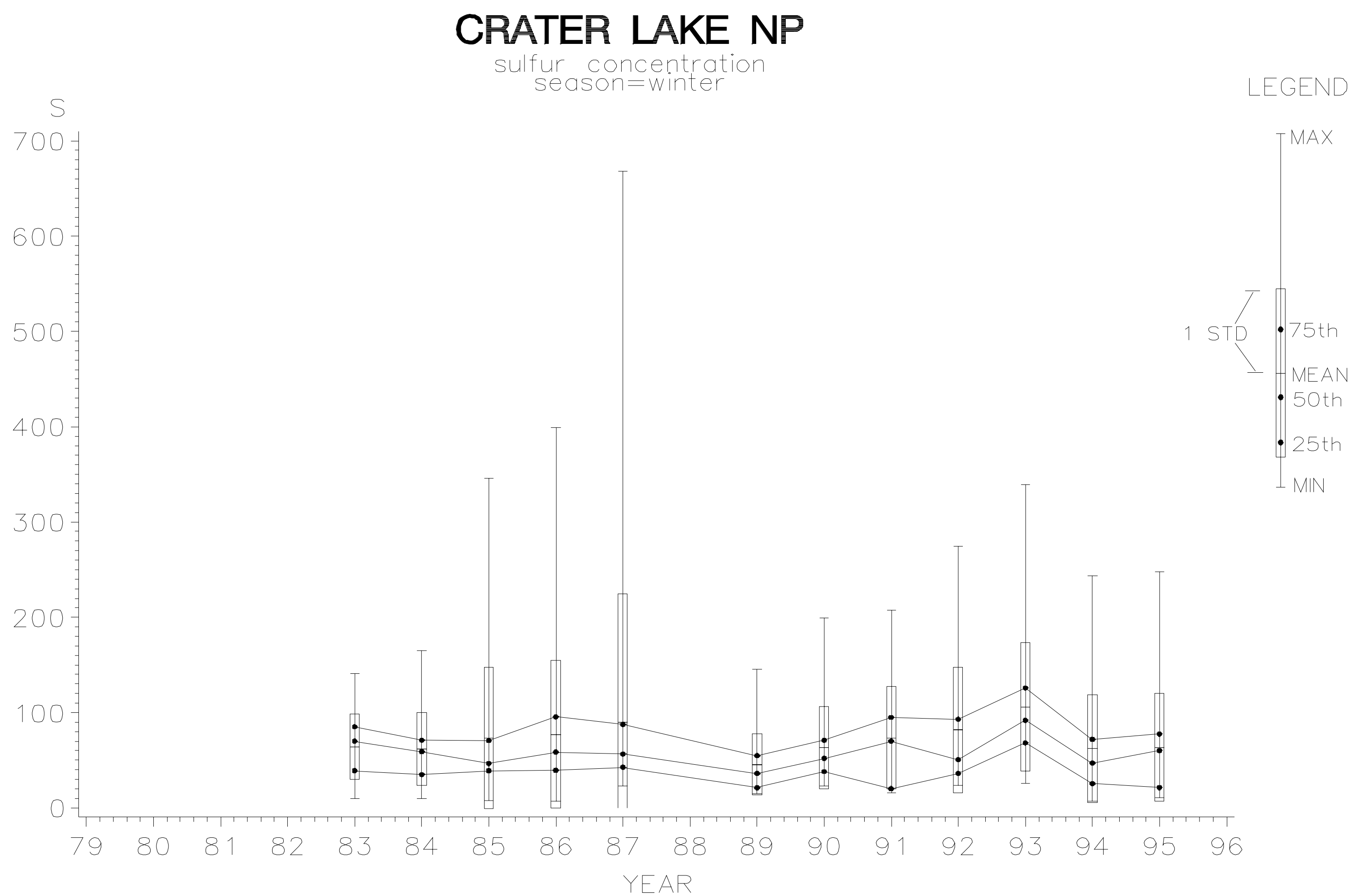

Figure 6.7b Monthly statistics for sulfur concentration (ng/m^3) at Crater Lake National Park in the winter.

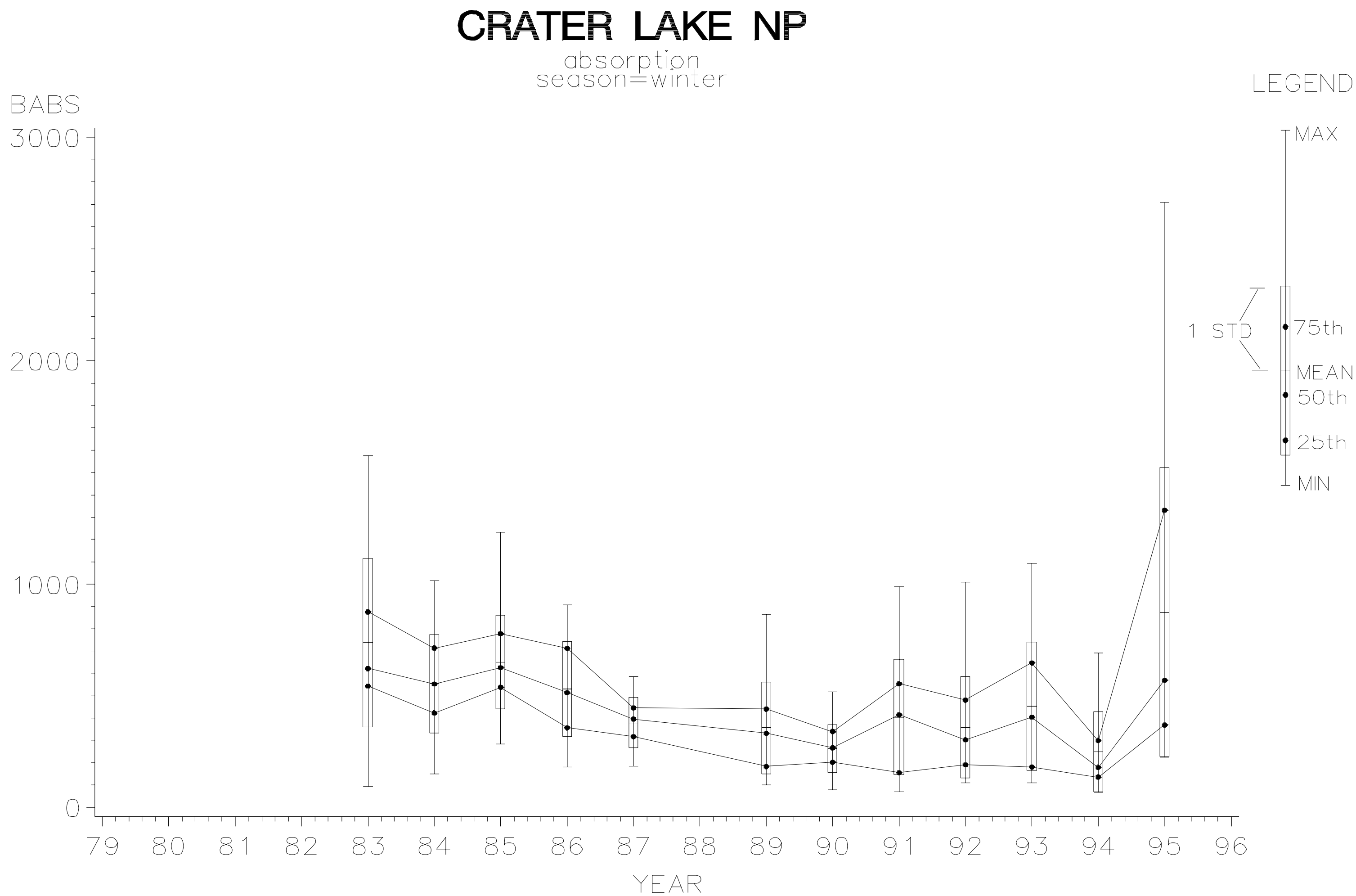

Figure 6.7c Monthly statistics for absorption (ng/m^3) at Crater Lake National Park in the winter.

6.4.5 Great Smoky Mountains National Park

Great Smoky Mountains in the autumn (Figure 6.8a) displays constant levels of fine mass concentrations for the 50th percentile at about 9000 ng/m^3. The 75th percentile obtains its maximum in 1990 at about 21000 ng/m^3 then drops steadily to 13000 ng/m^3 by 1995. There is a large decline in medium concentration coincident with the SFU to IMPROVE change in 1987-1988. However, because this type of change is not seen at other sites or at this site in other seasons, it is believed to be coincidental.

The median sulfur concentration (Figure 6.8b) is high in 1986 at about 1500 ng/m^3 then drops to a low of about 800 ng/m^3 in 1988. After 1988, with the exception of a sharp decrease in 1992, the median sulfur concentration increases to its maximum of about 1700 ng/m^3 in 1993 then pulls back to about 1100 ng/m^3 by 1994.

Absorption (Figure 6.8c) demonstrates an increasing trend. The median value, with slight variability, increased from about 900 ng/m^3 in the autumn of 1985 to greater than 1500 ng/m^3 in 1994. The 75th percentile shows a similar rise from about 1200 ng/m^3 in 1985 to almost 2000 ng/m^3 in 1991 and 1993. A similar trend is displayed by the 25th percentile, rising from about 600 ng/m^3 to almost 1000 ng/m^3. In 1994, the 75th and 50th percentiles decrease sharply from the high in 1993 to about 1600 ng/m^3 and 1200 ng/m^3, respectively, but only a slight decrease is seen for the 25th percentile.

6.4.6 Mesa Verde National Park

Fine mass concentrations during the summer at Mesa Verde (Figure 6.9a) demonstrates an interesting trend. The 25th percentile, beginning in 1986, increased dramatically from around 2200 ng/m^3 to 5000 ng/m^3 in 1990, then dropped off sharply to 3000 ng/m^3 by 1992. The same trend is closely mirrored by the 50th percentile and to a lesser extent by the 75th percentile, which rose from about 4000 ng/m^3 in 1985 to almost 8500 ng/m^3 in 1990 and then drops back to 4000 ng/m^3 in 1992. Since 1992 all percentiles have increased significantly; the 75th from 4000 ng/m^3 to 5000 ng/m^3; the 50th from about 3300 ng/m^3 to almost 4000 ng/m^3; and the 25th rose from about 3000 ng/m^3 to almost 3400 ng/m^3.

Median concentrations of sulfur at Mesa Verde (Figure 6.9b) are highest during the first two measurement summers of 1983 and 1984 at about 400 ng/m^3, then decrease to their minimum in 1987 at less than 200 ng/m^3. This same pattern is shown by the 25th percentiles and 75th percentiles, with the 25th percentile decreasing from 340 ng/m^3 to about 120 ng/m^3. After 1987 the 25th percentile increased every year except two, obtaining a level of about 280 ng/m^3 in 1994. The 50th percentile and 75th percentile rise to about 320 ng/m^3 and 440 ng/m^3 by 1990, respectively. After 1990 the 50th percentile essentially hovers about 320 ng/m^3 and the 75th percentile drops by to around 380 ng/m^3.

Absorption (Figure 6.9c) shows a similar trend as sulfur with its maximum median of about 650 ng/m^3 in 1983 and minimum median of 400 ng/m^3 in 1987. Median absorption then increases with sulfur to another high in 1990 of about 550 ng/m^3 then generally decreases to 450 ng/m^3. The 25th percentile decreased from 480 ng/m^3 in 1983 to 280 ng/m^3 in 1986 increased to

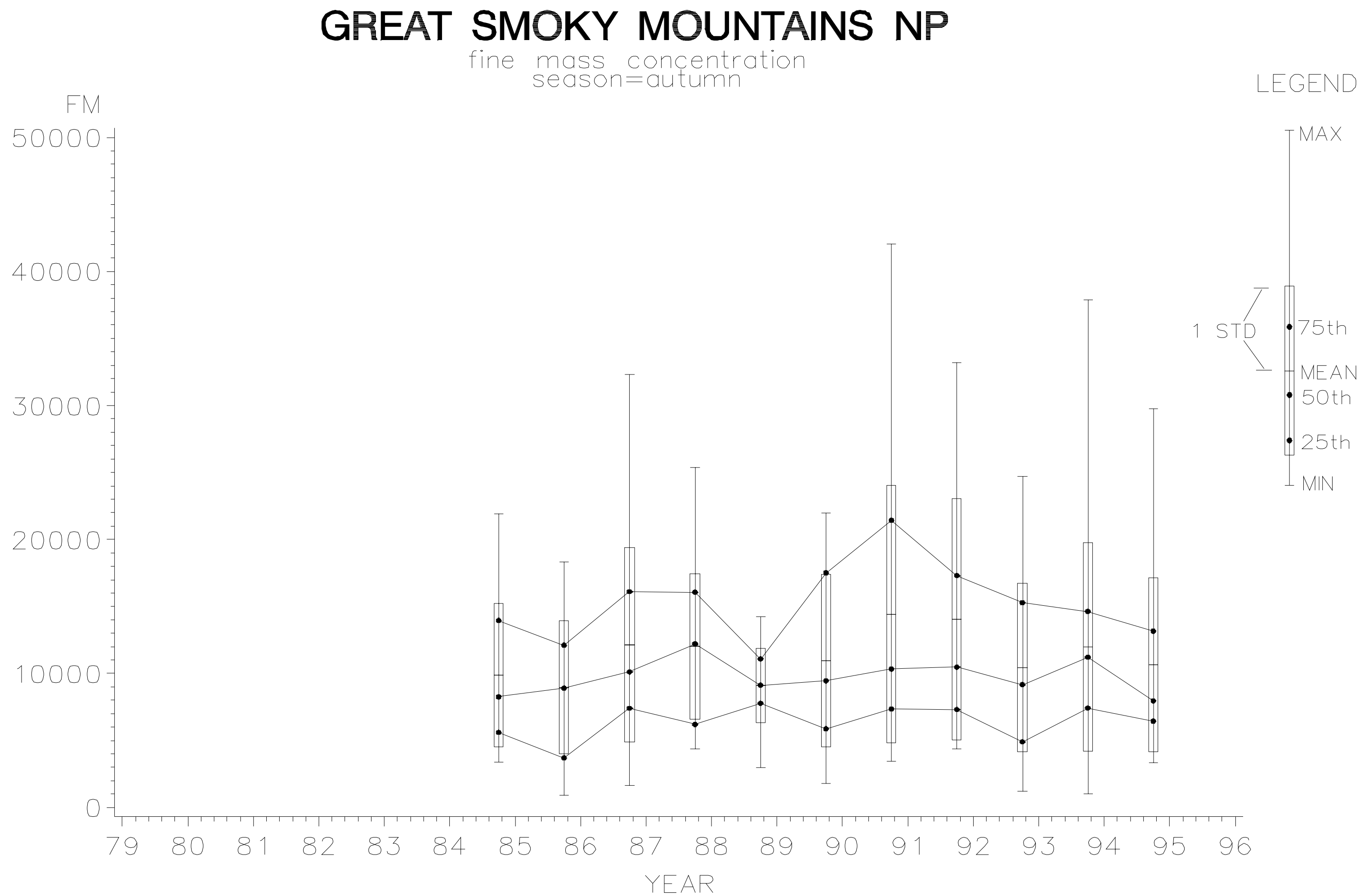

Figure 6.8a Monthly statistics for fine mass concentration (ng/m^3) at Great Smoky Mountains National Park in the autumn.

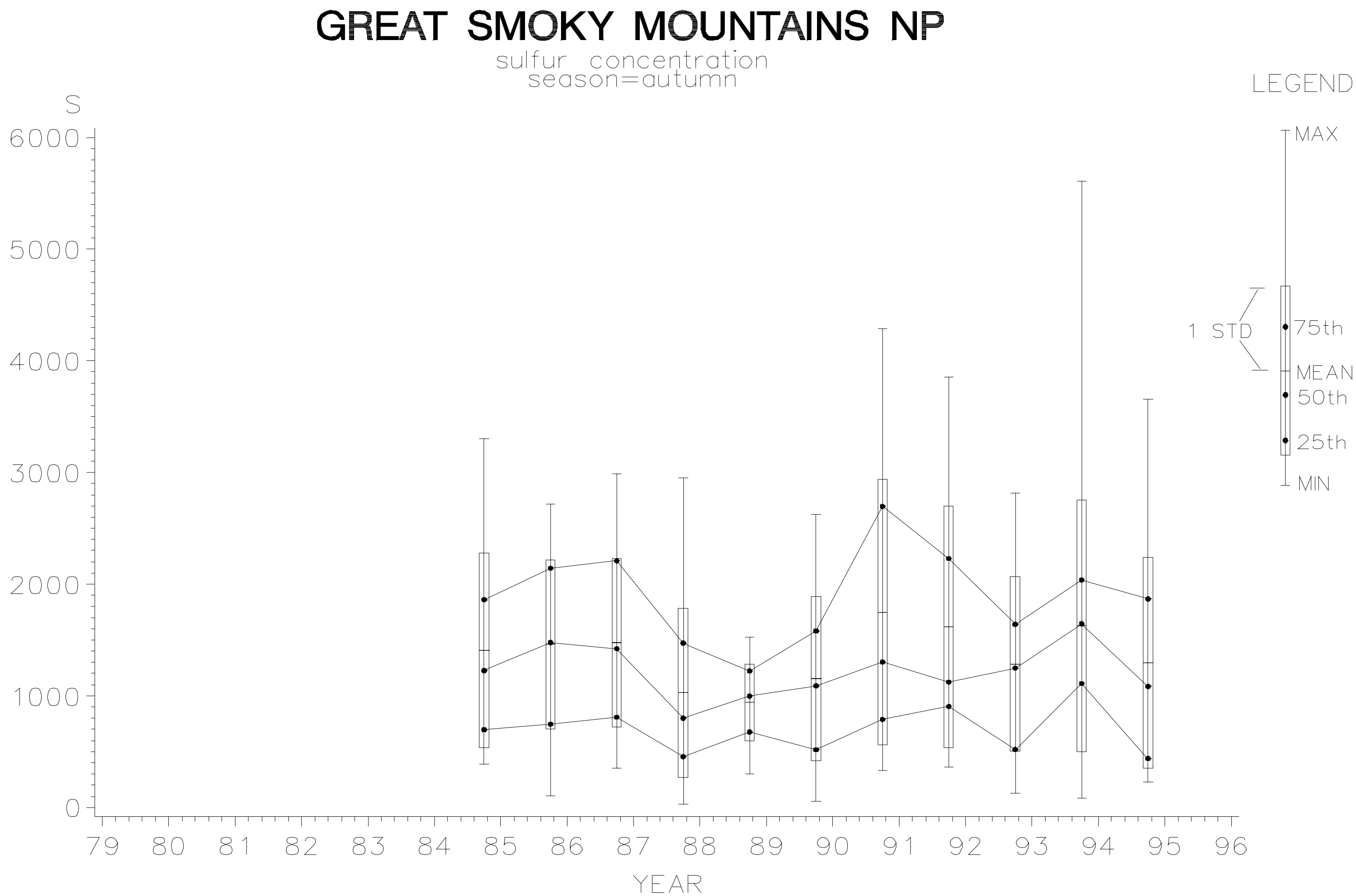

Figure 6.8b Monthly statistics for sulfur concentration (ng/m^3) at Great Smoky Mountains National Park in the autumn.

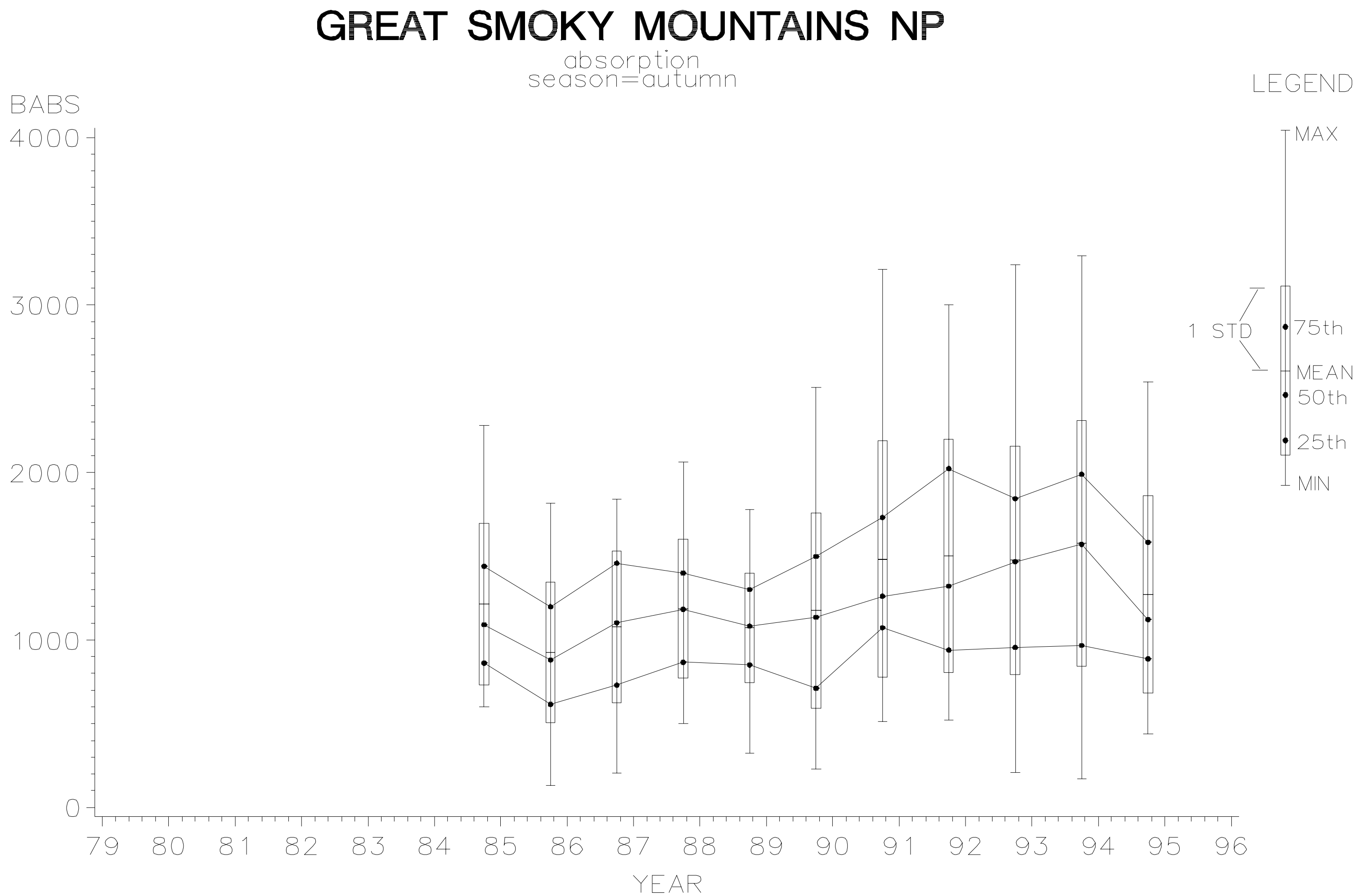

Figure 6.8c Monthly statistics for absorption (ng/m^3) at Great Smoky Mountains National Park in the autumn.

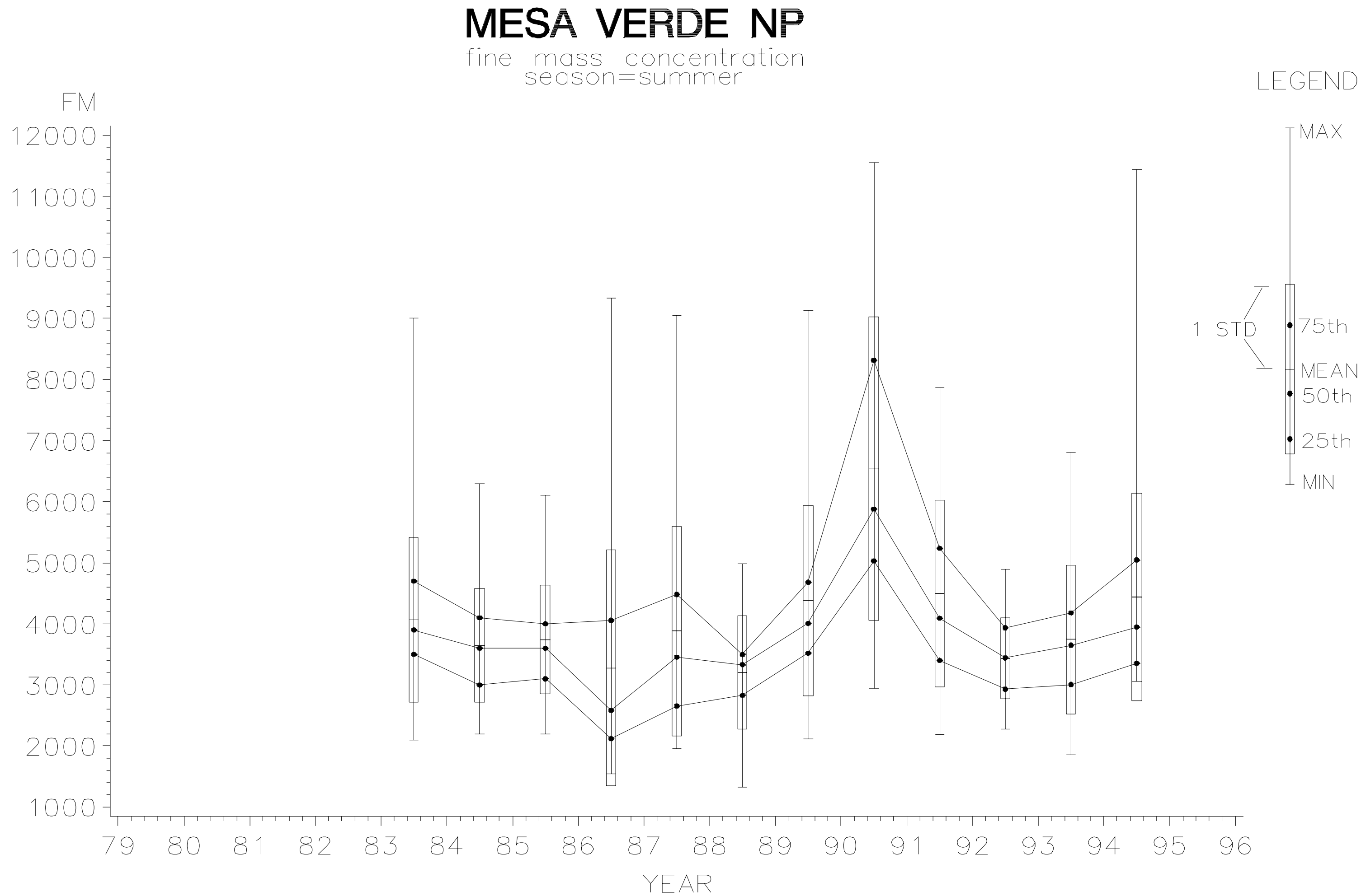

Figure 6.9a Monthly statistics for fine mass concentration (ng/m^3) at Mesa Verde National Park in the summer.

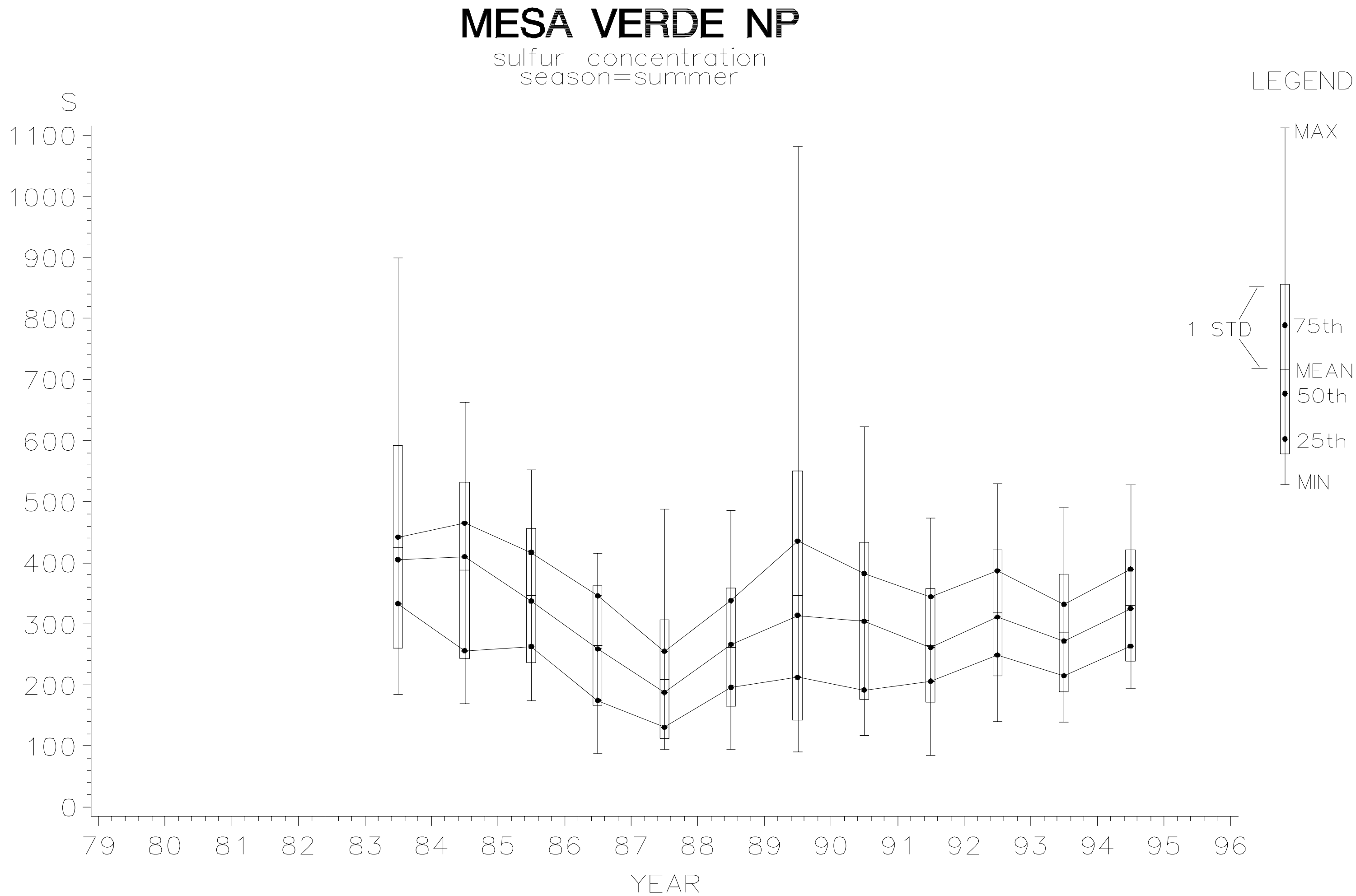

Figure 6.9b Monthly statistics for sulfur concentration (ng/m^3) at Mesa Verde National Park in the summer.

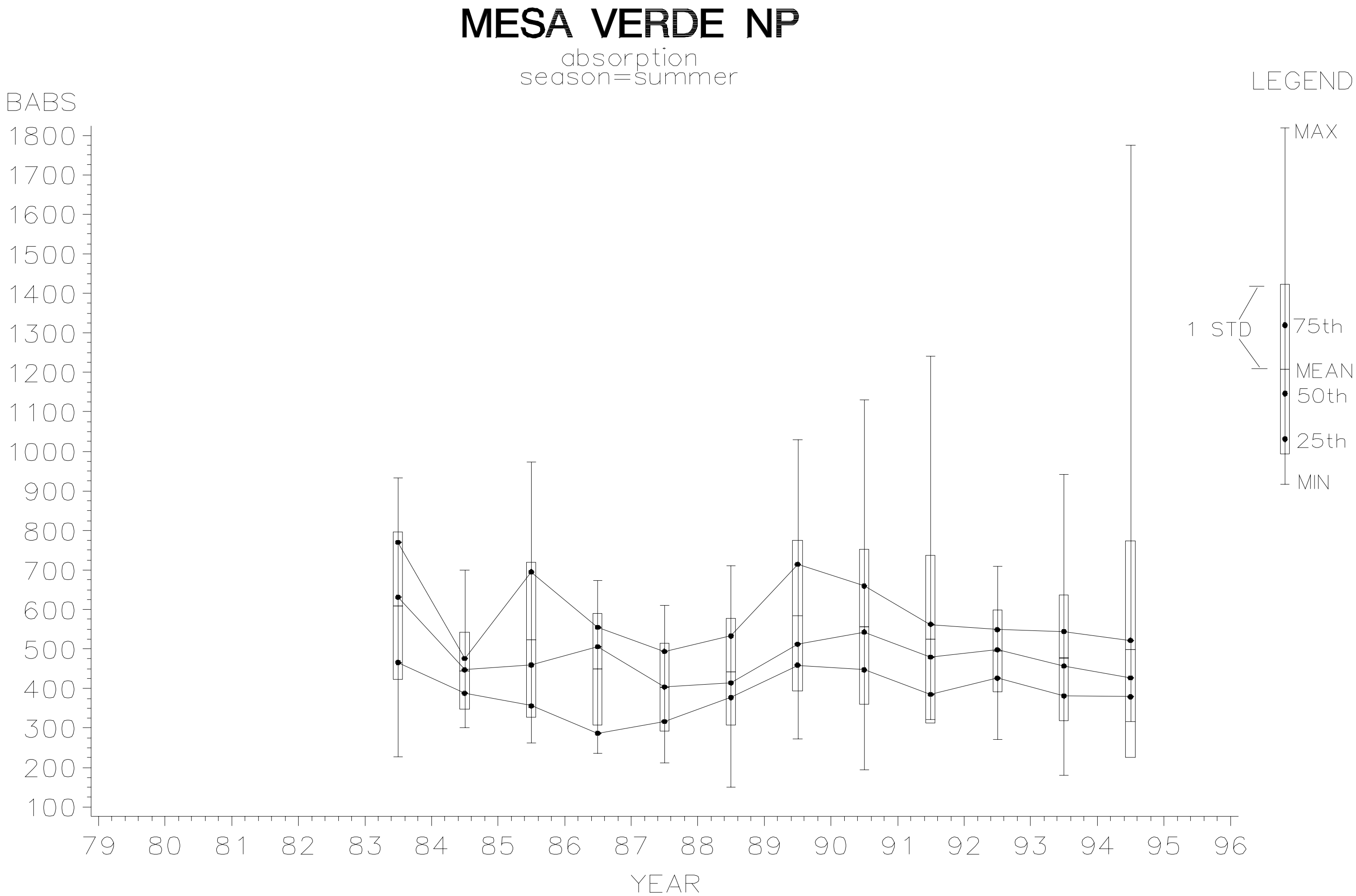

Figure 6.9c Monthly statistics for absorption (ng/m^3) at Mesa Verde National Park in the summer.

almost 460 ng/m^3 by 1989. The 75th percentile has a similar pattern with a high value of about 800 ng/m^3, then decreasing to 480 ng/m^3 in 1987 before rising again to almost 700 ng/m^3 in 1990. After 1990 the 75th percentile drops steadily to about 460 ng/m^3, the 50th and 25th percentile are trending down as well but not as dramatically.

6.4.7 Chiricahua National Monument

Fine mass concentrations at Chiricahua (Figure 6.10a) during the summer show little change. The only notable feature is the spike in 1990 for the 75th percentile at over 11000 ng/m^3, which then drops sharply to little more than 5000 ng/m^3 by 1992, followed by an increase to about 7500 ng/m^3 in 1994. The 25th and 50th percentiles do not demonstrate any trends. The 75th percentile varies between its high of almost 7000 ng/m^3 in the summer of 1981 and its low of about 4500 ng/m^3, while the 25th percentile varies between 5500 ng/m^3 in 1981 and 3000 ng/m^3 in 1987.

A particular point of interest is to what extent are changes in emissions reflected by changes in sulfur concentrations. Large fluctuations in smelter emissions have occurred in the desert southwest during the 1980s, providing an opportunity to study the relationship between emissions and aerosol sulfur concentrations. In the intermountain region between the continental divide and the Sierra Nevada, 90% of United States emissions were from 15 power plants and 12 smelters. Seven of the smelters were located in southern Arizona. Since the late 1980s, four of the seven Arizona smelters were shut down and the rest were controlled [Sisler and Malm, 1989; Oppenheimer, 1987; Epstein and Oppenheimer, 1986]. The reduction in smelter emissions is evident from the change in sulfur distributions at Chiricahua during the summer as shown in Figure 6.10b. Beginning in 1987 the variance drops considerably. There is no appreciable change in the minima and 25th percentile values, so the reduction in variance is attributed to reduced medians, means, 75th percentiles, and maxima. From 1988 through 1990 median concentrations increase from 350 ng/m^3 to about 650 ng/m^3 then drop to 400 ng/m^3 in 1991. Since 1991 there has been a steady increase to about 650 ng/m^3 by the median.

Absorption shows no consistent trend (Figure 6.10c). The median, from its high in 1983 of about 700 ng/m^3, decreases for the next three out of four years to its low in 1987 of 400 ng/m^3, then rises again to a high value of 700 ng/m^3 in 1989. Since 1989, there appears to have been a slight decline in median absorption.

6.4.8 Grand Canyon National Park - Winter

Figure 6.11a shows the winter distributions at Hopi Point in Grand Canyon for fine mass concentrations. Winter distributions are notable for the very high maxima in 1980 and 1987 at almost 25000 ng/m^3 and 18000 ng/m^3, respectively. There has been a significant increase in the 25th percentile, which starts out less than 1000 ng/m^3 then rising to almost 2000 ng/m^3 by 1989. After falling back slightly to 1500 ng/m^3, the 25th percentile essentially stays flat until 1994 when it drops back to about 1000 ng/m^3. The same behavior, although somewhat more variable, is displayed by the 50th percentile and 75th percentile, a maximum of about 4000 ng/m^3 and 2500 ng/m^3 are obtained in 1989, respectively. After 1989 the 75th and 50th percentiles drop to about 2000 ng/m^3 and 1500 ng/m^3, respectively.

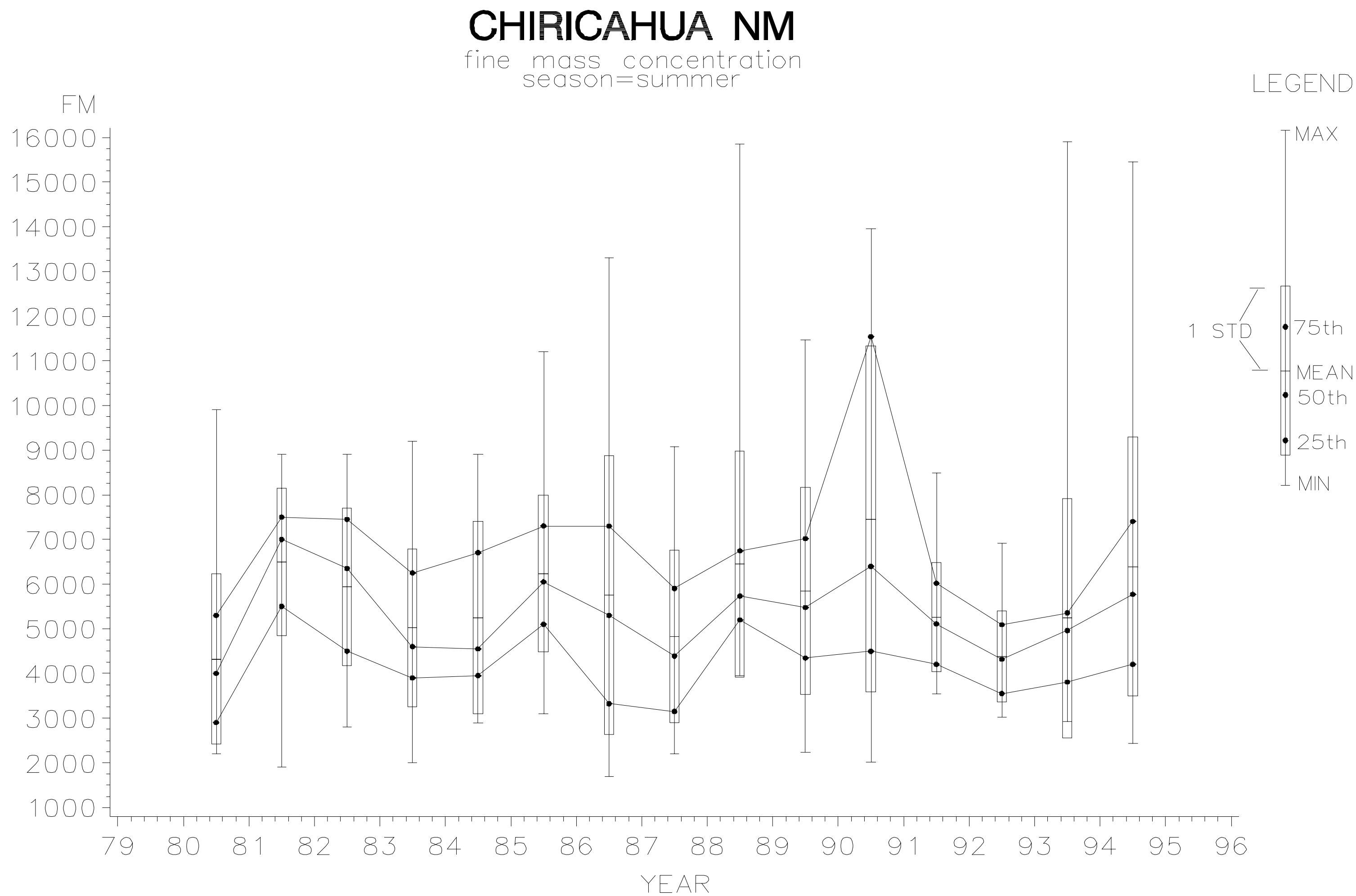

Figure 6.10a Monthly statistics for fine mass concentration (ng/m^3) at Chiricahua National Monument in the summer.

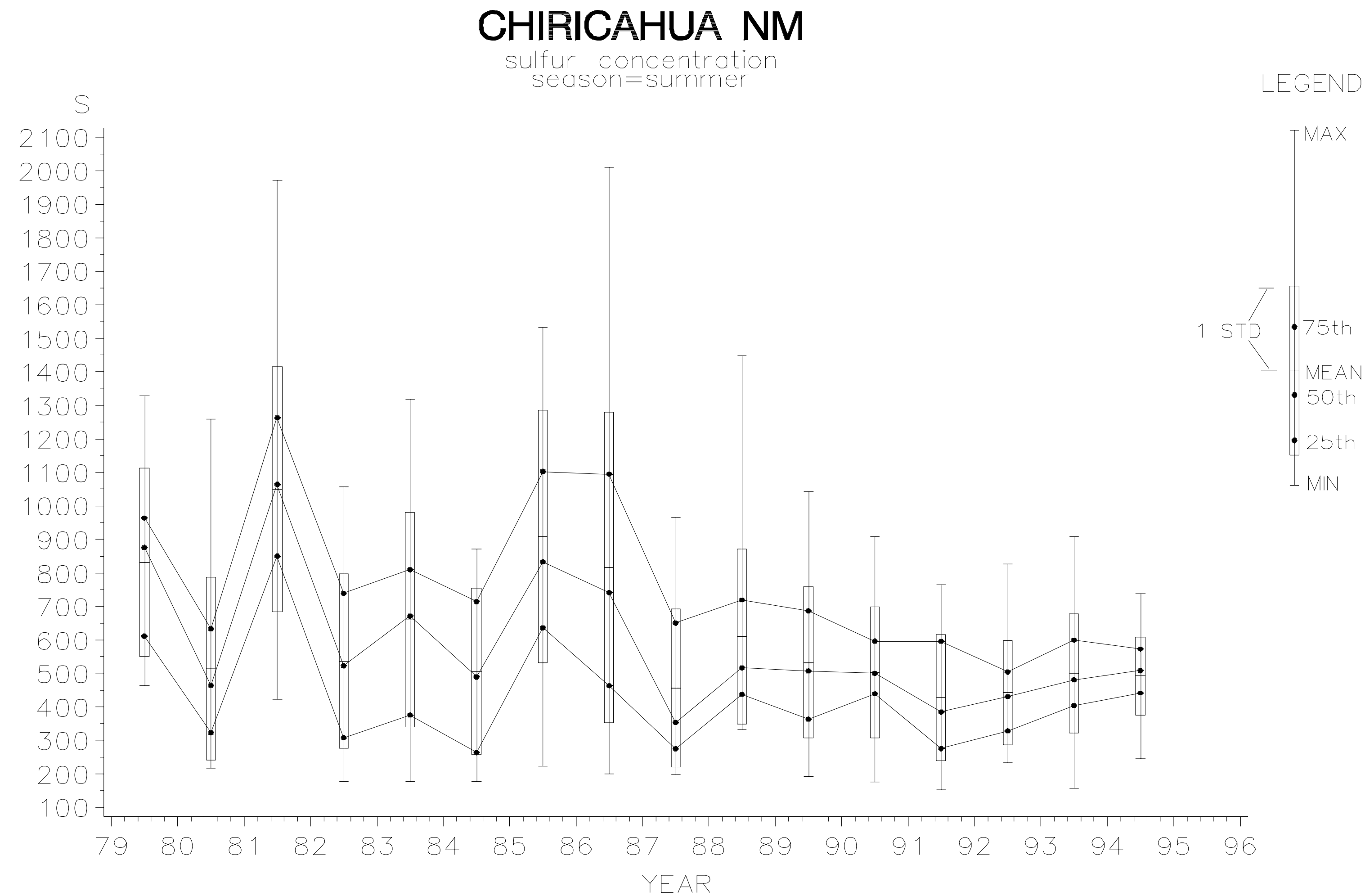

Figure 6.10b Monthly statistics for sulfur concentration (ng/m^3) at Chiricahua National Monument in the summer.

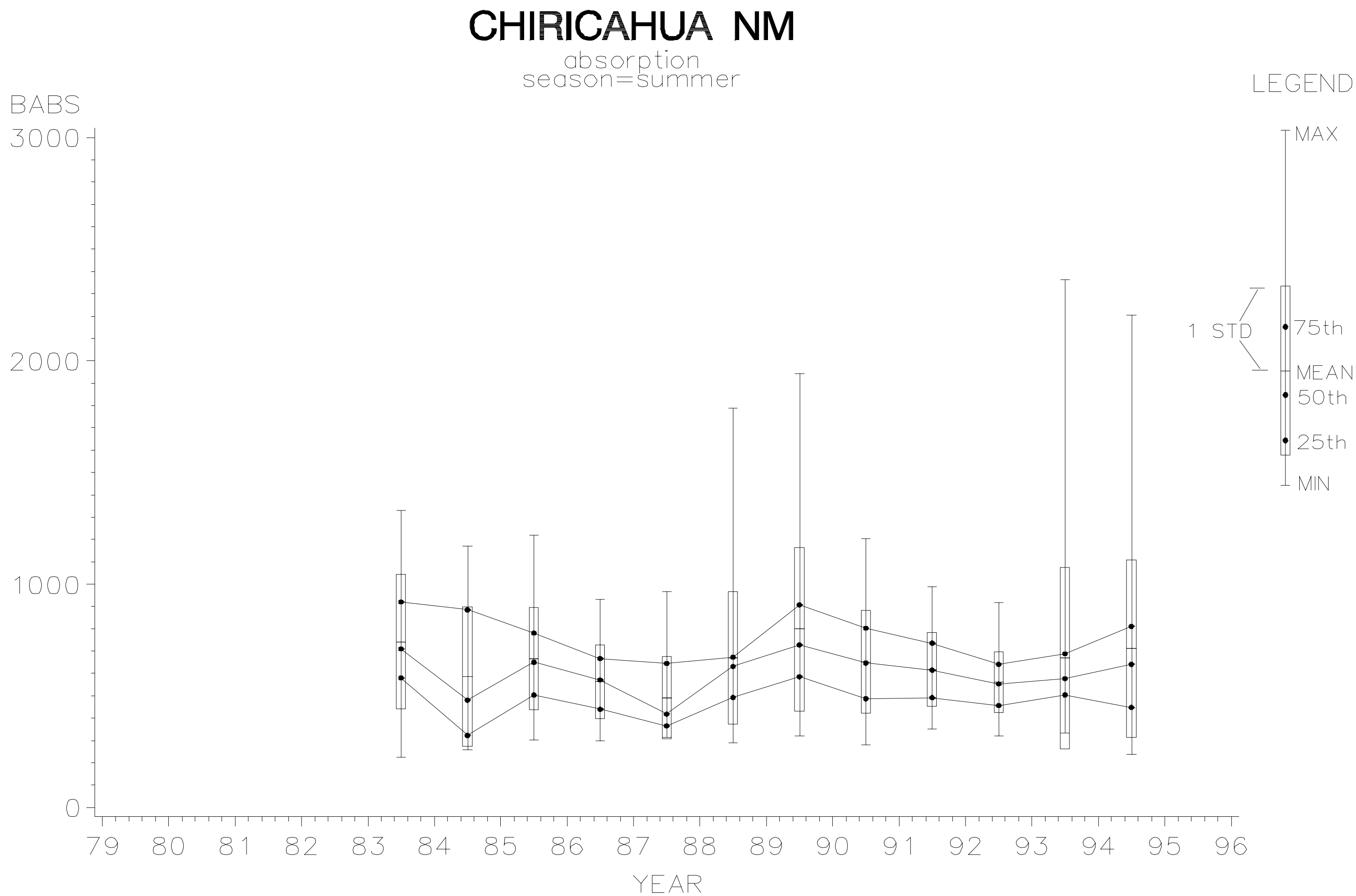

Figure 6.10c Monthly statistics for absorption (ng/m^3) at Chiricahua National Monument in the summer.

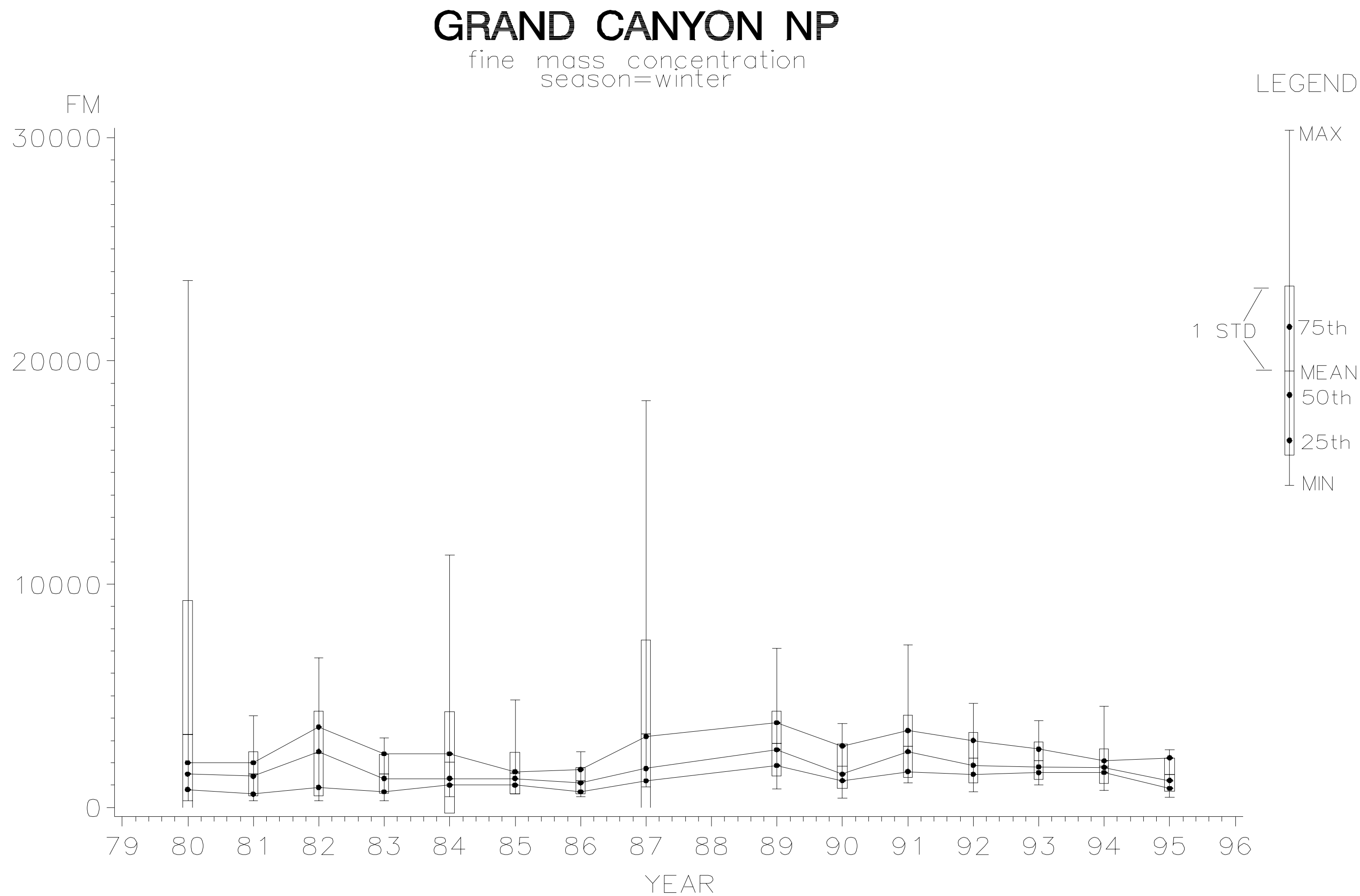

Figure 6.11a Monthly statistics for fine mass concentration (ng/m^3) at Grand Canyon National Park in the winter.

Sulfur concentrations show two distinct trends for the 25th percentile (Figure 6.11b). For the first four years the 25th percentile concentration is essentially flat at about 50 ng/m^3 then rises to over 120 ng/m^3 for 1991, 1992 and 1993. By 1995 it has dropped back to about 50 ng/m^3. This same pattern is displayed with more variance by the 50th percentile rising from its lowest value of about 60 ng/m^3 in 1982 to almost 200 ng/m^3 by 1992, then dropping off to 100 ng/m^3 by 1995. No trend is apparent for the 75th percentile.

Absorption (Figure 6.11c) shows a similar trend as sulfate. Levels start out low in 1983 and 1984 with concentrations about 100 ng/m^3, 200 ng/m^3, and 300 ng/m^3 for the 25th, 50th and 75th percentiles, respectively. By 1989 the 25th and 75th percentiles reach their maxima of 250 ng/m^3 and 550 ng/m^3, respectively, the 50th percentile obtains its maximum of about 400 ng/m^3 in 1991. After 1991 concentration levels drop significantly and steadily until 1995 to about 75 ng/m^3, 125 ng/m^3, and 200 ng/m^3 for the 25th, 50th and 75th percentile, respectively.

6.4.9 Grand Canyon National Park - Summer

Fine mass concentrations have significantly increased during the summers since 1980 (Figure 6.12a). It is particularly obvious by the rise in the 25th percentile almost doubling from about 1500 ng/m^3 in 1981 to almost 3000 ng/m^3 in 1994. A similar trend is seen for the 50th percentile, which has increased from about 2500 ng/m^3 in 1981 to about 4500 ng/m^3 in 1994. The 75th percentile, after some initial variance, has increased from 4000 ng/m^3 in 1984 to about 6000 ng/m^3 in 1994. This trend is also played out by the minima. In 1980 and 1981 the minima were about 500 ng/m^3, however during the last three years (1993-1995) the minima concentrations are about 3000 ng/m^3.

Figure 6.12b shows the summer distributions of sulfur at Hopi Point. Beginning in 1980, sulfur has median values that trend up from about 210 ng/m^3 to about 400 ng/m^3 in 1985, then fall to 200 ng/m^3 in 1987. From 1988 through 1993 the median for sulfur is quite stable and ranges between 250 ng/m^3 to about 325 ng/m^3. In 1994, the median increases to about 375 ng/m^3. The 25th percentile shows two clear trends; from a low of about 100 ng/m^3 in 1980 it increased to around 350 ng/m^3 in 1985, then drops sharply to 150 ng/m^3 in 1987. After 1987 the concentrations of the 25th percentile increase five years out of seven to more than 300 ng/m^3. A slight trend towards decreasing variability is evidenced by a decrease in standard deviations attributed to a decrease of maxima and an increase of minima.

The median value of absorption (Figure 6.12c) is lowest in 1984 at about 300 ng/m^3 then doubles to 600 ng/m^3 in 1985. From 1985 through 1994 the median remains relatively stable, ranging from a high of 700 ng/m^3 in 1989 to a low of 500 ng/m^3 in 1990, then dropping in 1995 to about 400 ng/m^3. The 25th and 75th percentiles essentially track the median rising and falling almost in lockstep. The 25th and 75th percentiles reach their maxima in 1989 of about 600 ng/m^3 and 900 ng/m^3, respectively then fall off by 1995 to about 500 ng/m^3 and 300 ng/m^3.

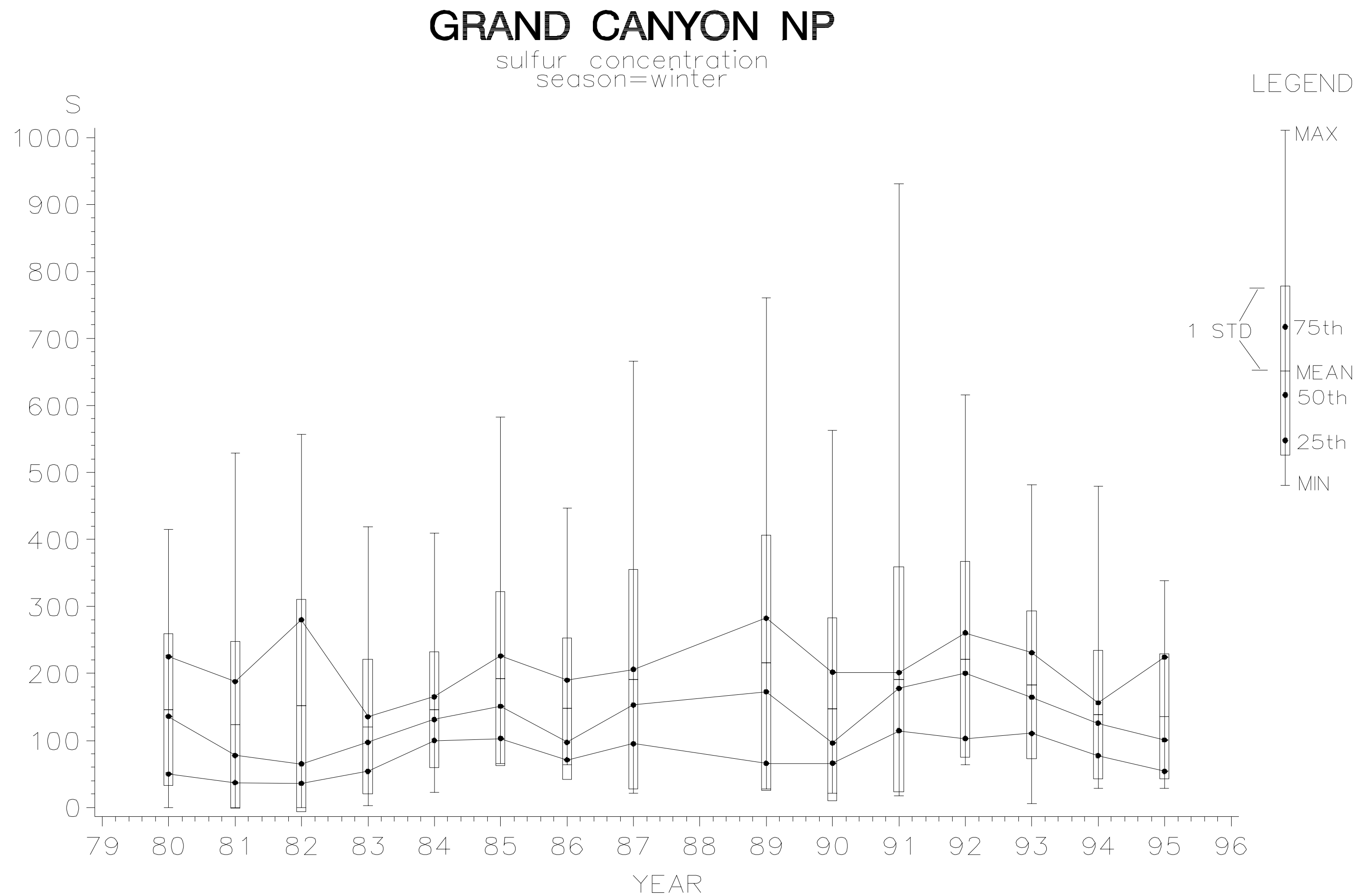

Figure 6.11b Monthly statistics for sulfur concentration (ng/m^3) at Grand Canyon National Park in the winter.

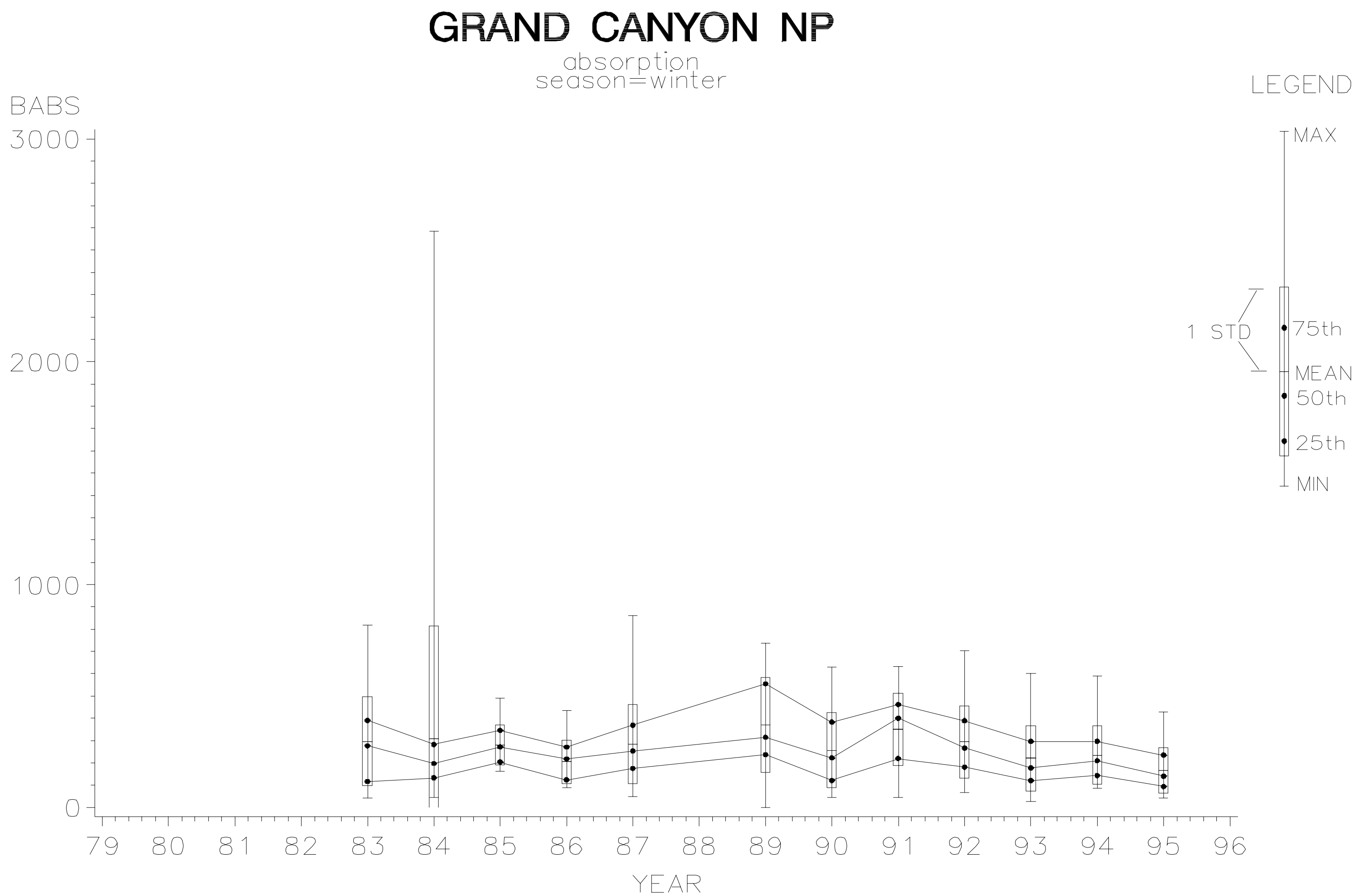

Figure 6.11c Monthly statistics for absorption (ng/m^3) at Grand Canyon National Park in the winter.

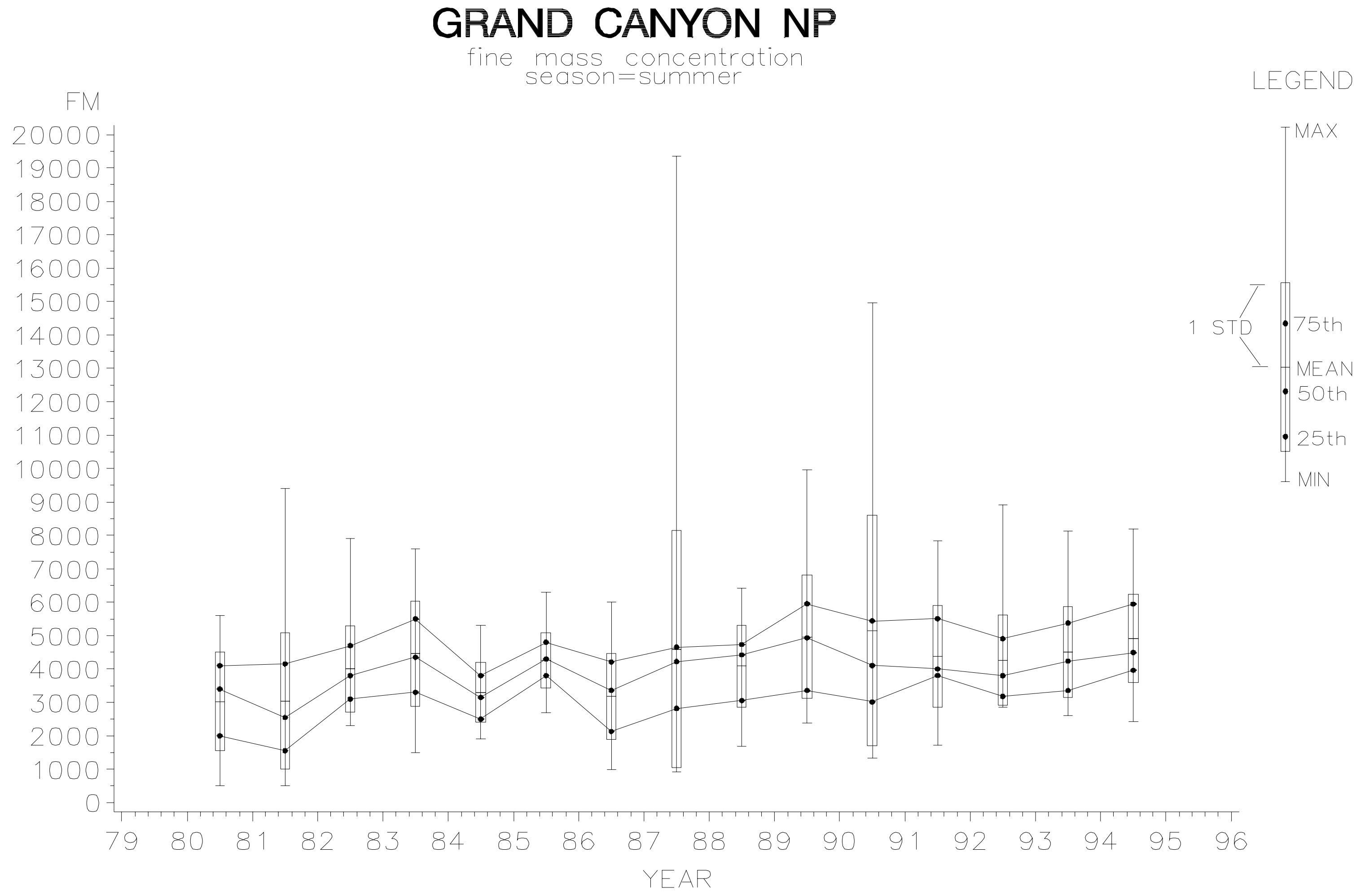

Figure 6.12a Monthly statistics for fine mass concentration (ng/m^3) at Grand Canyon National Park in the summer.

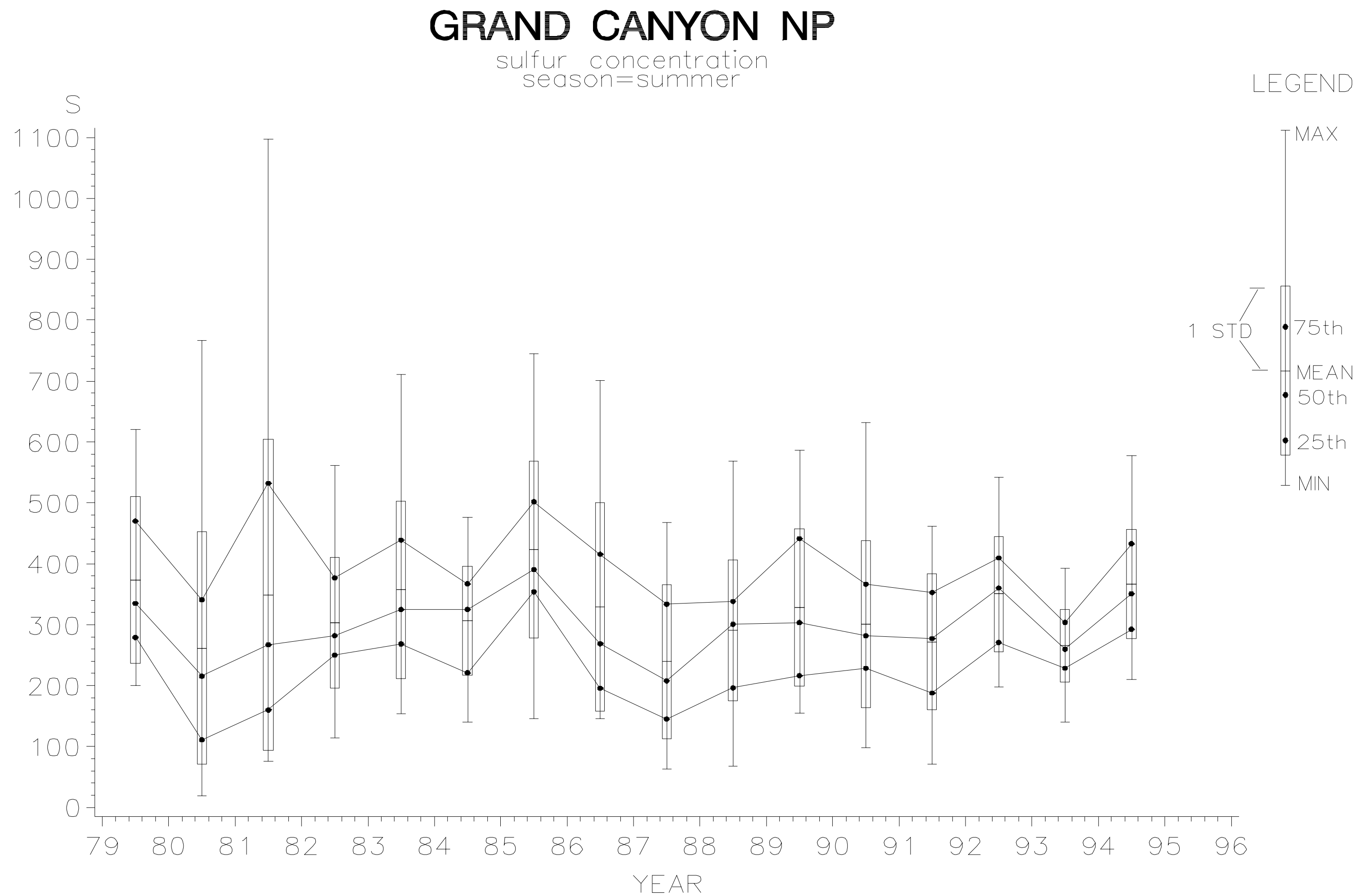

Figure 6.12b Monthly statistics for sulfur concentration (ng/m^3) at Grand Canyon National Park in the summer.

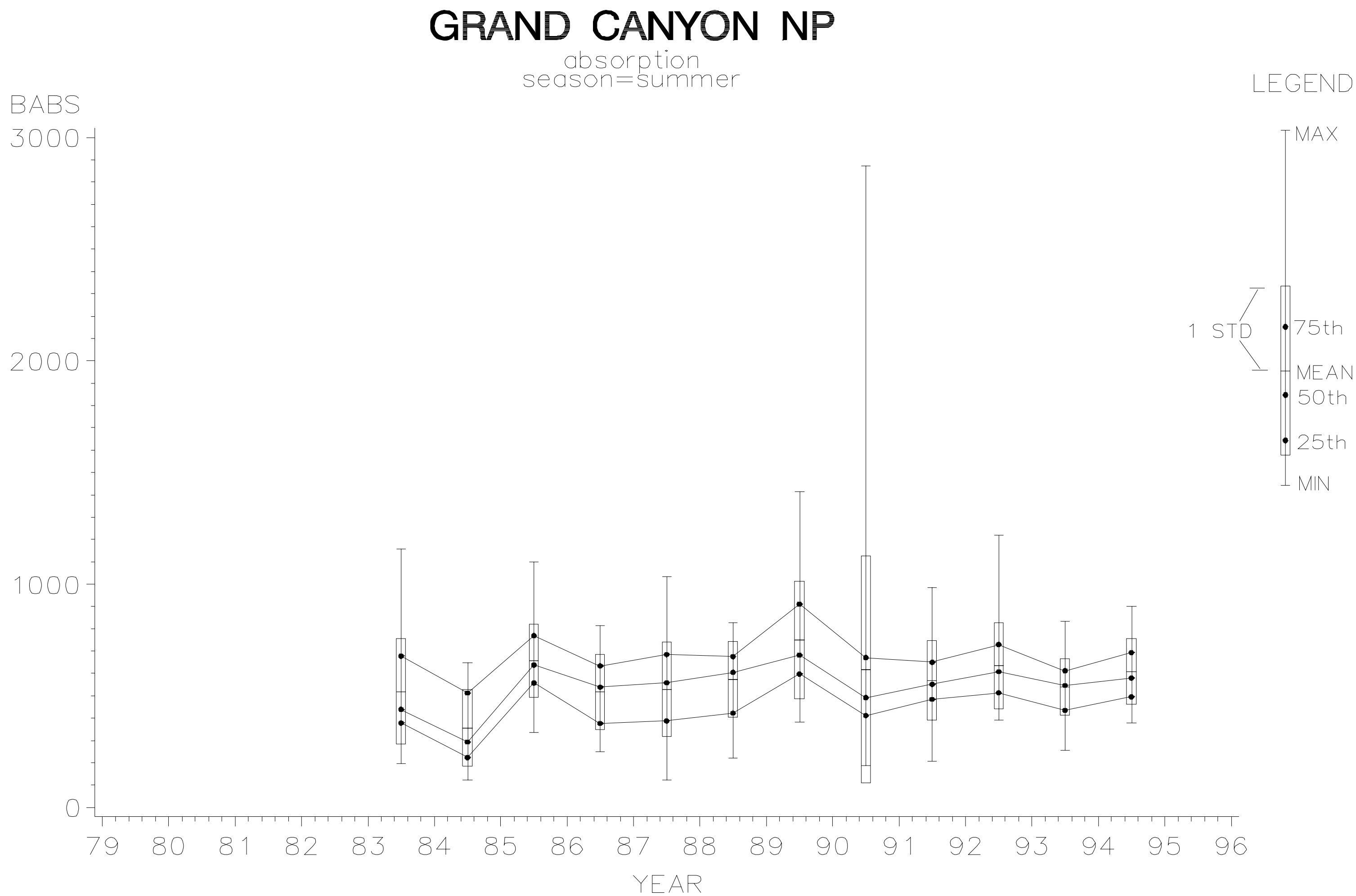

Figure 6.12c Monthly statistics for absorption (ng/m^3) at Grand Canyon National Park in the summer.

6.4.10 Grand Canyon National Park - Autumn

Fine mass concentrations (Figure 6.13a) have been trending upwards in the autumn at Hopi Point since obtaining their minimum in 1980. This is particularly evidenced by the 25th percentile and minima. In 1980, the minimum concentration was 200 ng/m^3, by 1993 it had increased to its maximum in excess of 1600 ng/m^3 before falling back to about 1000 ng/m^3 in 1994. The 25th percentile in 1980 was about 700 ng/m^3 and increased to almost 3000 ng/m^3 in 1992, then falls back to about 2000 ng/m^3 in 1994. Similar behavior by the 50th percentile is present with its minimum of 1200 ng/m^3 occurring in 1980; however, the 50th percentile obtains its maximum of about 4200 ng/m^3 in 1987 then remains relatively steady.

As with fine mass, sulfur has increased since 1980 when the 25th percentile obtained its minimum of about 60 ng/m^3 as shown by Figure 6.13b. By 1983 sulfur concentrations for the 25th percentile increase sharply to about 240 ng/m^3 then fall off to about 125 ng/m^3 in 1985. By 1990 the 25th percentile increases to almost 200 ng/m^3 and remains at this level with some variability through 1994. There is a trend towards decreased variability as evidenced by the standard deviation and is attributed to decreased maxima and increased minima.

Absorption displays little or no long-term trend (Figure 6.13c). Beginning in 1983 all three percentiles drop sharply by 1984; the 75th percentile moves from over 600 ng/m^3 to about 350 ng/m^3; the 50th percentile decreases from about 550 ng/m^3 to less than 250; and the 25th percentile drops from about 300 ng/m^3 to 200 ng/m^3. After 1984 all percentiles show steady increases by 1987 to their 1983 levels. From 1987 until 1993 the three percentiles are essentially steady with some variability at about 650 ng/m^3, 550 ng/m^3, and 350 ng/m^3 for the 75th, 50th, and 25th percentiles, respectively.

6.5 Interrelationships of Fine Mass, Sulfur and Absorption

Matrix scatter plots provide a useful tool for understanding the correlation of daily fine mass, b_{abs}, and sulfur, as well as for distinguishing differences between sites and seasons. Some correlation between fine mass and its constituents is expected, particularly in the case of sulfur where ammonium sulfate aerosol comprises a large fraction of the mass at many sites. By the same argument a limited amount of correlation between b_{abs}, sulfur, nitrate, organic carbon, and fine soil by virtue of their association with fine mass would not be unexpected. Sulfur and b_{abs} demonstrate the greatest amount of correlation between the constituent species. The strength of the correlation is variable and relatively strong at certain sites. Strong correlations suggest several possibilities including common anthropogenic sources or transport pathways and internally mixed aerosol. On the other hand, lack of correlation is indicative of different sources and externally mixed aerosols.

In the determination of b_{abs} a correction for "shadowing" is made. This is because as the filter becomes loaded with particles, the observed proportion of absorption to fine mass decreases. This is believed to be the case because some of the particles shadow others from the light source. Thus, a correction must be applied. If it is correct, then any correlation of b_{abs} with fine mass would be due to physical reasons. On the other hand, an over correction for fine mass would artificially increase absorption and the correlation of b_{abs} with fine mass [Campbell *et al.*, 1995].

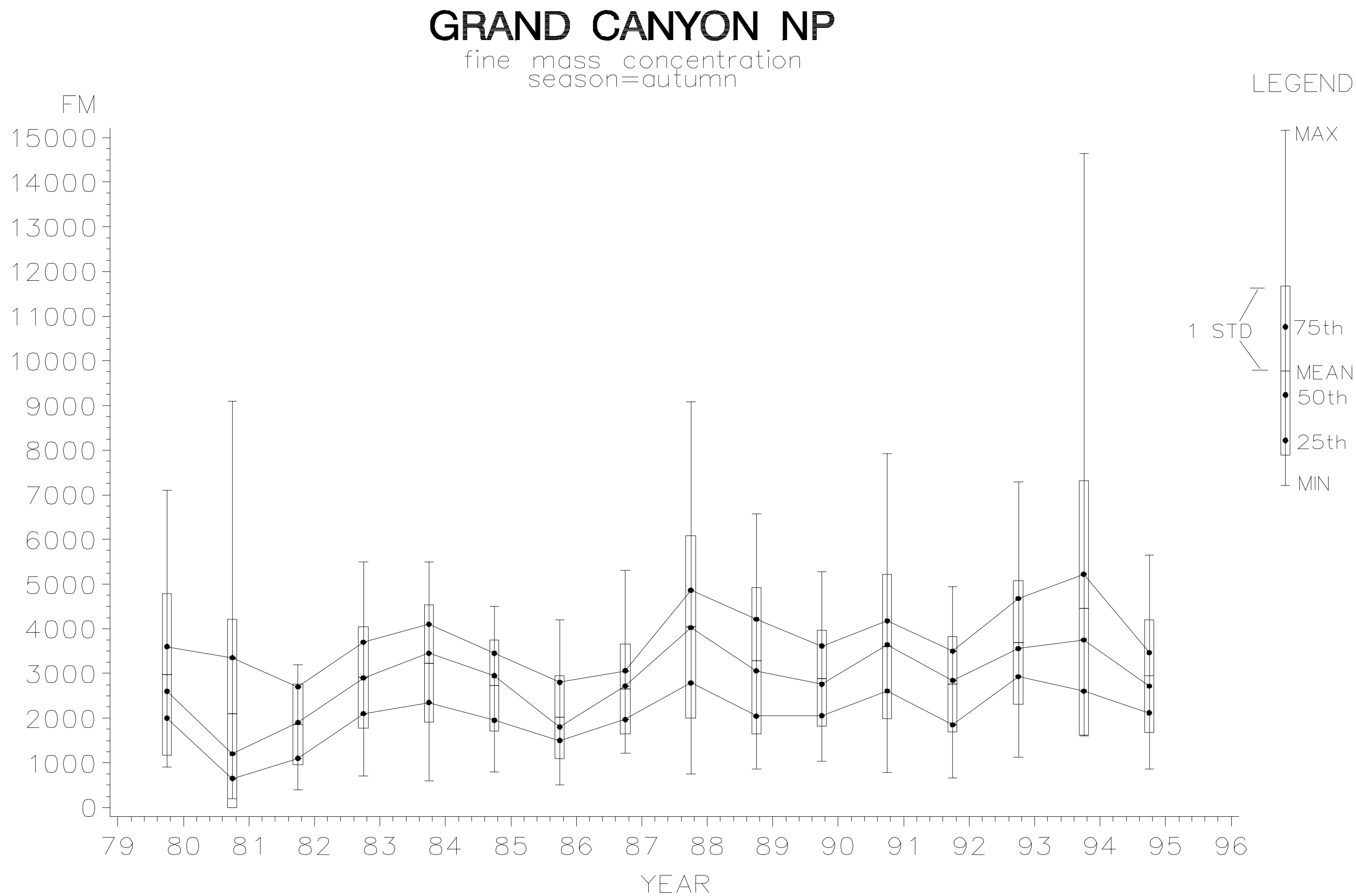

Figure 6.13a Monthly statistics for fine mass concentration (ng/m^3) at Grand Canyon National Park in the autumn.

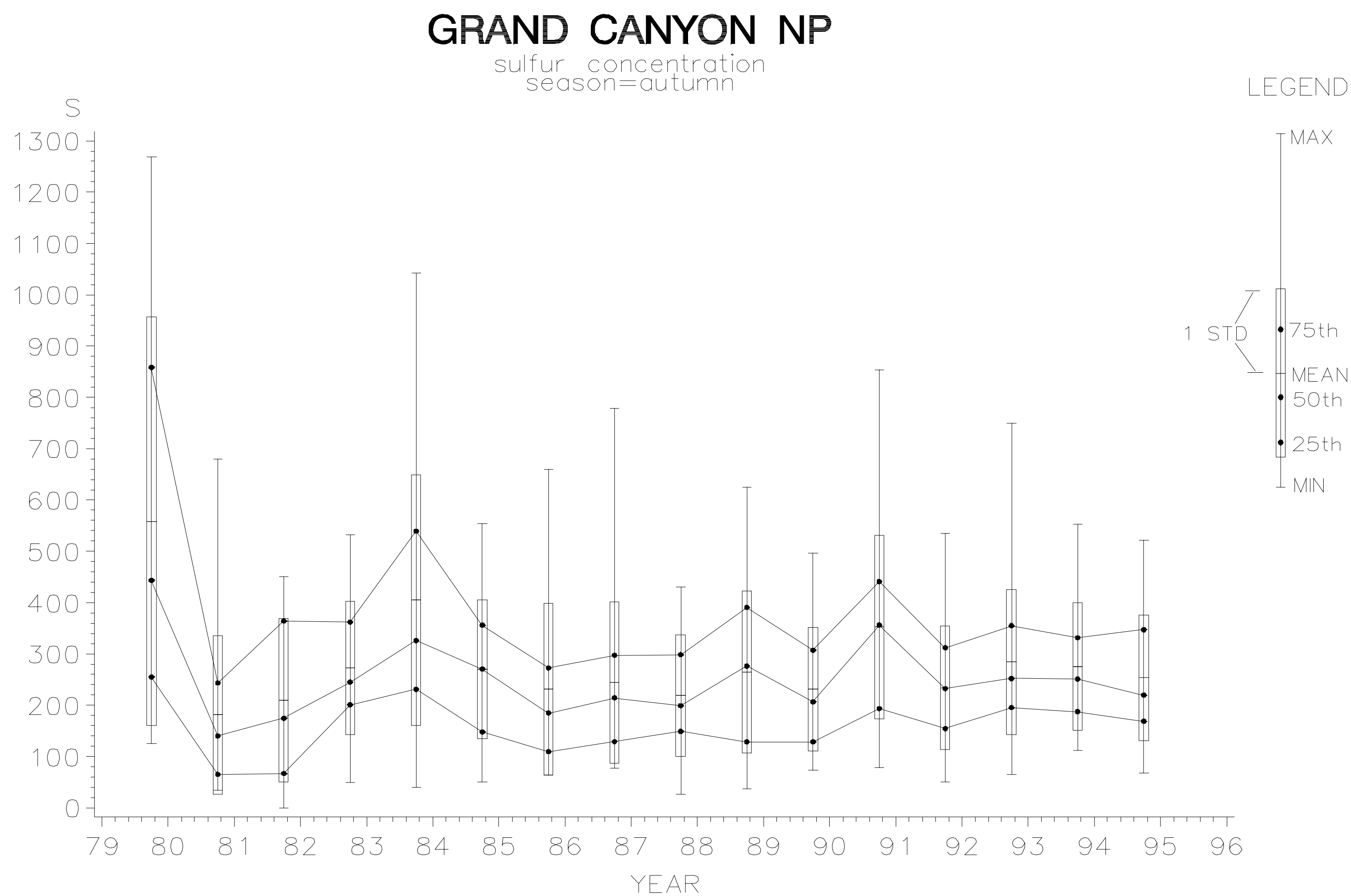

Figure 6.13b Monthly statistics for sulfur concentration (ng/m^3) at Grand Canyon National Park in the autumn.

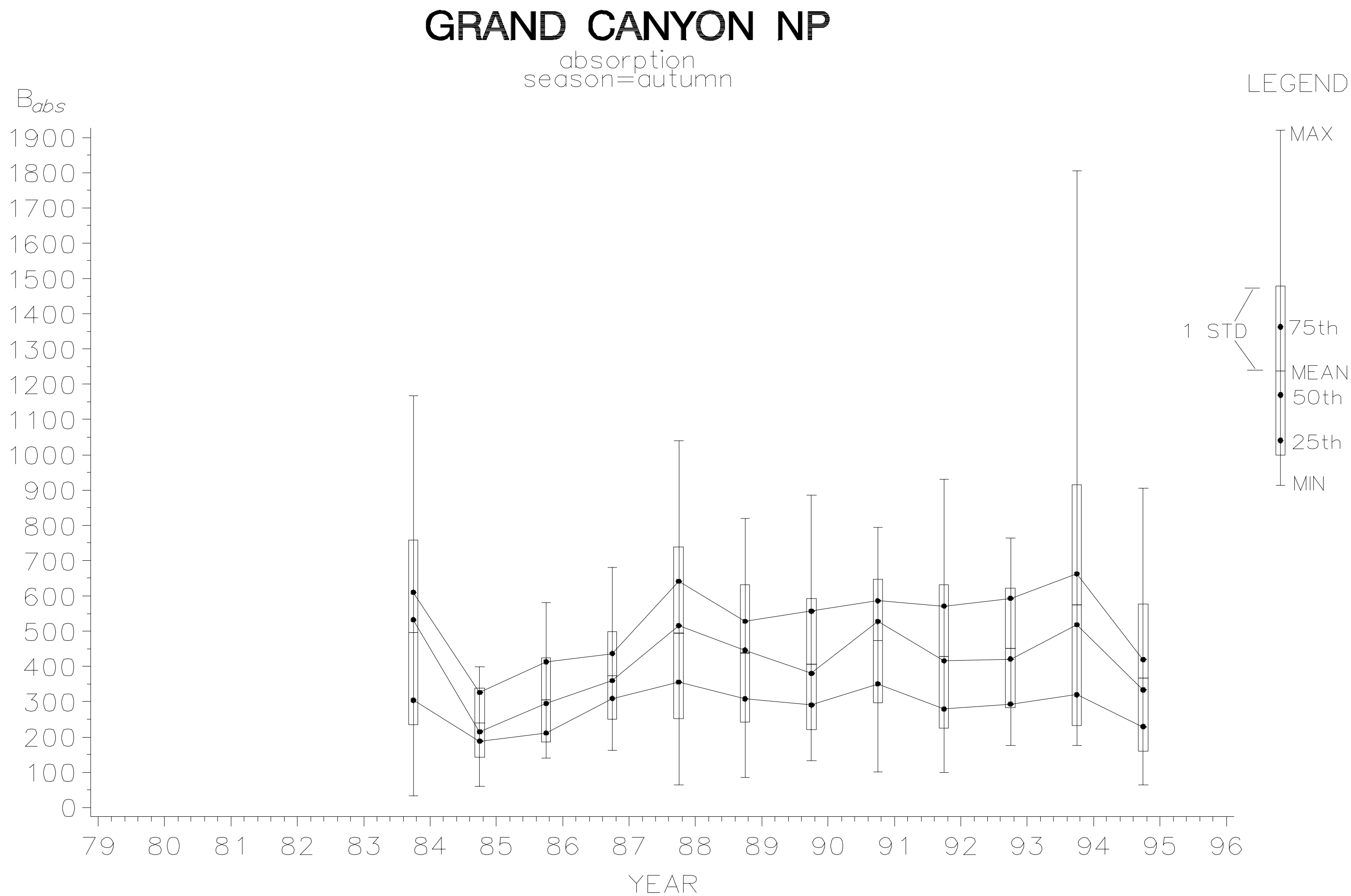

Figure 6.13c Monthly statistics for absorption (ng/m^3) at Grand Canyon National Park in the autumn.

6.6.1 Daily Scatter Plots

Appendix 3 has matrix scatter plots of fine mass, sulfur, and b_{abs} by season for all IMPROVE monitoring sites. Presented here are a representative subset of sites that demonstrate the variability, range, and character of the correlations with emphasis on differences between sites. Overlaid on each scatter plot are two sets of concentric ellipses. The major axis lies on the first principal component and the ellipse center lies on the mean value of both species. The ellipses define contours that enclose points that fall within the 50% and 90% of a bivariate normal distribution. A perfectly round ellipse indicates no correlation, and the oblateness indicates the degree of correlation. Perfect correlation would result in the ellipse collapsing into a straight line.

6.6.1 Shenandoah National Park

The scatter plots for Shenandoah (Figure 6.14) display many of the qualities expected for a site impacted by numerous anthropogenic sources. Sulfate constitutes a major fraction of the fine mass and accordingly the correlation of sulfur to fine mass is high, particularly in the autumn followed by the spring. Absorption is surprisingly correlated with fine mass even though b_{abs} composes a much smaller fraction of the mass. The correlation of b_{abs} with sulfur, although significant, especially in the winter, appears to be the weakest of the three relationships. Autumn is interesting because of the similarity of the scatter of b_{abs} against sulfur and fine mass. There is a readily identifiable subpopulation at lower concentrations and the appearance of a hard edge applies to both scatters. A hard edge is indicative of a strong influence from one source type or source area as evidenced by one ratio of b_{abs} to sulfur. The scatter away from the hard edge indicates occasional influx additional sulfur with proportionately less b_{abs} from other sources.

6.6.2 Glacier National Park

Glacier (Figure 6.15) is an interesting contrast to Shenandoah. The strongest correlations with fine mass are with b_{abs} rather than sulfur. The correlation of sulfur to b_{abs} is quite weak as evidenced by the roundness of the ellipse. This is especially evident during the spring and autumn with the strongest b_{abs} sulfur correlation occurring in the winter. The scatter plots of b_{abs} vs sulfur and sulfur vs fine mass suggest two types of days are being observed. One group of days has high b_{abs} and low sulfur. The other group has low b_{abs} and high sulfur.

6.6.3 Denali National Park

At Denali (Figure 6.16), many interesting features are evident. During the winter and spring correlations of b_{abs} with sulfur are the strongest of any site in the IMPROVE network. During the summer and autumn, when the correlations are lowest, the hard edges indicate two groups of days or "populations" dominated either by sulfur or by b_{abs} (similar to those discussed above for Glacier). Each population would most likely be associated with a distinct source type and/or region. The possibility of two populations during autumn and summer are also suggested by the scatter of sulfur against b_{abs}. The strongest correlation between b_{abs} and fine mass occurs during the summer. During the winter all three aerosol measures are relatively well correlated with each other.

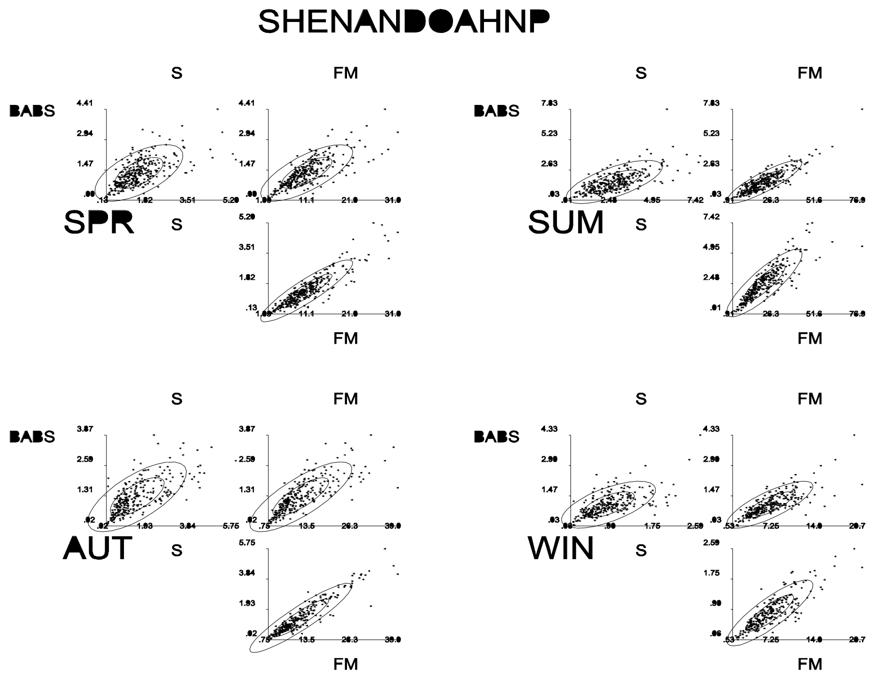

Figure 6.14 Matrix scatter plots of absorption (b_{abs}) sulfur (S) and gravimetric fine mass (FM) for the four seasons at Shenandoah National Park. Assuming an absorption efficiency of 10 m^2/gm all units are ìg/m^3.

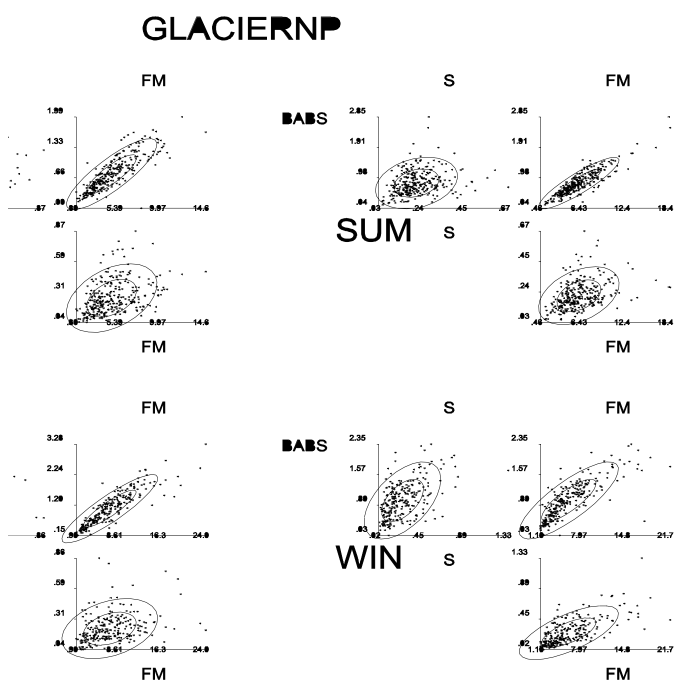

Figure 6.15 Matrix scatter plots of absorption (b_{abs}) sulfur (S) and gravimetric fine mass (FM) for the four seasons at Glacier National Park. Assuming an absorption efficiency of 10 m^2/gm all units are ìg/m^3.

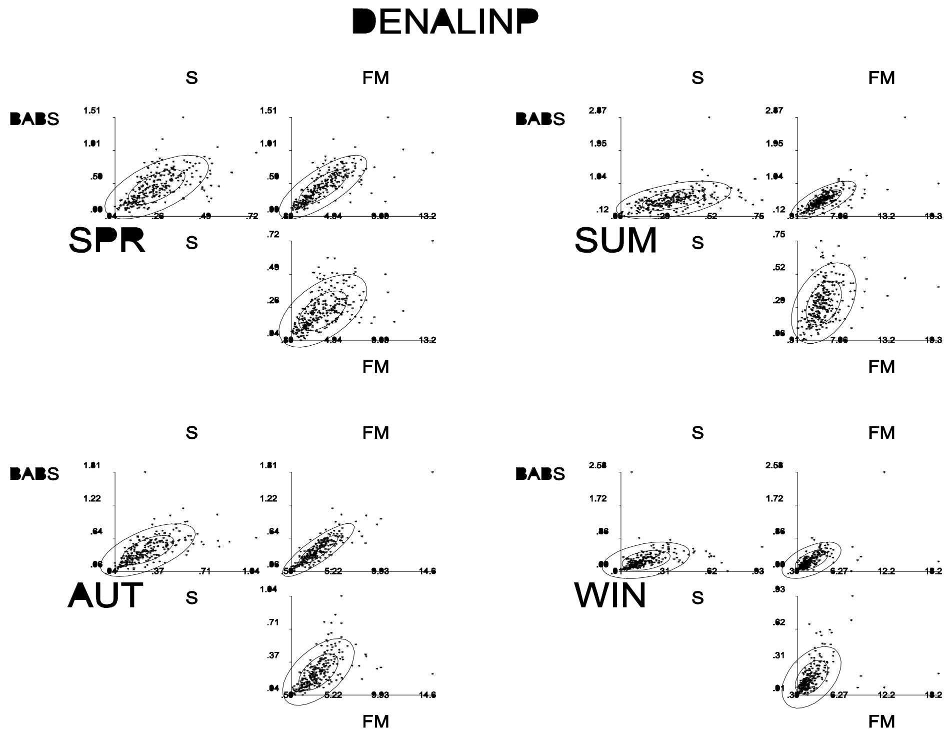

Figure 6.16 Matrix scatter plots of absorption (b_{abs}) sulfur (S) and gravimetric fine mass (FM) for the four seasons at Denali National Park. Assuming an absorption efficiency of 10 m^2/gm all units are ìg/m^3.

6.6.4 Bridger Wilderness Area

At Bridger (Figure 6.17), there are relatively moderate to strong correlations of all three aerosol measures with each other. The correlation of b_{abs} with sulfur is especially strong during the winter followed by the summer. The strongest correlations of b_{abs} with fine mass are during the spring and autumn. In the scatter of b_{abs} vs fine mass during the summer, two populations are evident. There is a population that appears very tight and then another group of days with elevated fine mass. This pattern is also seen to a lesser extent in the scatter between sulfur and fine mass.

6.7 Conclusions

Changes in sampling protocol, whether by sample duration (24-hour vs 72-hour) or sampler type (SFU vs IMPROVE) appear to have a minimal affect on observed concentrations of fine mass, sulfur or absorption. This is especially the case for sulfur where the noted changes were slight and variable between sites. The only site with a clear change between protocols was at Mount Rainier, which is coincident with a change in sampler location and altitude. For the case

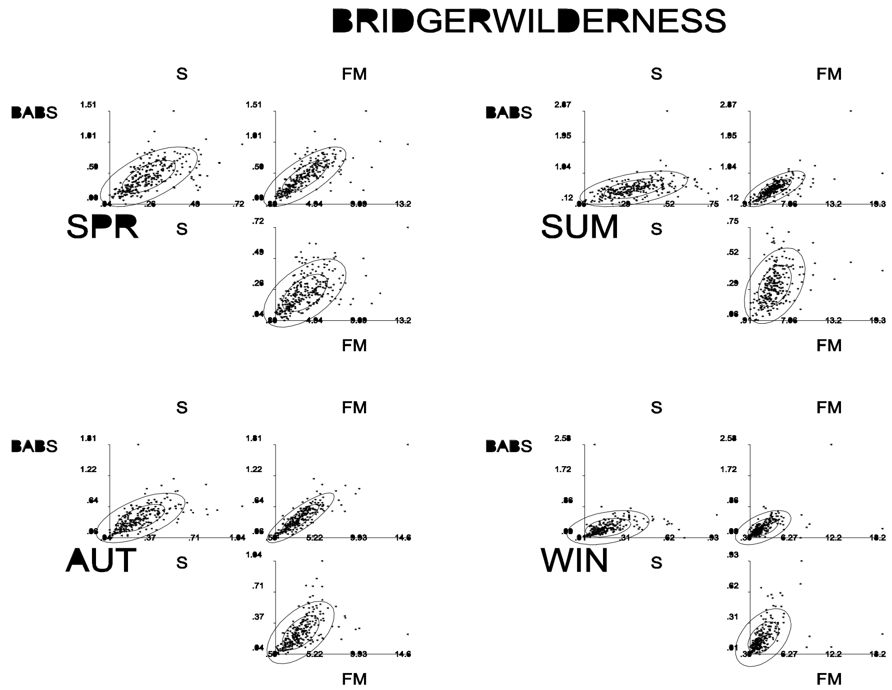

Figure 6.17 Matrix scatter plots of absorption (b_{abs}) sulfur (S) and gravimetric fine mass (FM) for the four seasons at Bridger Wilderness. Assuming an absorption efficiency of 10 m^2/gm all units are ìg/m^3.

of absorption, five sites demonstrate clear changes between sampler type, one of those sites is again at Mount Rainier, while the other sites show notable increases in absorption during most seasons.

Demonstrated long-term trends fall into three categories: increases, decreases, and variable. Sites that demonstrated decreases are at Crater Lake and Rocky Mountain National Parks where absorption dropped dramatically, and at Guadalupe Mountains National Park where sulfur is decreasing in the autumn. A clear demonstration of decreased sulfur concentrations as a result of emission reductions is in the desert southwest at Chiricahua. Two sites where increases have been observed are at the Grand Canyon in the autumn where the 25th percentile of sulfur concentrations have increased steadily since 1980, and at Great Smoky Mountains National Park where autumn concentrations of sulfur and absorption have increased. Other sites that demonstrate little or variable changes in sulfur concentrations are at Bryce Canyon, Rocky Mountain, and Crater Lake National Parks. Variable or little change in absorption was noted at the Grand Canyon National Park in the winter, and Chiricahua National Monument in the summer.

The most notable observation from a national perspective is the lack of a clear uniform trend of sulfur concentration or absorption. There are local success stories related to emission controls, and there are failures most likely associated with increased local emissions or long-range transport. The bulk of the sites show little or variable trends in the long run.

The matrix scatter plots demonstrate correlations ranging between slight to strong between gravimetric fine mass, b_{abs}, and sulfur. Some of the strongest correlations are between fine mass and b_{abs} even though light-absorbing material is a small fraction of fine mass suggesting an internal mixture of carbon with the primary constituents of the fine mass. The exceptions to this are sites in the eastern United States where sulfur is a large fraction of the fine mass; here sulfur shows strong correlations with fine mass indicative of strong sources. Weak correlations are usually manifested by 'fan shaped' scatters, some with hard edges, which suggest multiple sources with variable ratios of b_{abs} or sulfur.

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