

**Precipitation Chemistry at Mount Rainier (Paradise Ranger Station)
Collection Site
Final Report for Data collected between June 1, 2013 and May 30,
2014**

Cooperative Agreement between NPS and CWU, Agreement number
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Introduction

In order to understand the relationship between natural processes and perturbations brought about by human activities, precipitation chemistry must be studied over a long-term period. By sampling on a continuous basis with consistent techniques, we are seeking to accumulate valuable chemical precipitation data that will enable the atmospheric science community to track atmospheric changes that come as a consequence of modifications in anthropogenic emissions and land use both regionally and globally.

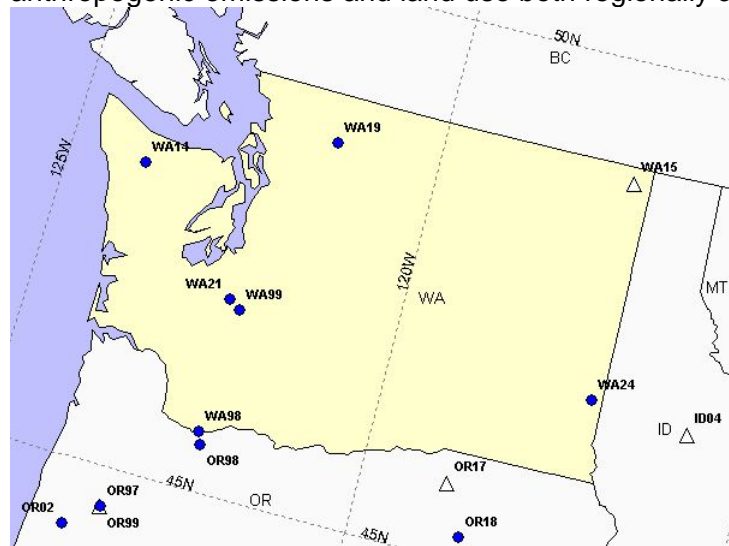


Figure 1: Map of Washington State with NADP sites

Our methods on Mt. Rainier closely resemble those of the existing NADP (National Atmospheric Deposition Program) sites in the state of Washington (depicted in Figure 1): Hoh (WA14), La Grande (WA21), Marblemount (WA19) and Tahoma Woods (WA99). The Hoh site (WA14) is located on the Olympic Peninsula, and is assumed not to include anthropogenic contaminants from the Seattle/Tacoma area. Marblemount (WA19) is located only 60 miles east of the Puget Sound in northwestern Washington along State Highway 20 and on the western face of the North Cascade Range at an elevation of 123 m. The two closest sites to our Mt. Rainier Paradise Ranger Station

(hereafter referred to as Mt. Rainier) site are: La Grande (WA21), which is located to the west of Mount Rainier just south of the town of Eatonville, at an elevation of 617 m, and nearby Tahoma Woods (WA99), at an elevation of 421 m and approximately 3 miles south east of the Paradise Ranger Station. While the first three sites have been operating since 1984, the Tahoma Woods site has only been active since fall 1999. Our site, Mt. Rainier Paradise Ranger Station, is located at 1654 m elevation and has been active for precipitation collection and analyses, on and off between 1989 and 2001 and consistently thereafter.

Experimental

Precipitation Collection

Collection of wet deposition in the form of rain and snow is carried out with large 5 gallon white plastic containers with an opening of 29 cm in diameter. During periods when there is no snow on the ground, a dry-wet collector of the same type as at the NADP sites is used, otherwise a bucket is placed on top of a collection tower at Paradise. During snowfall months, the bucket is capped with an inverted funnel with a smaller opening to prevent bucket over-filling during the one-week sampling period.

Weekly sample collection is performed by Mount Rainier National Park Biology Technician Rebecca Lofgren or assistants. This procedure consists of removal of the bucket containing 1-, and sometimes 2-weeks worth of precipitation, replacing it with a new cleaned one, and shipping the capped used bucket back to us for analysis. Buckets are received at CWU where the amount of collected precipitation is determined based on the mass difference of the full and empty bucket. It should be noted that between 12/5/07, i.e., sample M-07-35 and 5/28/13, i.e., sample M-13-17, a new preservation procedure was used in order to

assure that sample storage over longer time periods was feasible. For that purpose, the received sample is split among three 120 mL trace clean sample bottles. Conductivity, pH, and anions are determined from the original sample. Concentrated nitric acid is added to the second sample until a pH of 2.0 is reached to preserve the cations calcium, potassium, magnesium, and sodium until analysis. Similarly, concentrated sulfuric acid is added to the third sample until a pH of 2.0 is reached to ensure preservation of ammonium until analysis. Since sample M-13-18, which includes all samples in the current report, however, we started using our new Metrohm IC, which deemed to be problematic with the acidity of the samples for storage. Thus, we had to use the non-treated samples. Since we will be using the Metrohm IC for all future samples, we will ascertain that storage period for samples is held to a minimum and that samples are run once a month.

Before returning the bucket to Mt. Rainier, it thoroughly cleaned with DI water and boxed up. All procedures, including those described below are documented in detail in Standard Operating Procedures (SOPs) contained within our CWU Chemical Analysis Laboratory Quality Assurance/Quality Control Manual (QA/QC Manual, updated Feb. 2008).

Chemical and Data Analysis

Determination of inorganic cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) is accomplished by using a Metrohm Ion Chromatography (IC), with EPA Method 300.7. Inorganic anions (Cl^- , NO_3^- , SO_4^{2-}) are quantified by IC in anion mode using EPA Method 300.0. Conductivity and pH are measured using an YSI 3200 Conductivity Meter and an Orion model 420A pH Meter (EPA Methods 120.1 and 150.1, respectively). While the CWU Chemical Analysis Laboratory had been EPA accredited for pH since at least 1999, accreditation for the additional nine components was completed in spring 2006 and the laboratory has maintained accreditation since then.

Observed sample concentrations (C_i) are corrected for the potential loss of water by evaporation by multiplication with the ratio of collected precipitation volume (V_i) over the actual precipitation volumes as recorded at the Mt. Rainier ($V_{Mt.Rainier}$) site by NPS staff:

$$C_{i,corr} = \frac{C_i V_i}{V_{Mt.Rainier}} \quad (\text{Eqn. 1})$$

Note that when our measured volume, V_i , is larger than that predicted by the NOAA Paradise Station precipitation volume, $V_{Mt.Rainier}$, comparison is made with NRC data. If our volume still exceeds the predicted amount, no corrections are made and $V_{Mt.Rainier}$ is equaled to V_i in Eqn. 1. During the current sampling period this occurred in 11 out of the 38 collected samples, i.e., 29% of cases (see grey shaded entries in Table 1).

Quarterly volume weighted average concentrations are computed analogously to the other NADP sites:

$$C_{i,corr,quarter} = \frac{\sum C_{i,corr} V_{Mt.Rainier}}{\sum V_{Mt.Rainier}} \quad (\text{Eqn. 2})$$

Note that for pH, the quarterly volume weighted average value had been calculated analogously from the negative logarithm of the resulting volume weighted average proton (H^+) concentration as calculated with Eqn. 2. Since 2000, when all raw data was available to us, the measured, i.e., unadjusted, pH was also included in Table 1. This was motivated by the discrepancy observed between adjusted pH values for Mt. Rainier and those reported for Tahoma Woods. Typically it

is assumed that pH is buffered in this type of environmental sample, which means that some evaporation is not likely to change pH significantly.

Detection limits on the IC were established based on 3 x the standard deviations of the last 30 QC samples. Detectable quantities (i.e., values other than 0) that fell below this limit are highlighted in blue in Table 1. In the trend analysis portion of this report these values were still used, as omission or replacement with zeros would skew the data more strongly.

Deposition loads for all anions and cations for the years 1993-present are computed for each quarter and totaled annually where data is available for all four quarters of the year. The following equation was used to estimate quarterly deposition loads:

$$DepositionLoad_{Quarterly} = \sum \frac{C_i \cdot V_i \left(\frac{1 \mu mol}{|z|} \right) \left(\frac{1 mol}{1000000 \mu mol} \right) MW_{ion} \left(\frac{1 kg}{1000 g} \right)}{A_{Opening} \cdot \frac{1 Hectare}{10000000 cm^2}} \quad (Eqn. 3)$$

C_i is the sample concentration expressed in $\mu eq/L$, z is the charge of the ion, and $A_{opening}$ is the area of the opening of the bucket, which varies with year and precipitation type. Where information was lacking, assumptions were made based on reports and bucket logs from previous years including the following: pre-10/98 bucket opening area=440.0 cm^2 , post-10/98 bucket opening area=660.5 cm^2 , funnel #2 opening area=146.3 cm^2 , funnel #3 opening area=128.7 cm^2 , and funnel #4 opening area = 201.1 cm^2 . Information was not available pertaining to the area of funnel #1, therefore, data prior to Summer 1993 was not included. Reference to critical load values could only be found for SO_4^{2-} and these were specific for the Rocky Mountains [Fox et al., 1989] where the reported value of 20.0 $kg ha^{-1} yr^{-1} SO_4^{2-}$ critical load is by a factor of 11.5 larger than the values that we determined in the reported period.

Statistical Analysis

Time Series Analysis and Student t-Test

A sequence of observations recorded over time, such as the present one, is known as a time series. Precipitation time series are affected by three basic components: the underlying trend (T), seasonal variations (S) and random events (residual, R). Estimates of T, S, and R, are obtained through the time series decomposition of quarterly volume weighted average concentrations ($C_{i,corr,quarter}$) with the statistical software MINITAB15 [MINITAB 15, 2007]. Assumptions include a multiplicative model:

$$C_{i,corr,quarter} = T \times S \times R \quad (Eqn. 3)$$

and a linear trend:

$$T = b + m \cdot year \quad (Eqn. 4)$$

Time series decomposition outputs (model and trend line with equation) and the observed data are plotted in Figures 2 through 7 for important anthropogenic species, in addition to pH and the ratio of cationic over anionic charges. The significance of the trend and seasonality for each component is computed by the model and can be judged by the P-values that are noted within each graph.

P-values represent the probability that the null hypothesis is true, e.g., a p-value of .05 indicates that there is a 5% probability for the null hypothesis, i.e., a significance of the observed

trend or seasonal variation at the 95% confidence interval (C.I.). In this study, the standard P-value of ≤ 0.05 is used to determine if a significant trend is observed in the overall data.

Data for Tahoma Woods, which has been active for 16 years as of the current sampling period, are shown at the bottom of each Figure. Due to the proximity of this site to Mt. Rainier, Mt. Rainier data are included in this plot (dotted) for direct visual comparison. Furthermore, paired student t-tests are performed on all ten components for both sites to determine if significantly different chemical characteristics are observed within the 95% C.I., i.e., P-values ≤ 0.05 demonstrate significant difference.

Results and Discussion

Data

Results from the 2013-2014 Mt. Rainier precipitation monitoring study are presented in Table 1, arranged in a quarterly format consistent with the NADP's quarter system: summer is June-August, fall is September-November, winter is December-February, and spring is March-May. Collection Date refers to start date of collection for that particular sample. During the 2013-2014 52-week period, 40 samples were collected. When precipitation was very low, e.g., in the summer, no sample was obtained. This occurred 9 times during the current report period. In other instances, for a variety of pertinent reasons, the bucket contained 2-week samples. Four 2-week samples were collected during this year.

The resulting 4 new seasonal data points, in orange cells in Table 1, are plotted along with all previously determined seasonal results in the corresponding plots in Figures 2 through 8 for a subset of each of the parameters. Analogous data for the other 4 NADP sites are presented in Tables 3 through 7. Figure 8 shows additional analytes with significant trends.

Paired student t-tests are performed on data from the two nearby locations, Mt. Rainier and Tahoma Woods. P-values for quarterly and monthly averaged data are presented in Table 8. Results show that nitrate, protons, calcium, magnesium and sodium are significantly different in Tahoma Woods compared to Mt. Rainier. Potassium is only different when analyzing the quarterly data.

Component	P-Value Quarterly Data*	P-Value Monthly Data**
SO ₄ ²⁻	0.322	0.635
NO ₃ ⁻	0.000	0.000
H ⁺	0.551	0.097
NH ₄ ⁺	0.091	0.981
Ca ²⁺	0.000	0.000
Cl ⁻	0.362	0.146
Mg ²⁺	0.037	0.015
Na ⁺	0.007	0.001
K ⁺	0.037	0.633
(+)/(-)	0.086	0.152

*Sample: n = 57, **Sample n = 153
Bold indicates values are significantly different (i.e. P \leq 0.05).

Trend and Seasonality Analyses

Trend and seasonality analyses of selected atmospheric pollutant indicators for the Hoh, La Grande, Marblemount, Mt. Rainier and Tahoma Woods sites are presented graphically in Figures 2 through 7. To ease comparative visual interpretation between each site, each figure presents the data for one species at all five sites. Figures display observed and modeled data in addition to the linear trend line and its equation. Significance of the null hypothesis in the trend appears immediately after the trend line equation within the plot and the significance of seasonality is also reported. Each Figure, i.e., component, is presented and discussed separately in the following section. In addition, Figure 8 shows other analytes from the sites that display significant trends.

SO_4^{2-} is typically considered anthropogenic in nature, but can also have volcanic, sea-salt, and biogenic contributions. The latter two sources are assumed to be of minor significance in the present case due to the distance from the coast, except for at the Hoh site. Volcanic activity was present from Mt. St. Helens during the fall of 2004, particularly in early October, but no clear signal was observed during the corresponding monitoring period [Kittelson *et al.*, 2006]. The anthropogenic source is mainly from sulfur contained in fossil fuel that is first oxidized to gaseous SO_2 during combustion and then further oxidized to SO_4^{2-} thus generating two protons in the process and increasing acidity.

Concentrations are plotted in Figure 2 and show a decreasing trend for all sites except Hoh. The rates of decrease are largest in La Grande ($0.36 \mu\text{eq/L year}^{-1}$), and smallest at Mt. Rainier ($0.22 \mu\text{eq/L year}^{-1}$). The other sites are similar in value to Mt. Rainier. All slopes are smaller in magnitude by approximately 5-10% compared to last year's report, which indicates a general leveling out of SO_4^{2-} . There seem to be significant seasonal patterns at all sites, where minima occur in the winter, probably due to higher amounts of precipitation which lead to more rainout of pollutants and dilution of chemical components.

The paired student t-test on the Tahoma Woods and Mt. Rainier SO_4^{2-} seasonal data shows that there is no significant difference between the two sites (Table 8b).

NO_3^- is an oxidation product of NO_x species produced in high temperature combustion processes and is thus predominantly anthropogenic in origin. These data, presented in Figure 3, show significant decreasing trends in all sites except Hoh. The rate of decrease is smaller for all sites compared to sulfate, ranging from 0.08 at La Grande to $0.19 \text{ ueq/L year}^{-1}$ at Tahoma Woods. Mt. Rainier nitrate decreased at $0.12 \text{ ueq/L year}^{-1}$, which is close to the value observed at Marblemount, $0.10 \text{ ueq/L year}^{-1}$. Analogous to SO_4^{2-} , the Hoh site displays the lowest overall concentrations compared to the other sites, and concentrations for Tahoma Woods and Mt. Rainier are similar and fall between the low concentrations observed at Hoh and the higher concentrations observed at Marblemount and La Grande. Seasonal fluctuations are significant at all sites except Tahoma Woods.

Mt. Rainier and Tahoma Woods data show a significant difference in NO_3^- concentrations over the complete 16-year period (Table 8).

H^+ and pH (the negative logarithm of the activity of H^+) are direct measures of acidity and are plotted in Figures 4a and 4b, respectively. Note that an additional graph in the lower right of the panel is shown in these two figures. They show H^+ and pH that were corrected for evaporation, which, as indicated in the experimental section did not seem appropriate as we are likely dealing with a buffered system. Thus, for as far back as we could dig up raw data, i.e. since 2000, we decided to also inspect the actual measured pH and found it was closer in value to Tahoma Woods than the one corrected for evaporation. Nevertheless, both measured and adjusted values are plotted in each figure.

The formation of SO_4^{2-} and NO_3^- in the atmosphere is associated with the production of H^+ , thereby lowering pH. Since SO_4^{2-} and NO_3^- display decreasing trends at all sites, except Hoh, H^+ is expected to decrease and pH is expected to increase at these other sites. This is what we observe: significant negative pH trends and significant positive H^+ trends. Interestingly, the rate of measured H^+ decrease is the largest at Mt. Rainier at $0.68 \text{ ueq/L year}^{-1}$ compared with $0.32 \text{ ueq/L year}^{-1}$ at Tahoma Woods and the lowest rate of $0.14 \text{ ueq/L year}^{-1}$ observed at Marblemount. The adjusted H^+ rate of decrease for Mt. Rainier falls within the range of the other sites at $0.24 \text{ ueq/L year}^{-1}$. At Hoh, a significant positive trend is observed for H^+ and, conversely, negative trend for pH.

In terms of pH values, La Grande and Marblemount display the lowest pH averaging around 5.1, which is significantly lower than the pH of unpolluted water in equilibrium with the current atmosphere (pH 5.6). The overall increasing trend in measured pH is the largest at Mt. Rainier, with $0.052 \text{ pH units per year}$ (since 2000), which compares to $0.021 \text{ pH units per year}$ to the adjusted pH, and $0.019 \text{ pH units per year}$ to the rate of decrease observed at Tahoma Woods. Seasonal patterns are significant for pH and H^+ at all sites.

Measured H^+ at Tahoma Woods and Mt. Rainier are not significantly different (Table 8).

NH_4^+ is derived from gaseous ammonia (NH_3), which is primarily emitted from soils, industry and animal waste, and it contributes to acid neutralization ($\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$). This data is plotted in Figure 5. The Hoh and Marblemount sites show significant negative trends. Mt. Rainier, however, shows an almost significantly positive trend ($P=0.053$) and is the only site with such a trend. This trend may in part be driven by a few high values including the most recently collected Summer 2013 entry which seems to correlate with a spike in ammonium at La Grande and less so at Marblemount. There is no apparent reason for this observation. Hoh exhibits the smallest concentrations and fluctuations. Hoh and Tahoma Woods are the only sites that do not display a significant seasonal pattern. There is no significant difference between Mt. Rainier and Tahoma Woods from the paired student-t test.

Ca^{2+} is a tracer for limestone that can reach the atmosphere in the form of suspended dust, but it can also reach the atmosphere from emissions of coal combustion. It is typically associated with CO_3^{2-} or O^{2-} , which have the ability to take up protons thus buffering the system against pH drop. Ca^{2+} is plotted in Figure 6 and shows a significant upward trend at Hoh and downward trends at Mt. Rainier. Seasonal trends are observed at Hoh and La Grande. Comparisons between the Mt. Rainier and Tahoma Woods data reveal significant differences between the two sites, however, the change in trend at Mt. Rainier since ~2007 may be bringing Ca^{2+} concentrations closer in those two sites.

[+]/[-] is defined as the ratio between the summed up positive and summed up negative charges in precipitation. Figure 7 depicts this data for the five sites. Carbonate species, which cannot be detected by the IC, are the only missing major components that have not been taken into consideration in the determination of this parameter. Significant increases in the charge ratio are observed at all sites except Hoh. The increase can be explained by the drops in both SO_4^{2-} and NO_3^- . Mt. Rainier displays the most extreme charge ratio in that there is a downward trend up until 2003 followed by a steep upward trend that has flattened out since 2011. The decrease observed at Mt. Rainier prior to 2004 could be attributed to contamination amount of Cl^- due to the acid cleaning procedure of the bucket that we have since changed. Seasonal fluctuations are significant at all sites except Hoh and Tahoma Woods, and display opposite maxima and minima to anionic species, thus also indicating that the negatively charged anions play a major role in the seasonal variations observed for the charge ratio. Ratios for Mt. Rainier and Tahoma Woods are not significantly different.

Additional graphs presented in Figure 8 are those that display significant trends of species that are not plotted in the previous figures. Specifically, conductivity in the first row, K^+ in the second row, Mg^{2+} in the third row, and Na^+ in the fourth row. Conductivity is decreasing at La Grande, Marblemount and Mt. Rainier, in accordance with decreased SO_4^{2-} and NO_3^- at these sites. Increased K^+ trends at Hoh, La Grande and Marblemount may stem from biomass burning as K^+ is a tracer for particles emitted during the combustion of plant material. Interestingly, Mg^{2+} shows a decreasing trend at Marblemount while an upward trend at Tahoma Woods. Mg^{2+} is frequently associated with Ca^{2+} when stemming from soil dust sources. While for Marblemount this may be the case, the opposite trend for those to species at Tahoma Woods indicate that they are not clearly associated with each other.

Conclusions

In agreement with previous reports, precipitation chemistry at Paradise, Mt. Rainier, seems to fall between the low contaminant levels at Hoh and the higher levels at La Grande and Marblemount [Agren *et al.* 2011&2012; Baker and Johansen, 2004; Bolstad and Duncan, 2000; Johansen and Lenington, 2003; Kittelson *et al.*, 2006; Lenington *et al.*, 2005; Sorey and Johansen, 2007; Sorey *et al.*, 2008; Rybka *et al.*, 2009; Nieber *et al.* 2010]. Significant negative trends can be identified for sulfate and nitrate for all sites except Hoh. Associated with these trends are also the positive trends in pH at all sites except Hoh, where pH values have decreased significantly. These observations support the fact that emissions regulations are effective and apparent at this high elevation site.

For all Mt. Rainier components presented in the graphs (except the charge ratio) the seasonal pattern is significant, with concentrations at a minimum during the winter months. In comparing the Tahoma Woods site with Mt. Rainier, there seem to be statistically significant differences for NO_3^- , Na^+ , Mg^{2+} , Ca^{2+} , and K^+ for the quarterly. It is feasible that Tahoma Woods is closer to anthropogenic pollutant sources and thus concentrations for the anions and the proton are higher there.

Although there is no direct evidence for Asian pollution reaching the Pacific Northwest, the continued collection and analysis of long-term and consistent data is essential in determining the impact that intercontinental atmospheric transport of pollutants exerts on pristine areas such as Mt. Rainier. With the recent increase in frequency of wildfires in the Pacific Northwest, it is likely that a chemical signature becomes apparent, in particular in increased K^+ concentrations in the next few years.

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Tables and Figures

Table 1: Summary of Weekly Precipitation Data for 2013/2014 at Mount Rainier Paradise Ranger Station

Summer 2013

Sample ID	Collection Date	Week (sum.'13)	Collection Volume	Precipitation Volume	Conductivity	Measured pH	Adjusted pH	Measured H ⁺	Adjusted H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	SO ₄ ²⁻	NO ₃	Cl ⁻	[+]/[-]	
	(M/D/Y)		(L)	(L)	(µS/cm)			(µmol/L)	(µmol/L)					(µeq/L)					
M-13-18	5/29/2013	1	0.9215	1.39	2.88	6.19	6.37	0.65	0.43	0.76	1.12	1.13	2.71	13.45	7.33	5.07	1.86	1.37	
M-13-19	6/4/2013	2	0.5994	0.84	8.09	6.79	6.94	0.16	0.12	1.72	3.86	4.94	13.46	49.88	12.61	3.13	5.62	3.46	
M-13-20	6/13/2013	3	0.2594	0.40	37.90	7.59	7.78	0.03	0.02	3.03	17.76	3.40	78.94	244.26	30.40	3.21	7.18	8.52	
M-13-21	6/19/2013	4	4.2129	4.21	2.58	5.90	5.90	1.26	1.26	0.65	0.87	1.36	2.76	6.75	5.67	6.00	2.58	0.96	
	6/25/2012	5		0.92															
	7/4/2012	6		0.02															
	7/10/2013	7		0.00															
	7/17/2013	8		0.00															
M-13-22	7/24/2013	9	0.888	0.89	7.30	5.50	5.50	3.16	3.16	7.12	2.58	2.32	4.66	40.75	13.74	18.08	3.55	1.71	
	8/1/2013	10		0.54															
	8/7/2012	11		0.54															
	8/14/2013	12-13		0.18															
M-13-23	8/21/2013	14	1.8596	1.86	5.29	5.63	5.63	2.34	2.34	5.08	1.68	2.00	1.70	16.24	11.03	16.08	3.07	0.96	
M-13-24	8/28/2013	15	0.5959	1.92	2.23	5.30	5.81	5.01	1.56	3.29	1.09	4.16	1.14	5.92	5.98	6.82	1.77	1.18	
Volume weighted average concentrations Summer 2013:					4.20	4.94	5.04	1.69	1.18	2.08	1.69	1.94	4.96	19.34	7.37	6.95	2.43	1.30	
Total Volume:			9.34	13.71															
Sample count:			7																

Fall 2013

Sample ID	Collection Date	Week (fall '13)	Collection Volume	Precipitation Volume	Conductivity	Measured pH	Adjusted pH	Measured H ⁺	Adjusted H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	SO ₄ ²⁻	NO ₃	Cl ⁻	[+]/[-]	
	(M/D/Y)		(L)	(L)	(µS/cm)			(µmol/L)	(µmol/L)					(µeq/L)					
M-13-25	9/5/2013	16	3.89	4.33	2.84	7.00	7.05	0.10	0.09	0.76	0.00	0.76	0.80	0.99	4.00	6.85	1.54	0.27	
M-13-26	9/11/2013	17	1.41	1.41	3.45	5.63	5.63	2.34	2.34	2.90	2.17	6.94	3.51	13.17	15.26	8.85	7.70	0.98	
M-13-27	9/18/2013	18	4.49	4.50	3.35	5.65	5.65	2.24	2.24	0.54	1.56	8.33	0.36	1.45	5.83	0.98	9.43	0.89	
M-13-28a	9/25/2013	19-20	20.21	27.83	2.61	5.45	5.59	3.55	2.58	0.67	1.15	5.64	0.55	0.69	4.43	1.13	6.59	0.93	
	10/19/2013	21		0.00															
M-13-28b	10/23/2013	22	2.42	2.42	1.61	5.98	5.98	1.05	1.05	0.61	0.47	0.29	8.25	0.00	2.77	0.00	0.90	2.92	
M-13-29	10/30/2013	23	6.76	9.84	3.42	5.71	5.87	1.95	1.34	0.00	0.25	1.08	0.00	0.51	4.59	0.00	22.44	0.12	
M-13-30	11/6/2013	24	6.52	6.52	2.25	5.61	5.61	2.45	2.45	0.76	2.50	13.99	0.49	0.34	4.12	1.42	1.80	2.80	
M-13-31	11/13/2013	25	7.20	9.28	2.77	5.69	5.80	2.04	1.58	0.63	0.39	2.34	0.37	0.00	3.31	0.66	12.51	0.32	
M-13-32	11/22/2013	26	6.98	6.98	1.80	5.99	5.99	1.02	1.02	6.12	2.36	2.26	1.70	5.63	2.56	0.57	3.14	3.04	
Volume weighted average concentrations Fall 2013:					2.67	5.71	5.80	2.41	1.90	1.14	1.12	4.75	0.87	1.30	4.32	1.33	8.42	1.14	
Total Volume:			59.87	73.11															
Sample count:			9																

Winter 2013-14

Sample ID	Collection Date	Week (winter '13-'14)	Collection Volume	Precipitation Volume	Conductivity	Measured pH	Adjusted pH	Measured H ⁺	Adjusted H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	SO ₄ ²⁻	NO ₃	Cl ⁻	[+]/[-]	
	(M/D/Y)		(L)	(L)	(µS/cm)			(µmol/L)	(µmol/L)					(µeq/L)					
M-13-33	12/6/2013	27	0.21	2.35	0.29	5.78	6.84	1.66	0.14	0.05	0.04	0.08	0.07	0.02	0.89	0.26	0.22	0.29	
M-13-34	12/11/2013	28-29	2.45	2.70	1.31	5.92	5.96	1.20	1.09	1.55	4.93	24.10	1.84	0.46	2.23	0.00	0.82	11.11	
M-14-01	12/19/2013	30	1.96	2.08	1.48	5.45	5.48	3.55	3.35	0.00	0.00	0.67	0.00	0.00	2.03	0.15	0.57	1.46	
M-14-02a	12/25/2013	31-32	0.16	0.23	2.45	5.43	5.59	3.72	2.58	2.83	1.00	1.85	1.01	0.86	4.25	3.45	2.04	1.04	
M-14-02b	1/1/2014	33	0.47	0.62	1.46	5.84	5.96	1.45	1.11	1.77	0.73	1.88	0.70	0.57	2.49	0.55	1.85	1.38	
M-14-03	1/8/2014	34	1.64	2.61	2.13	5.42	5.62	3.80	2.39	0.61	1.71	9.17	0.25	0.30	2.57	0.23	10.85	1.06	
	1/15/2014	35		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
M-14-04	1/22/2014	36	0.58	0.60	1.46	5.61	5.63	2.45	2.37	0.79	0.31	0.97	0.27	0.47	2.44	0.26	0.69	1.53	
M-14-05	1/29/2014	37	1.03	1.03	1.67	5.78	5.78	1.66	1.66	0.48	0.00	0.72	0.00	0.35	2.55	0.73	0.92	0.77	
M-14-06	2/5/2014	38	1.13	1.67	1.18	5.77	5.94	1.70	1.15	0.43	0.30	1.18	0.16	0.42	1.86	0.38	1.28	1.04	
M-14-07	2/11/2014	39	2.34	3.78	1.51	5.63	5.84	2.34	1.45	0.46	0.79	4.57	0.00	0.00	1.79	0.07	5.05	1.05	
M-14-08	2/24/2014	40	0.39	0.42	1.47	5.99	6.02	1.02	0.96	1.55	0.44	0.85	0.52	1.41	3.04	0.01	0.89	1.45	
M-14-09	2/26/2014	41	2.63	3.63	1.86	5.58	5.72	2.63	1.91	0.51	0.59	3.09	0.25	0.53	2.22	0.04	3.29	1.24	
Volume weighted average concentrations Winter 2013-14:					1.44	5.03	5.14	2.17	1.63	0.62	1.13	5.72	0.36	0.30	1.97	0.18	3.14	2.28	
Total Volume:			15.00	21.71															
Sample count:			12																

Spring 2014

Sample ID	Collection Date	Week (spring '14)	Collection Volume	Precipitation Volume	Conductivity	Measured pH	Adjusted pH	Measured H ⁺	Adjusted H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	SO ₄ ²⁻	NO ₃	Cl ⁻	[+]/[-]	
	(M/D/Y)		(L)	(L)	(µS/cm)			(µmol/L)	(µmol/L)					(µeq/L)					
M-14-10	3/6/2014	42	1.78	1.78	1.49	5.82	5.82	1.51	1.51	0.45	0.00	0.74	0.00	0.24	2.21	0.00	0.66	1.02	
M-14-11	3/12/2014	43	1.25	1.29	3.52	5.83	5.84	1.48	1.44	1.44	2.66	12.79	0.42	1.00	4.84	0.88	14.91	0.96	
M-14-12	3/19/2014	44-45	0.60	0.74	2.62	5.62	5.71	2.40	1.93	1.05	1.00	4.23	0.31	2.33	5.10	2.15	4.80	0.90	
M-14-13	3/27/2014	46	0.82	0.91	6.65	5.55	5.60	2.82	2.54	1.29	0.75	1.87	0.30	2.20	4.37	2.17	1.85	1.07	
M-14-14	4/2/2014	47	1.03	1.03	2.35	5.65	5.65	2.24	2.24	0.78	0.34	0.75	0.29	1.11	4.77	1.94	0.88	0.73	
M-14-15	4/9/2014	48	0.45	0.45	4.39	5.61	5.61	2.45	2.45	2.08	2.47	11.48	0.72	4.64	7.30	4.65	12.34	0.98	
M-14-16	4/16/2014	49	1.13	1.24	3.16	5.71	5.75	1.95	1.77	1.88	1.88	7.40	0.44	2.00	5.70	2.92	8.28	0.91	
M-14-17	4/23/2014	50	1.71	1.93	2.12	5.77	5.82	1.70	1.50	0.77	0.98	4.37	0.21	1.07	3.27	1.02	4.87	0.97	
M-14-18	4/30/2014	51	0.75	0.75	2.29	5.75	5.75	1.78	1.78	1.10	0.63	2.39	0.25	0.65	4.02	1.67	2.56	0.82	
M-14-19	5/7/2014	52	0.91	1.13	2.25	5.65	5.74	2.24	1.81	2.66	1.22	1.40	1.54	1.25	5.06	2.55	1.43	1.09	
M-14-20	5/21/2014	53	1.30	1.76	2.21	5.68	5.81	2.09	1.55	2.42	0.87	1.50	0.29	1.74	4.80	2.88	1.75	0.89	
M-14-21	5/28/2014	54	0.18	0.57	4.06	5.28	5.78	5.25	1.67	3.47	3.65	11.03	0.92	2.81	8.77	5.56	12.51	0.88	
Volume weighted average concentrations Spring 2014:					2.66	5.39	5.45	1.97	1.65	1.43	1.12	4.07	0.39	1.33	4.26	1.85	4.56	0.89	
Total Volume:			11.91	13.58															
Sample count:			12																

Samples in gray boxes indicate cases when collection volume was used as precipitation volume because numbers derived from NOAA Paradise data were lower or evaporation was unlikely.

Numbers in blue indicate the values that fell below the Method Detection Limit before evaporation correction.

Table 7: Tahoma Woods NADP Site Seasonal Precipitation Data

Season	Year	Conductivity	pH	H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	[+]/[-]
		µS/cm											
Fall	1999.75	2.99	5.33	4.67	0.60	0.33	1.65	0.13	0.55	2.23	1.84	1.92	1.32
Winter	2000.00	3.97	5.26	5.52	0.90	0.82	4.39	0.13	0.72	2.77	2.79	4.80	1.21
Spring	2000.25	6.78	5.05	8.95	1.75	2.63	12.31	0.43	1.94	8.44	4.52	13.91	1.04
Summer	2000.50	10.12	4.79	16.41	1.45	2.47	12.44	0.46	1.33	14.58	4.77	13.88	1.04
Fall	2000.75	7.05	4.89	12.94	0.95	0.66	3.31	0.15	0.83	10.54	3.60	3.98	1.04
Winter	2001.00	6.02	5.08	8.36	2.00	1.73	8.70	0.28	1.39	5.79	5.36	9.73	1.08
Spring	2001.25	6.95	4.99	10.35	1.90	1.73	7.22	0.41	1.83	9.44	5.44	8.10	1.02
Summer	2001.50	5.41	5.01	9.73	1.30	0.49	1.83	0.28	1.88	7.87	3.69	2.31	1.12
Fall	2001.75	5.39	5.09	8.13	1.10	1.07	5.26	0.26	1.66	6.48	3.26	6.23	1.09
Winter	2002.00	4.21	5.28	5.25	1.00	1.48	7.79	0.20	0.83	2.92	2.65	9.39	1.11
Spring	2002.25	5.45	5.21	6.18	1.35	1.89	9.44	0.38	1.66	5.33	4.13	10.89	1.03
Summer	2002.50	5.41	5.24	5.77	1.25	1.73	5.79	6.01	2.38	5.79	5.32	7.36	1.24
Fall	2002.75	10.34	4.79	16.11	2.00	1.15	5.61	0.28	7.21	12.85	14.50	6.15	0.97
Winter	2003.00	3.28	5.34	4.59	0.75	0.82	4.00	0.13	0.83	2.00	2.00	4.85	1.26
Spring	2003.25	4.61	5.27	5.40	1.70	1.32	5.87	0.38	2.94	4.35	4.94	6.88	1.09
Summer	2003.50	7.91	5.13	7.43	3.94	1.32	2.96	1.53	19.46	11.79	17.10	3.67	1.13
Fall	2003.75	4.89	5.23	5.87	1.50	1.65	8.44	0.36	1.83	4.54	3.56	9.85	1.09
Winter	2004.00	3.68	5.30	5.05	0.85	0.90	5.31	0.18	0.78	2.02	2.89	6.26	1.17
Spring	2004.25	4.82	5.20	6.37	1.70	1.23	6.09	0.46	3.49	5.60	5.11	6.97	1.09
Summer	2004.50	3.52	5.26	5.55	0.75	0.33	1.74	0.31	1.66	3.94	3.29	2.17	1.10
Fall	2004.75	5.61	5.15	7.08	1.45	2.22	10.96	0.41	0.89	5.00	3.48	13.77	1.03
Winter	2005.00	6.51	5.00	10.05	1.25	1.48	7.53	0.26	1.33	2.75	3.11	14.36	1.08
Spring	2005.25	3.95	5.29	5.13	2.50	0.82	3.13	0.28	2.27	3.87	3.24	5.05	1.16
Summer	2005.50	6.83	5.00	10.00	1.90	1.32	5.05	0.54	4.71	8.62	7.39	5.98	1.07
Fall	2005.75	5.55	5.12	7.60	1.50	1.56	7.61	0.33	0.94	4.02	2.92	11.17	1.08
Winter	2006.00	3.81	5.32	4.75	2.40	0.99	5.13	0.20	0.28	2.02	1.63	7.28	1.26
Spring	2006.25	5.56	5.12	7.66	2.25	0.90	2.92	0.51	3.77	5.44	6.61	4.85	1.07
Summer	2006.50	5.54	5.07	8.55	2.79	0.66	2.22	0.77	2.94	5.04	4.39	5.53	1.20
Fall	2006.75	4.03	5.21	6.17	0.85	1.23	6.09	0.33	0.67	4.00	2.10	7.59	1.12
Winter	2007.00	4.56	5.34	4.58	1.90	2.63	13.09	0.36	0.44	3.46	1.87	15.74	1.09
Spring	2007.25	5.15	5.12	7.66	1.85	1.48	6.57	0.56	2.11	4.79	5.36	7.70	1.13
Summer	2007.50	6.60	4.99	10.33	1.80	1.07	4.13	0.84	5.99	7.96	7.66	5.92	1.12
Fall	2007.75	4.55	5.19	6.40	1.30	1.32	6.96	0.38	1.77	5.08	2.95	8.44	1.10
Winter	2008.00	3.35	5.36	4.38	1.00	0.99	6.09	0.21	0.39	1.79	1.65	7.53	1.19
Spring	2008.25	5.76	5.19	6.49	2.00	2.14	9.88	0.44	2.44	6.90	4.11	12.81	0.98
Summer	2008.50	6.12	4.98	10.57	1.30	0.91	4.44	0.56	0.67	7.73	4.23	4.88	1.18
Fall	2008.75	3.48	5.27	5.33	0.80	0.82	4.09	0.31	1.16	2.88	2.82	5.28	1.24
Winter	2009.00	3.00	5.32	4.78	0.90	0.82	4.44	0.21	0.50	2.35	1.73	12.75	1.08
Spring	2009.25	4.89	5.32	4.81	3.14	2.47	11.01	0.51	1.77	6.21	2.92	2.40	1.14
Summer	2009.50	5.67	5.06	8.77	1.55	0.66	2.18	0.46	7.76	8.73	7.61	2.40	1.14
Fall	2009.75	4.35	5.27	5.42	1.35	1.81	9.44	0.36	1.00	3.81	2.40	11.12	1.12
Winter	2010.00	2.94	5.36	4.37	1.90	0.91	4.35	0.18	0.78	1.98	2.08	5.05	1.37
Spring	2010.25	5.09	5.34	4.59	3.44	2.55	11.31	0.51	3.33	5.67	4.79	12.98	1.10
Summer	2010.50	6.39	5.03	9.44	1.55	1.56	6.92	0.46	3.94	7.62	6.73	7.98	1.07
Fall	2010.75	4.02	5.26	5.45	1.00	1.48	7.31	0.31	0.55	3.31	2.15	9.00	1.11
Winter	2011.00	3.52	5.34	4.53	0.75	1.65	7.57	0.26	0.67	2.48	1.90	8.94	1.16
Spring	2011.25	4.12	5.32	4.75	1.70	1.81	7.05	1.05	3.38	4.29	3.27	8.18	1.25
Summer	2011.50	6.42	5.04	9.23	1.45	1.89	6.96	0.74	5.77	8.52	7.13	8.04	1.10
Fall	2011.75	4.68	5.29	5.15	0.95	2.88	12.53	0.38	0.89	3.94	1.97	14.61	1.11
Winter	2012.00	5.42	5.40	4.00	1.70	4.11	18.92	0.59	0.83	3.75	2.24	22.43	1.06
Spring	2012.25	2.91	5.37	4.27	1.40	0.91	3.39	0.28	1.94	2.63	2.26	4.03	1.37
Summer	2012.50	4.09	5.41	3.88	1.85	0.82	2.22	1.25	8.65	4.29	8.23	1.81	1.30
Fall	2012.75	3.75	5.26	5.56	0.80	1.65	6.96	0.28	0.94	2.92	2.18	8.60	1.18
Winter	2013.00	3.98	5.32	4.80	1.00	2.30	10.01	0.28	0.55	3.00	1.95	11.65	1.14
Spring	2013.25	3.78	5.42	3.80	1.75	1.81	7.13	0.44	2.83	4.02	2.76	8.41	1.17
Summer	2013.50	4.55	5.37	4.29	1.85	0.99	2.05	1.82	9.59	5.83	6.24	2.31	1.43
Fall	2013.75	5.03	5.33	4.68	1.20	2.96	12.79	0.46	1.77	4.48	2.90	14.98	1.07
Winter	2014.00	4.18	5.41	3.91	0.80	2.80	12.18	0.33	0.55	2.52	1.45	14.33	1.12
Spring	2014.25	3.16	5.44	3.67	1.30	1.15	4.57	0.36	2.77	2.94	2.21	5.19	1.34

Data acquired at Central Washington University

Each entry is a volume weighted average concentration of a three month period (Eqn. 2). Winter 199x is defined as Dec 199x-1 through Feb 199x.

Spring is defined as Mar 199x through May 199x. Summer is defined as June 199x through Aug 199x. Fall is defined as Sept 199x through Nov 199x.

The column headed "[+]/[-]" is the ratio of cation to anion concentration

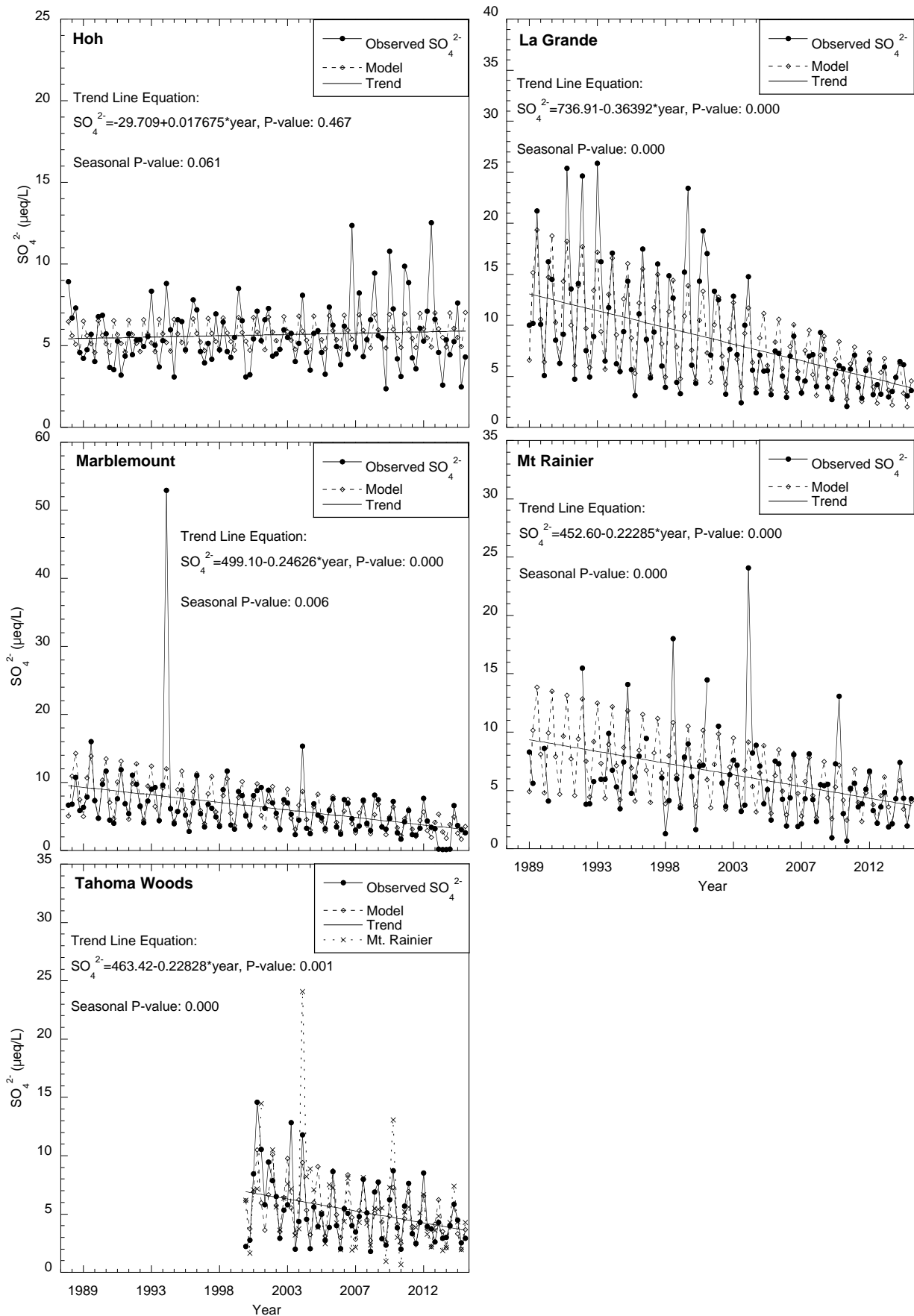


Figure 2: Observed, Modeled and Trend including Trend Line Equation for SO_4^{2-} precipitation concentrations at 4 NADP sites and at Mt. Rainier.

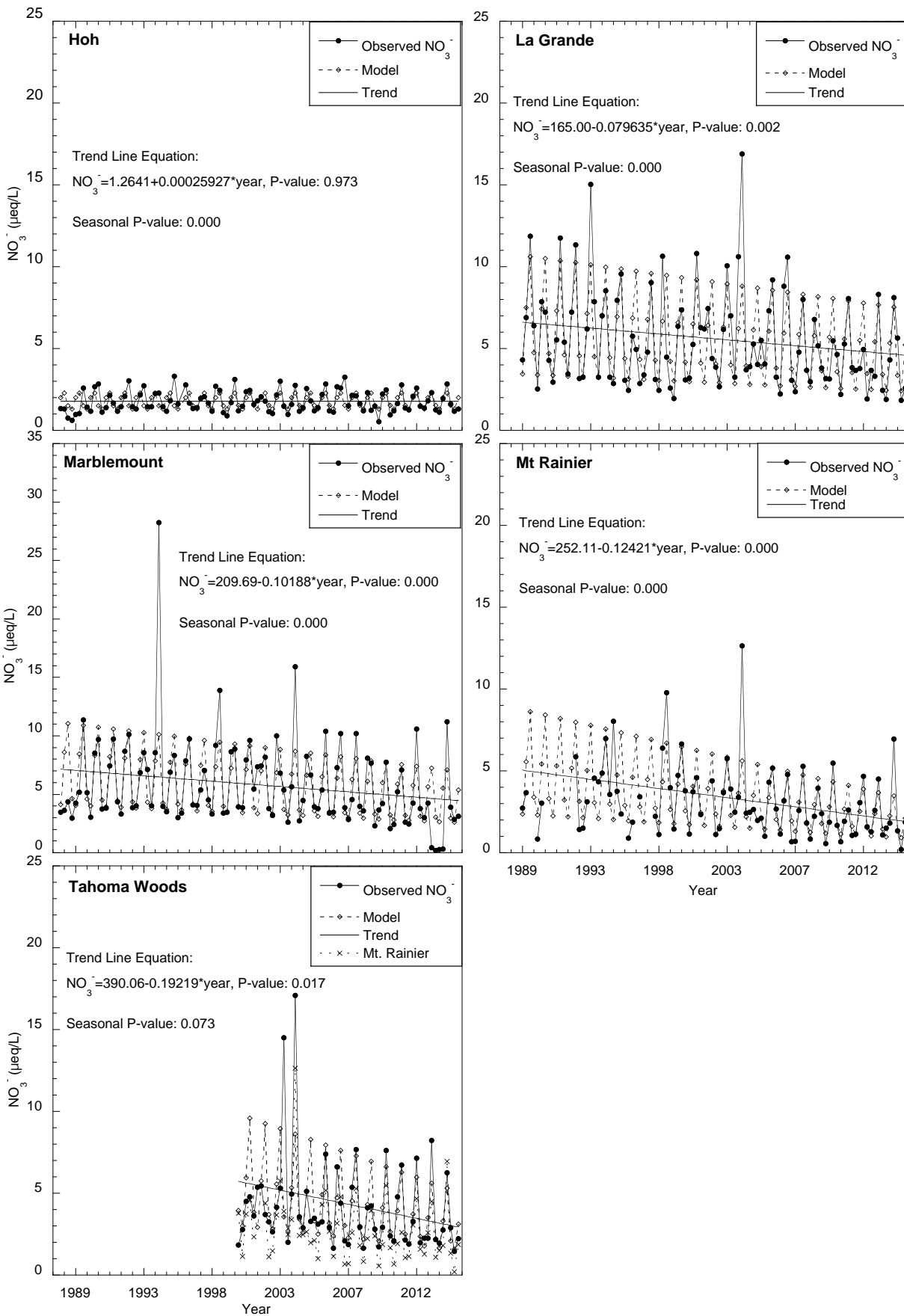


Figure 3: Observed, Modeled and Trend including Trend Line Equation for NO_3^- precipitation concentrations at 4 NADP sites and at Mt. Rainier.

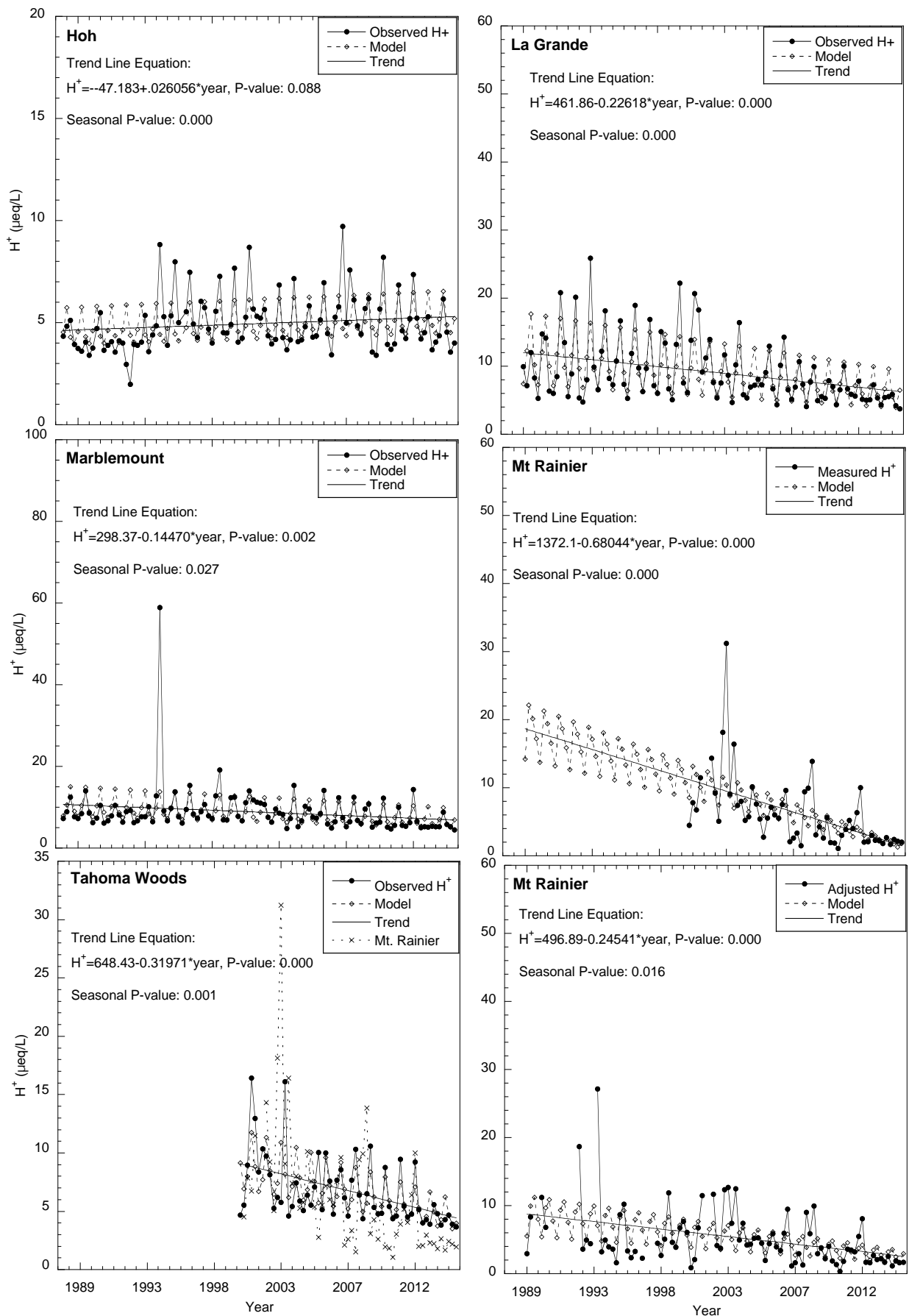


Figure 4a: Observed, Modeled and Trend including Trend Line Equation for H^+ precipitation concentrations at 4 NADP sites and at Mt. Rainier.

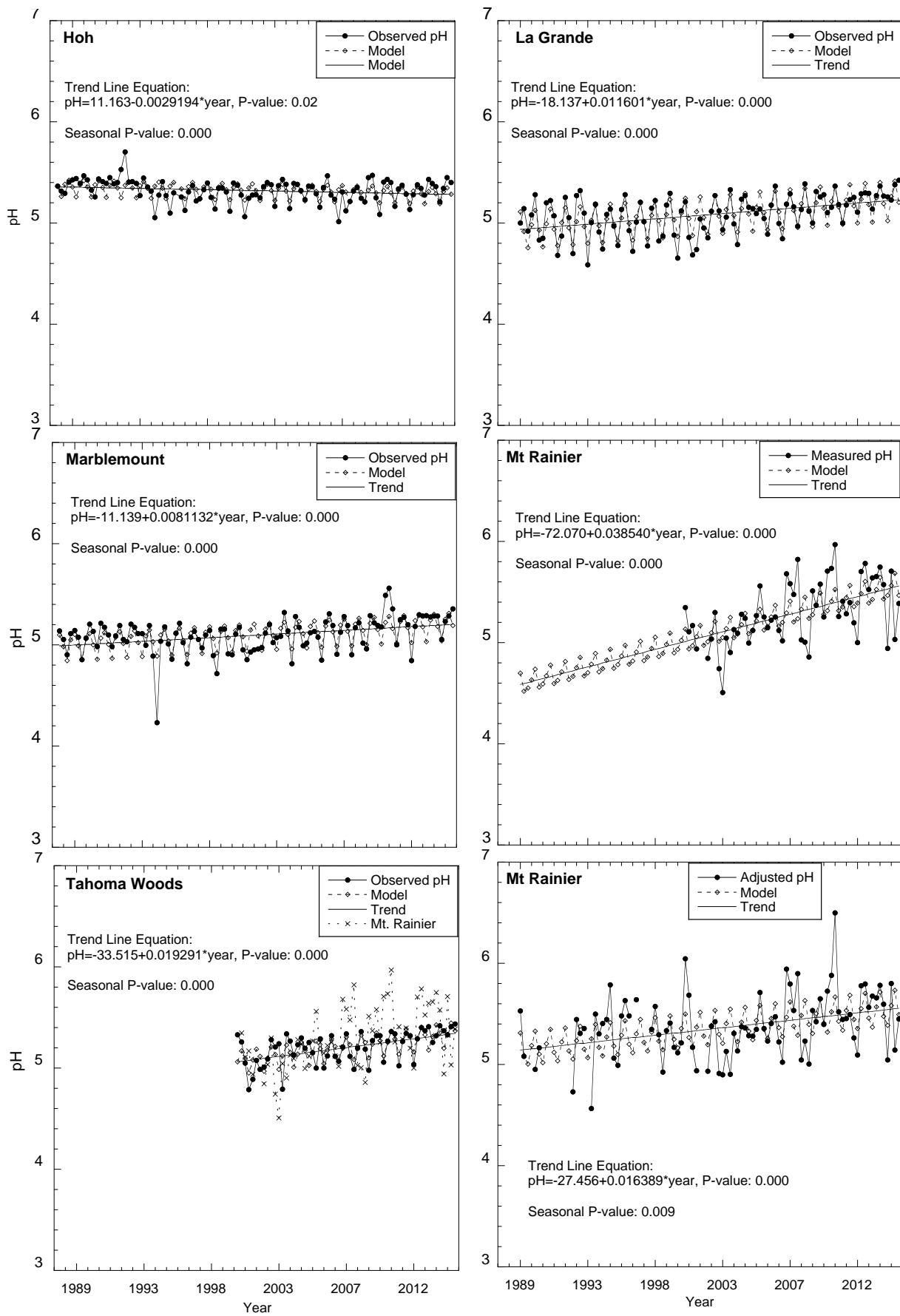


Figure 4b: Observed, Modeled and Trend including Trend Line Equation for pH values of precipitation at 4 NADP sites and at Mt. Rainier.

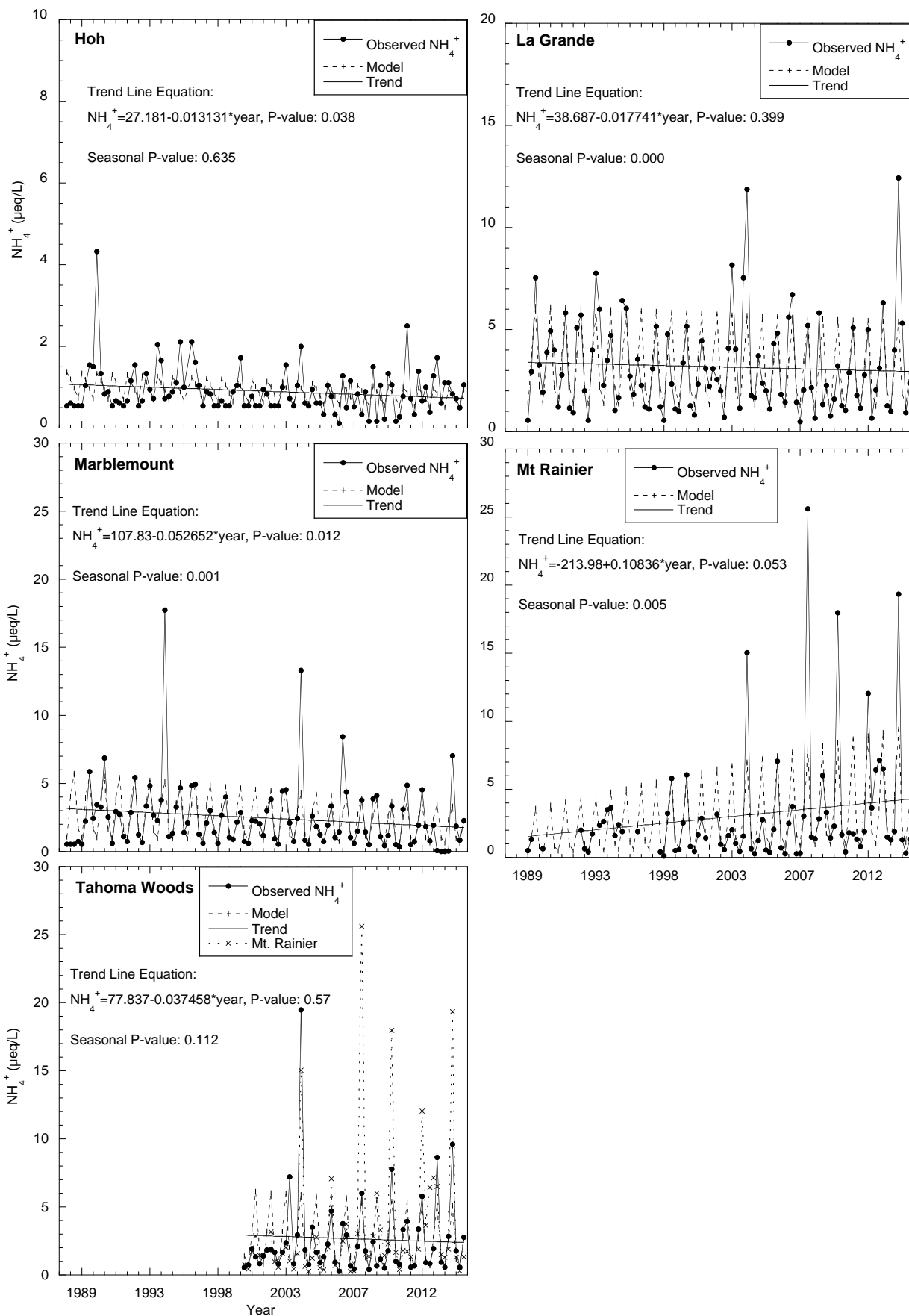


Figure 5: Observed, Modeled and Trend including Trend Line Equation for NH_4^+ precipitation concentrations at 4 NADP sites and at Mt. Rainier.

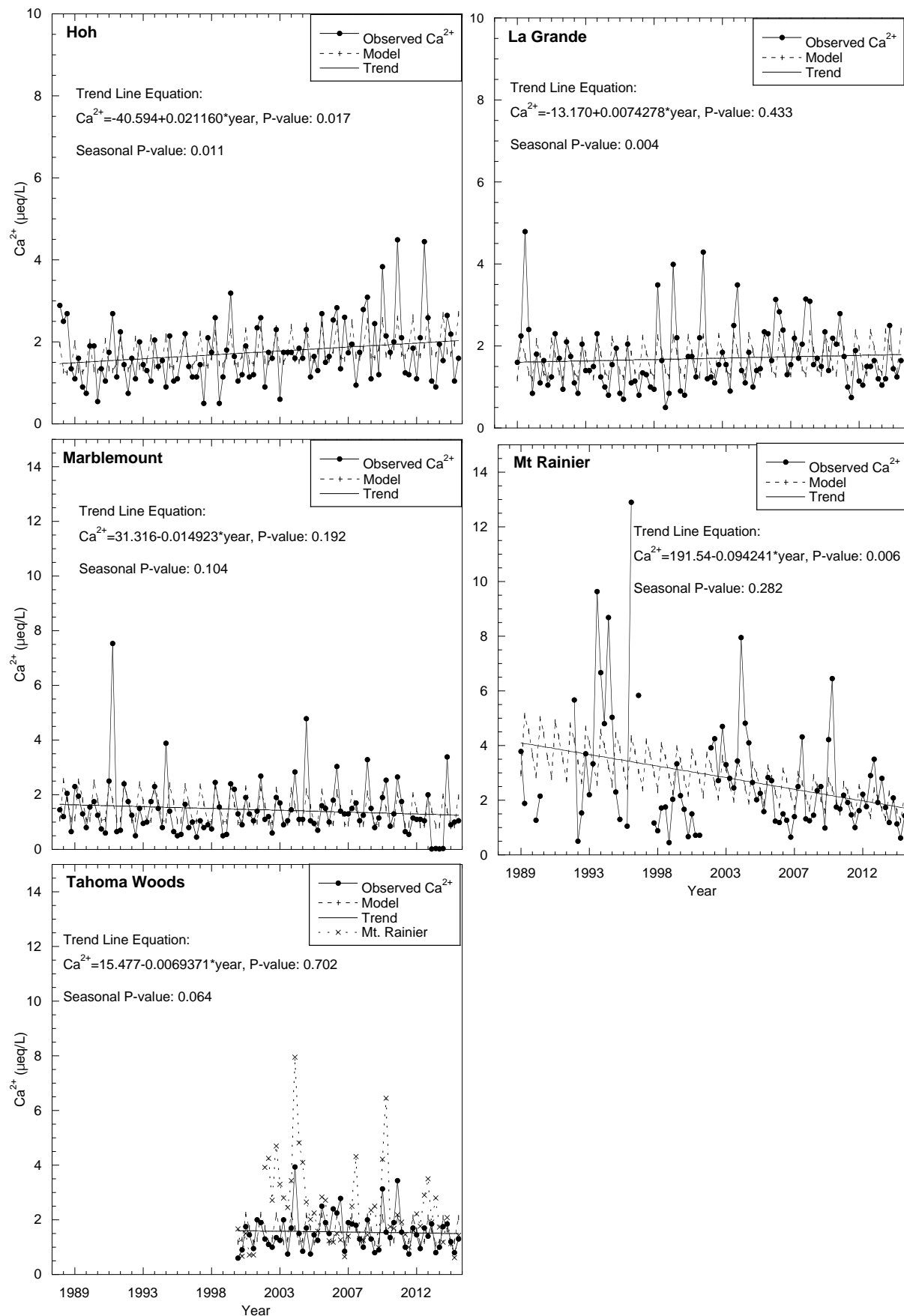


Figure 6: Observed, Modeled and Trend including Trend Line Equation for Ca^{2+} precipitation concentrations at 4 NADP sites and at Mt. Rainier.

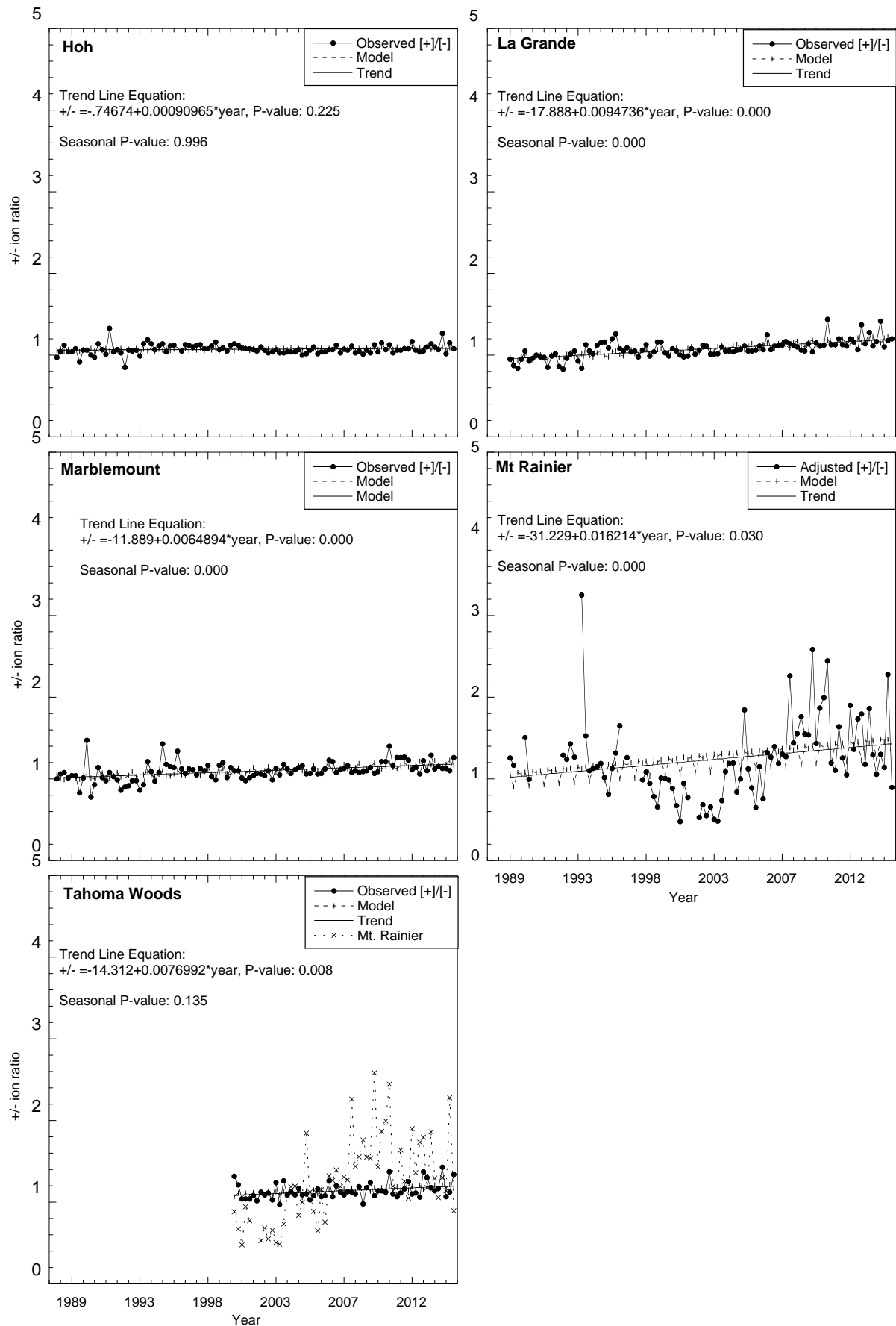


Figure 7: Observed, Modeled and Trend including Trend Line Equation for [+]/[-] charge ratio in precipitation at 4 NADP sites and at Mt. Rainier.

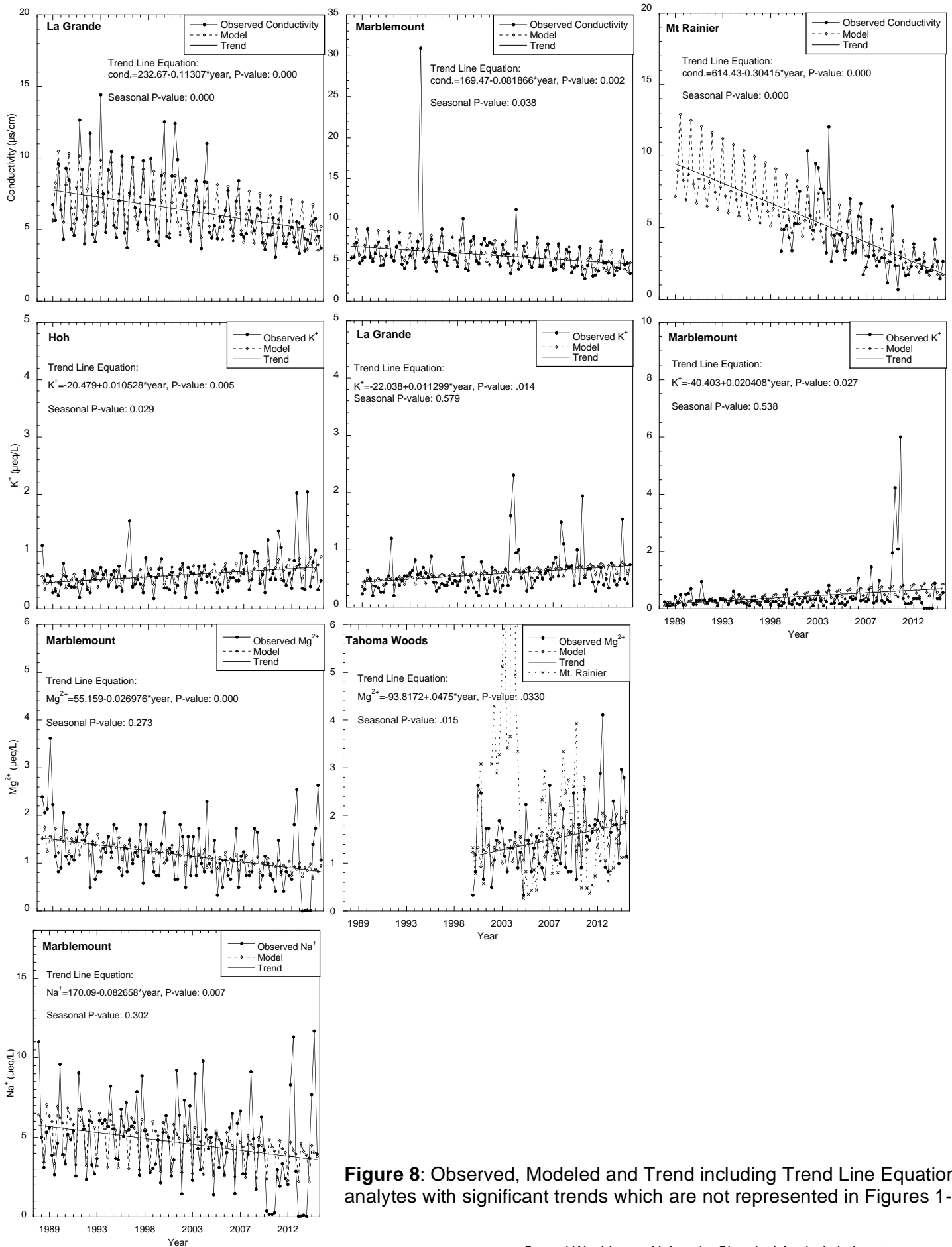


Figure 8: Observed, Modeled and Trend including Trend Line Equation for analytes with significant trends which are not represented in Figures 1-7