CHAPTER 8

EXPLORATION OF RELATIONSHIPS AMONG AEROSOLS

This chapter explores the relationship between the various aerosol species using multivariate techniques. In the first section, the relationship between variables is explored in a qualitative way using factor analysis techniques.[1,2] In the next section, relationships between variables are investigated using regressional techniques.

The investigation of relationships between aerosol species is complicated by the inherent interdependence between variables due to underlying common physical processes. For instance, at high elevation sites, a whole array of species may rise and fall together because of the diurnal variation of mixing height. As the air, which is trapped in nighttime inversions, mixes up to higher elevation monitoring sites, concentrations of all aerosol species may rise together. However, not all observables vary together. They are also influenced by spatial locations of sources and receptors and relative winds.

8.1 FACTOR ANALYSIS

The following factor analysis is exploratory in nature, seeking to find relationships among variables that may have underlying physical interpretations. Because sulfates and carbon species are usually responsible for most of the visibility reduction, it is of interest to explore relationships between these variables and various trace element species. Furthermore, much of the measured nitrate may be anthropogenic in nature and some attention will be given to how nitrates relate to other species. Specifically, the following questions will be explored:

Are there relationships between sulfur and trace element species?
Are there relationships between carbon species and trace element species?
Are there relationships between nitrates and trace element species?
Are there relationships between sulfur and nitrates and relative humidity?
Are there any distinctive sources associated with aerosol concentrations at the receptor sites?

The underlying development of factor analysis methodologies will not be presented here. There are a number of excellent treatments of the subject.[1,2] For the application here, factors are extracted and followed by a varimax orthogonal rotation.

The objective of factor analysis is to reduce the number of variables explaining the variance among the variables' underlying structure in the data set. Furthermore, by examining the variables with large weighting it is often possible to associate a component with a physical process or with specific source types. It also reveals underlying collinearity between variables.

8.1.1 THE DATA SET

Figures 8-1a through 8-1d and 8-2a through 8-2d present the variables used in the factor analysis for Tahoma Woods and Paradise. Figures 8-1a through 8-1d and 8-2a through 8-2d show fine mass, elemental sulfur, nitrate ion interpreted as ammonium nitrate, hydrogen and absorption in units of $\mu g/m^3$. b_{abs} is presented in terms of equivalent carbon mass assuming an absorption efficiency of 10 m^2/g. The remainder of the trace elements are in units of ng/m^3. Temporal presentations of the various carbon species can be found in Figures 7-1 and 7-3 in Chapter 7. Tables 8-1 and 8-2 are statistical summaries of the variables shown in Figures 8-1 and 8-2. However, in Tables 8-1 and 8-2 sulfur has been multiplied by 4.125 and should be interpreted as equivalent to ammonium sulfate mass. Temporal plots of relative humidity can be found in Chapter 6. Factor or other multivariate analysis was not carried out on the Marblemount data set because the high sensitivity analysis using XRF was not carried out at that site.

There is one large nitrate episode at Tahoma Woods starting on Julian day 190 (July 9) and ending about Julian day 205 (July 24). Sulfur, on the other hand, is not as episodic. It stays uniformly elevated at about 0.7-1.0 $\mu g/m^3$ from Julian day 190 to 230 (August 18), when it becomes more episodic in nature. Carbon species are more episodic with about a 7-10 day cycle.

At Paradise, the data set is somewhat abbreviated in that the monitoring site was snowed in until mid July. However, unlike the Tahoma Woods data set sulfur is episodic. Three sulfur episodes exceed 1.5 $\mu g/m^3$ of sulfur: JD=224-226 (Aug 12-13), JD=234-236 (Aug 22-23), and JD=244-246 (Sept 1-3). On the other hand, nitrate concentrations are less than 0.5 $\mu g/m^3$ except for two "spikes" on JDs 228 (Aug 16) and 232 (Aug 20).

8.1.2 FACTOR ANALYSIS OF TAHOMA WOODS AND PARADISE DATA SETS

Tables 8-3 and 8-4 present the results of factor extraction followed by a Varimax rotation. The tables list the factors in descending order according to the amount of variance explained. Only those factors corresponding to eigenvalues of the correlation matrix greater than one are retained.

Factor loadings greater than 0.60 are highlighted for reference. At Tahoma Woods factor 1 explains 7.57 (35%) of the variance and consists of trace elements normally associated with urban areas or transportation (See Appendix 5). Pb, Mn, Zn, and Ni are all associated with factor loadings greater than 0.8. High temperature organic carbons and low temperature light absorbing carbon are loaded highest in factor 1. This suggests an urban influence.

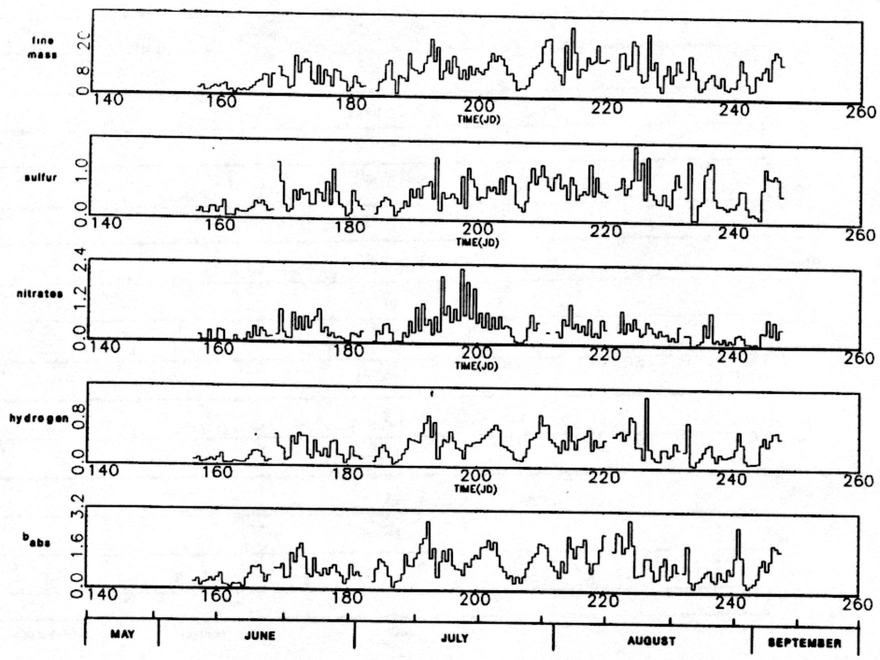

Figure 8-1a. Tahoma Woods: Temporal plot of fine mass, sulfur, ammonium nitrate, hydrogen, and optical absorption. All are presented in concentration units of μg/m^3. Optical absorption "mass" is calculated assuming an absorption efficiency of 10 m^2/g.

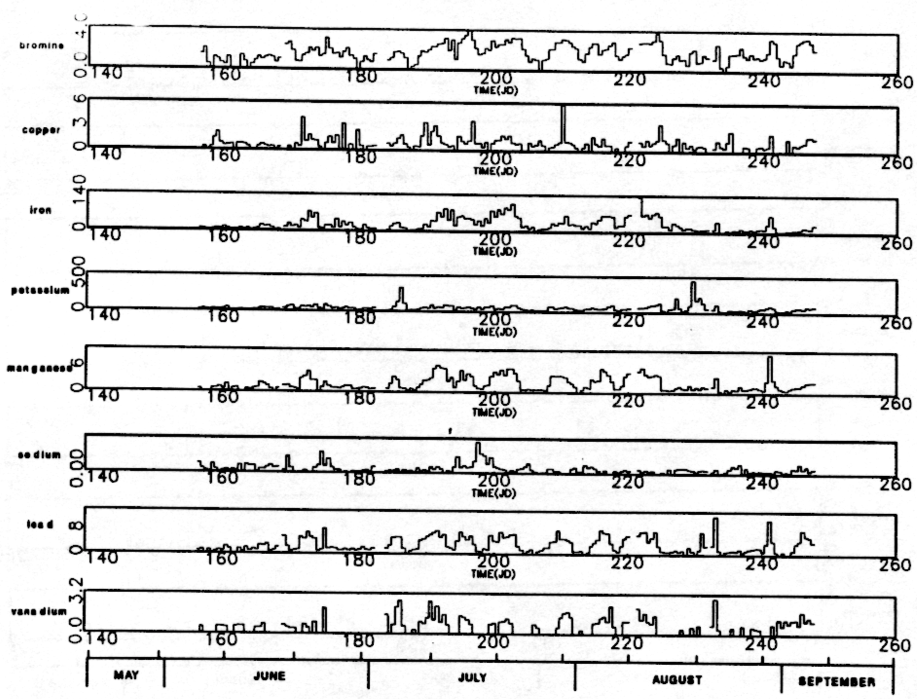

Figure 8-1b. Tahoma Woods: Temporal plot of Br, Cu, Fe, K, Mn, Na, Pb, and V. All are presented in concentration units of ng/m^3.

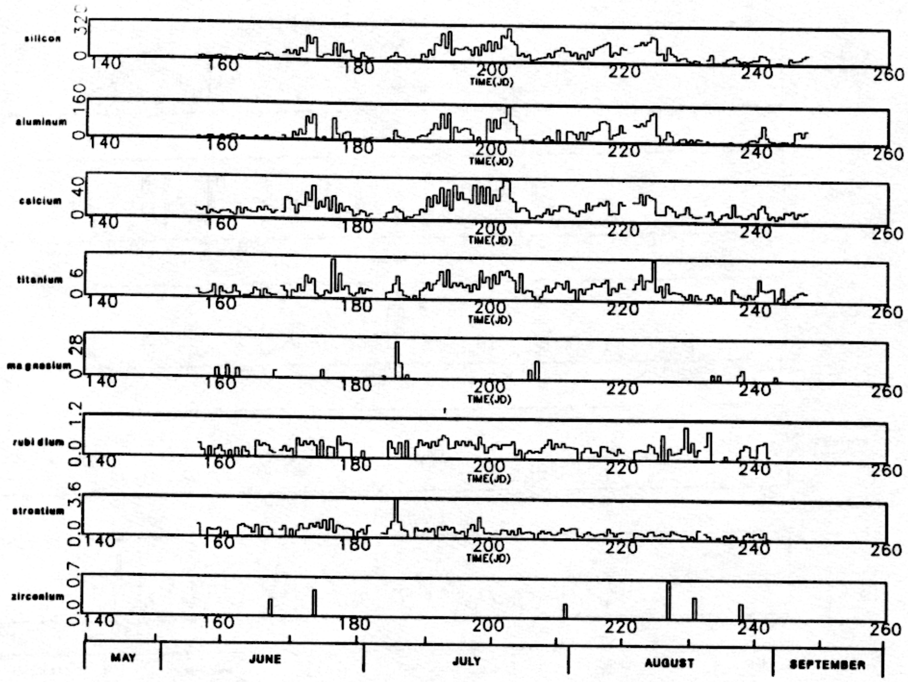

Figure 8-1c. Tahoma Woods: Temporal plot of Si, Al, Ca, Ti, Mg, Rb, Sr, and Zr. All are presented in concentration units of ng/m^3.

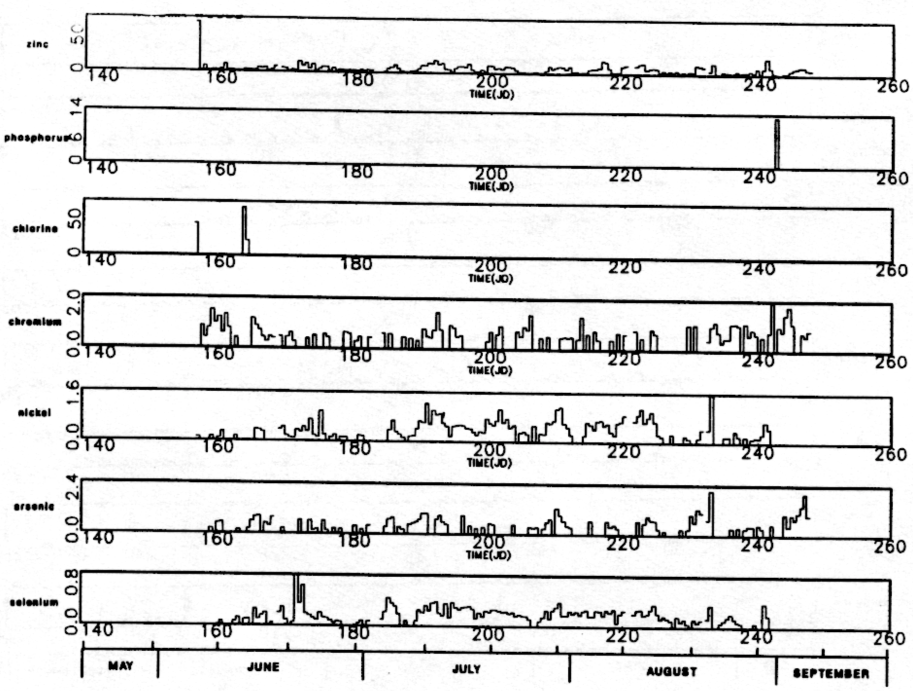

Figure 8-1d. Tahoma Woods: Temporal plot of Zn, P, Cl, Cr, Ni, As, and Se. All are presented in concentration units of ng/m^3.

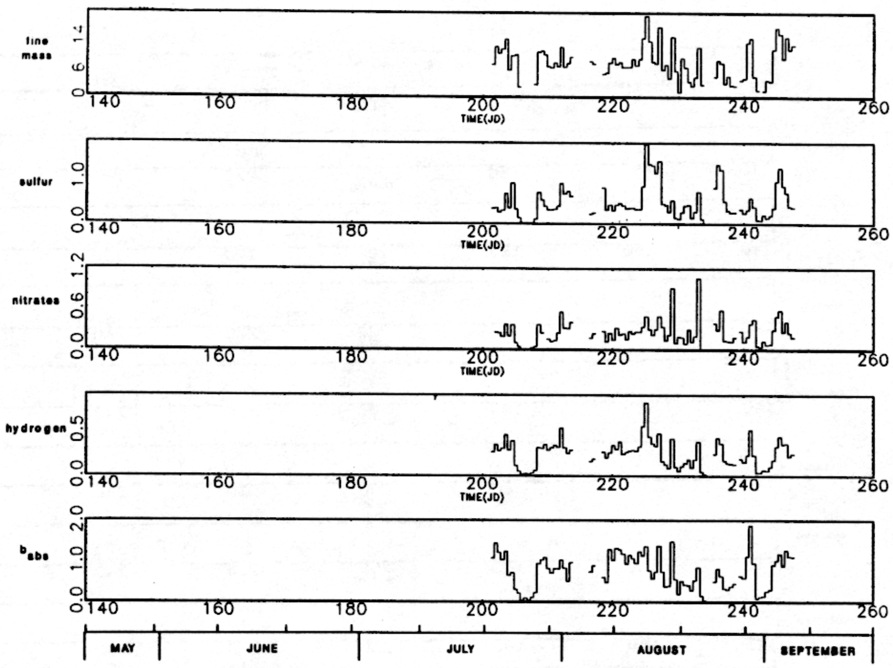

Figure 8-2a. Paradise: Temporal plot of fine mass, sulfur, ammonium nitrate, hydrogen, and optical absorption. All are presented in concentration units of μg/m^3. Optical absorption "mass" is calculated assuming an absorption efficiency of 10 m^2/g.

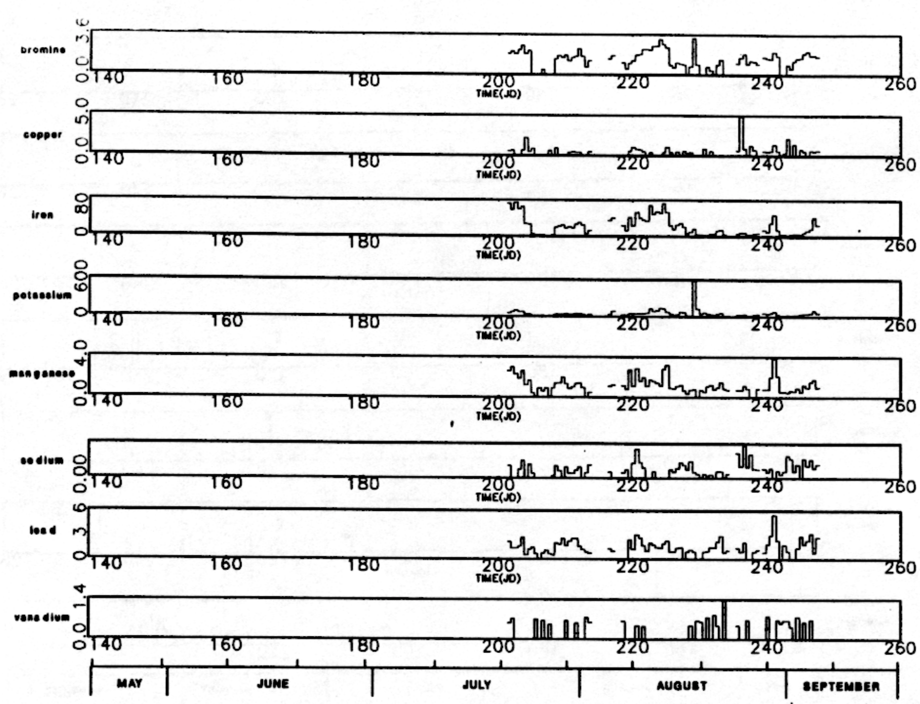

Figure 8-2b. Paradise: Temporal plot of Br, Cu, Fe, K, Mn, Na, Pb, and V. All are presented in concentration units of ng/m^3.

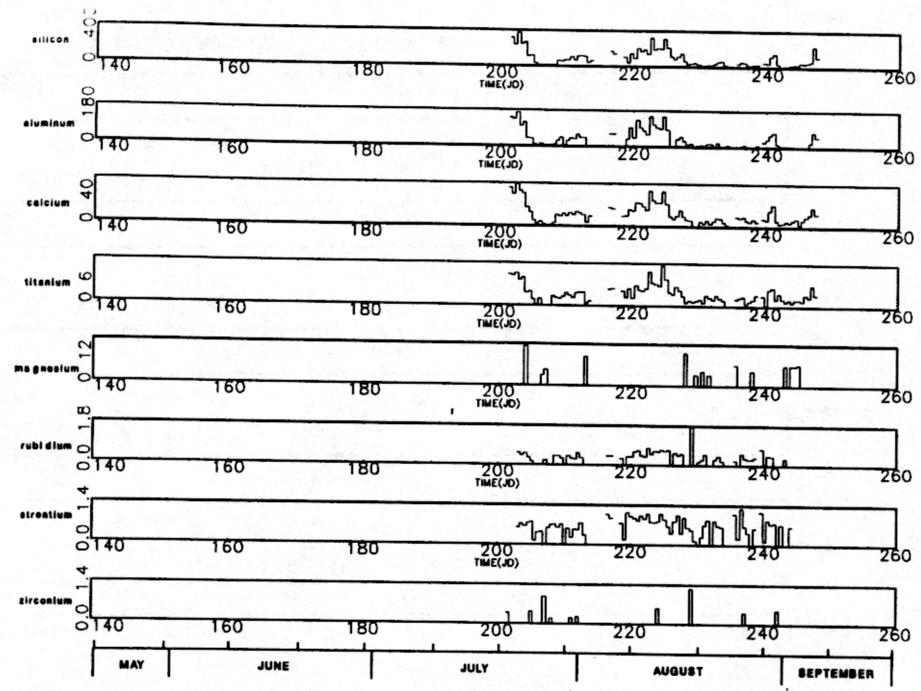

Figure 8-2c. Paradise: Temporal plot of Si, Al, Ca, Ti, Mg, Rb, Sr, and Zr. All are presented in concentration units of ng/m^3.

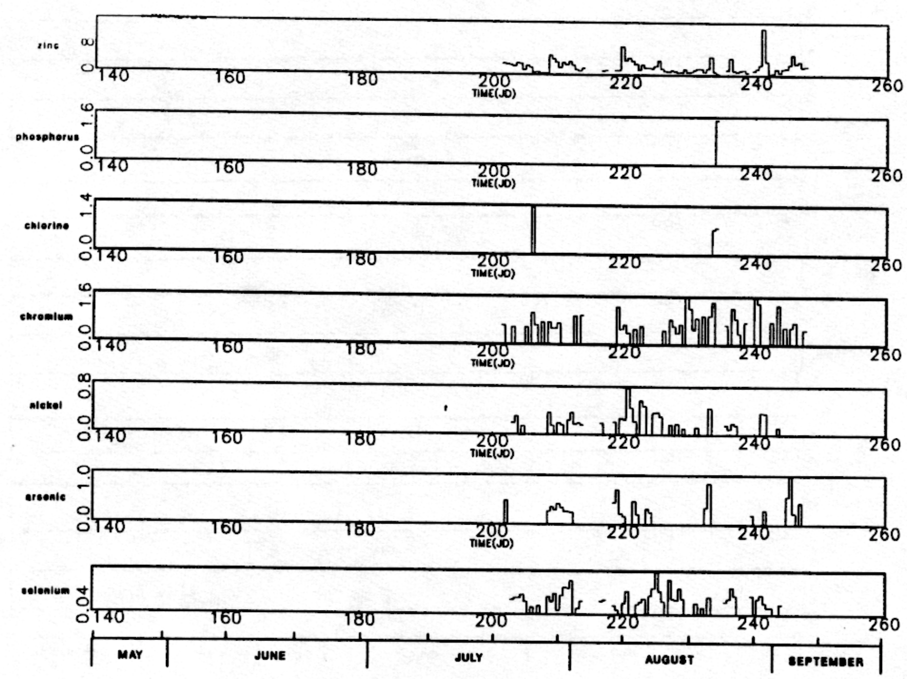

Figure 8-2d. Paradise: Temporal plot of Zn, P, Cl, Cr, Ni, As, and Se. All are presented in concentration units of ng/m^3.

Table 8-1. Statistical summary of aerosol mass concentrations measured at Tahoma Woods and used in a factor analysis.

VARIABLE	MEAN	STD DEV	MINIMUM	MAXIMUM	VALID
fine mass (μg/m^3)	9.72	5.66	0.86	28.18	177
$(NH_4)_2SO_4$ (μg/m^3)	2.44	1.47	0.20	7.16	177
NH_4NO_3 (μg/m^3)	0.44	0.38	0.00	2.28	170
H (μg/m^3)	0.35	0.23	0.04	1.27	177
b_{abs} (μg/m^3)	0.998	0.60	0.08	2.87	177
Br (ng/m^3)	1.75	0.91	0.00	4.00	177
Cu (ng/m^3)	0.87	0.86	0.00	5.88	177
Fe (ng/m^3)	26.37	24.46	0.97	134.88	177
K (ng/m^3)	51.92	49.26	6.37	451.04	177
Mn (ng/m^3)	1.97	1.70	0.00	9.32	177
Na (ng/m^3)	0.05	0.06	0.00	0.41	177
Pb (ng/m^3)	2.84	2.49	0.00	12.49	177
V (ng/m^3)	0.52	0.65	0.00	2.85	177
Si (ng/m^3)	71.16	62.72	0.00	296.70	177
Al (ng/m^3)	28.40	34.26	0.00	155.77	177
Ca (ng/m^3)	17.99	11.94	2.36	58.62	177
Ti (ng/m^3)	2.95	2.27	0.00	11.58	177
Mg (ng/m^3)	0.89	3.69	0.00	36.06	177
Rb (ng/m^3)	0.29	0.20	0.00	1.01	164
Sr (ng/m^3)	0.59	0.43	0.00	3.56	164
Zr (ng/m^3)	0.01	0.08	0.00	0.67	177
Zn (ng/m^3)	6.16	6.81	0.00	73.57	177
Cr (ng/m^3)	0.49	0.52	0.00	2.33	177
Ni (ng/m^3)	0.37	0.36	0.00	1.78	164
As (ng/m^3)	0.35	0.45	0.00	2.51	177
Se (ng/m^3)	0.19	0.16	0.00	1.00	164

Factor 2, explaining 5.9 (27%) of the variance, seems to be a soil factor. Furthermore, relative humidity is loaded negatively. Relative humidity is a good indicator of time of day; as daytime temperatures rise the relative humidity decreases while during the evening hours the relative humidity nearly always approaches 100% in most cases. The negative loading on RH suggests that as RH increases concentrations of trace elements in factor 2 decreases. Therefore, transport of trace elements associated with factor 2 into the Tahoma Woods area may be occurring during daytime hours.

An interesting aspect of factor 2 is that sulfur is loaded highest, although weakly, in this factor. Elemental fine sulfur is not normally associated with soil. There are a number of possible explanations: sulfur may be associated with soil; sulfur is being transported into Tahoma Woods during daylight hours and is thus collinear with soil trace elements; or "soil trace elements" are associated with coal-fired power plant emissions. The fine mass source profile for a coal-fired power plant, shown in Appendix 5, is rich in trace elements found in soil dust. Source profiles of a number of dust samples are also presented in Appendix 5.

The third factor consists of two variables which are highly loaded; nitrate and elemental sodium. Sodium is normally thought to be associated with sea salt, whereas, nitrates are not. However, there are a number of source profiles that are rich in Na and nitrates. These include lime, cement kilns, and oil combustion.

Other factors are less interesting. Factor 5 is primarily associated with low temperature organic carbon, and factor 7 with Zr.

At Paradise, factor 1, apparently the soil factor, is similar to factor 2 at Tahoma Woods. All the soil elements are loaded greater than 0.9, while relative humidity is loaded negatively at 0.82. Again the negative loading associated with RH suggests soil is transported into the area during daylight hours. However, at Paradise sulfur is not associated with the soil factor as it was at Tahoma Woods.

Factor 2 is associated with Rb, Zr, K, and low temperature light absorbing carbon. Examination of source profiles in Appendix 5 shows a number of sources emitting these trace elements. However, a unique source does not stand out.

Factor 3 is similar to factor 1 at Tahoma Woods. A number of the variables that load in the Tahoma Woods factor 1 are found in factor 3. This is the factor that is apparently associated with urban or transportation emissions. Some elements found in Tahoma Woods factor 1 are missing in Paradise factor 3. For some elements this may happen because those missing elements are below the detectable limit for much of the time. Vanadium is one example where this is apparently the case.

Factor 4 is associated with sulfur, nitrate, and Se. There are a number of sources associated with Se including coal-fired power plants. The Kraft recovery furnace, cement kiln (coal fired), oil-fired power plant, and wood-fired boiler all have source profiles that contain some Se.

Factors 5 and 7 essentially contain the single elements of Cu and Na, respectively. Interestingly Na is not associated with any other variable at Paradise. It is however, associated with nitrate at Tahoma Woods. Factor 6 contains low-temperature organic carbon and As with factor loadings of about 0.75.

Two common profiles that stand out at both Tahoma Woods and Paradise are soil dust and transportation or urban influence.

8.2 REGRESSION ANALYSIS

Linear regression analysis is often used to empirically relate a variable of interest, such as sulfates, to other aerosol species or to other atmospheric variables such as wind speed and direction. The relationships may have underlying physical interpretations such as when the wind blows from source A to receptor B, emissions from the source are transported to the receptor. Also, a source may directly emit sulfates or precursors to sulfates and a number of trace elements. The usual goal of multiple regression on observables is to find the best regression; the equation containing the fewest number of variables; and explaining the greatest variation in the independent variable. A number of regressional techniques, such as stepwise multiple linear regression, are available to meet this objective.[3] However, when applying regression analysis to environmental variables caution must be exercised because a number of variables may be highly correlated with each other.

An alternative to merely searching for the combination of variables that explain the maximum variance is to select unique aerosol species that are known to be associated with one or more sources, or to estimate the fraction of a species associated with a specific source and use the derived or unique variable in the regression analysis. Discussion and application of various apportionment schemes, their assumptions and relationship to physical processes is discussed in Appendix 1. In the following section, relationships among variables will be explored in an empirical way and where possible physical interpretations will be proposed.

Two strategies for selecting variables in the regression analysis were used. In the first approach, one variable was selected to represent each of the factors presented in Tables 8-3 and 8-4. Furthermore, if a variable was known to represent a potential source, and wasn't loaded in one of the factors, it was included in the regression. In the second approach, composite variables were formed by adding together those variables in each of the factors and weighting them according to their factor loadings. All variables and only those with weighting greater than 0.70 were used. However, neither of these approaches yielded results different from just using one variable to represent each factor. Therefore, the results of only the single variable approach will be presented here.

The variables used in the regressions are extracted from Tables 8-3 and 8-4. For Tahoma Woods, Pb was used to represent factor 1, Si for factor 2, Na for factor 3, K for factor 4, and Zr for factor 7. In addition, Br was included as a variable because it is known to be associated with automobile emissions; Se because of its association with coal-fired power plants, and ECHT because of its apparent association with sulfur. (This association was discussed in Chapter 7.)

Table 8-2. Statistical summary of aerosol mass concentrations measured at Paradise and used in a factor analysis.

VARIABLE	MEAN	STD DEV	MINIMUM	MAXIMUM	VALID
fine mass ($\mu g/m^3$)	8.19	3.97	1.03	19.39	78
$(NH_4)_2SO_4$ ($\mu g/m^3$)	1.91	1.51	0.02	7.32	84
NH_4NO_3 ($\mu g/m^3$)	0.24	0.18	0.00	1.06	82
H ($\mu g/m^3$)	0.25	0.15	0.01	0.82	84
b_{abs} ($\mu g/m^3$)	0.75	0.42	0.02	1.88	84
Br (ng/m^3)	1.30	0.84	0.00	3.33	84
Cu (ng/m^3)	0.42	0.67	0.00	4.94	84
Fe (ng/m^3)	26.93	25.59	0.00	93.78	84
K (ng/m^3)	47.27	68.13	0.00	599.74	84
M (ng/m^3)	1.18	0.79	0.00	3.92	84
Na (ng/m^3)	0.03	0.03	0.00	0.11	84
Pb (ng/m^3)	1.40	0.96	0.00	5.52	84
V (ng/m^3)	0.23	0.33	0.00	1.37	84
Si (ng/m^3)	90.11	87.07	3.59	376.76	84
Al (ng/m^3)	36.03	44.18	0.00	169.89	84
Ca (ng/m^3)	16.85	13.60	0.00	59.39	84
Ti (ng/m^3)	3.24	2.39	0.00	11.53	84
Mg (ng/m^3)	1.45	3.58	0.00	17.05	84
Rb (ng/m^3)	0.30	0.29	0.00	1.76	73
Sr (ng/m^3)	0.60	0.35	0.00	1.30	73
Zr (ng/m^3)	0.06	0.20	0.00	1.26	84
Zn (ng/m^3)	2.48	2.04	0.36	14.38	84
Cr (ng/m^3)	0.47	0.53	0.00	1.79	84
Ni (ng/m^3)	0.14	0.19	0.00	0.87	73
As (ng/m^3)	0.14	0.25	0.00	1.19	84
Se (ng/m^3)	0.10	0.09	0.00	0.40	73

Table 8-3. Results of factor analysis on the Tahoma Woods data set. Factor extraction was followed by a Varimax rotation. Variables with factor loadings greater than 0.6 are shaded for easy reference.

TAHOMA WOODS	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4	FACTOR 5	FACTOR 6	FACTOR 7
$(NH_4)_2SO_4$	0.09	0.66	0.13	0.21	-0.09	0.25	-0.01
NH_4NO_3	0.27	0.50	0.77	0.06	-0.00	-0.09	-0.02
OCLT	0.11	0.08	0.05	-0.01	0.92	0.01	0.09
OCHT	0.72	0.50	-0.08	0.17	0.15	-0.02	-0.01
ECLT	0.85	0.41	-0.00	0.15	-0.04	0.10	0.08
ECHT	0.23	0.37	-0.13	-0.04	0.69	-0.05	-0.10
b_{abs}	0.69	0.56	-0.08	0.14	0.18	0.10	0.11
Br	0.60	0.55	0.16	0.17	0.15	0.15	0.07
Cu	0.52	0.12	0.04	-0.04	-0.11	-0.52	0.01
Fe	0.57	0.74	0.07	-0.01	0.23	-0.10	-0.01
K	0.19	0.10	-0.02	0.73	-0.09	-0.07	0.30
Mn	0.84	0.43	-0.05	-0.04	0.11	-0.00	-0.02
Na	-0.10	0.02	0.94	-0.01	-0.06	0.06	0.05
Pb	0.92	0.15	-0.01	0.08	0.15	0.00	0.03
V	0.75	-0.06	-0.00	0.30	0.15	0.07	-0.17
Zn	0.86	0.20	0.02	0.08	-0.01	-0.07	0.02
Si	0.40	0.85	0.01	0.05	0.22	-0.10	-0.01
Al	0.45	0.74	-0.14	-0.02	0.20	-0.15	0.05
Ca	0.40	0.72	0.40	0.09	0.18	-0.13	0.01
Ti	0.24	0.83	0.04	0.15	0.12	-0.19	-0.11
Rb	0.38	0.25	-0.02	0.59	-0.05	0.01	0.01
Sr	-0.05	0.03	0.31	0.64	0.18	-0.40	-0.31
Zr	-0.06	-0.09	0.03	0.10	0.04	-0.04	0.92
Cr	0.07	-0.08	0.05	-0.14	-0.04	0.63	-0.03
Ni	0.81	0.32	0.10	0.14	0.12	0.19	-0.05
As	0.34	-0.14	-0.16	0.43	0.00	0.47	-0.03
Se	0.60	0.31	0.25	0.12	0.03	-0.20	-0.17
RH	-0.09	-0.67	-0.29	0.11	0.01	0.24	0.11

Variance explained by each factor						
FACTOR1	FACTOR 2	FACTOR 3	FACTOR 4	FACTOR 5	FACTOR 6	FACTOR 7
7.57	5.90	2.04	1.83	1.73	1.41	1.16

Table 8-4. Results of factor analysis on the Paradise data set. Factor extraction was followed by a Varimax rotation. Variables with factor loadings greater than 0.6 are shaded for easy reference.

PARADISE	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4	FACTOR 5	FACTOR 6	FACTOR 7
$(NH_4)_2SO_4$	0.07	0.03	0.10	0.86	0.20	-0.08	0.13
NH_3NO_3	-0.09	0.52	0.24	0.66	-0.04	0.28	0.16
OCLT	0.21	-0.08	0.18	-0.17	0.15	0.74	0.02
OCHT	0.59	0.42	0.35	0.31	0.13	0.06	-0.24
ECLT	0.26	0.71	0.52	0.12	-0.04	0.02	0.07
ECHT	0.38	-0.11	0.22	0.58	0.15	0.25	-0.17
b_{abs}	0.53	0.42	0.57	0.25	0.10	0.14	0.03
Br	0.60	0.54	0.19	0.22	0.22	0.04	0.01
Cu	-0.18	-0.18	0.24	0.07	0.79	-0.19	0.18
Fe	0.92	0.16	0.27	0.15	0.05	0.03	-0.09
K	0.06	0.94	0.02	0.01	-0.01	-0.05	-0.08
Mn	0.57	0.01	0.68	0.30	-0.02	0.01	-0.11
Na	-0.10	-0.08	-0.02	0.16	0.03	-0.16	0.87
Pb	0.33	0.04	0.81	0.17	-0.00	0.09	0.01
V	-0.38	-0.26	0.01	-0.19	-0.57	-0.35	-0.17
Zn	0.11	0.02	0.91	0.05	0.26	0.16	-0.05
Si	0.94	0.10	0.19	0.17	0.05	0.02	-0.05
Al	0.94	0.05	0.27	0.02	0.01	0.02	-0.02
Ca	0.94	0.01	0.22	0.10	0.09	0.00	0.02
Ti	0.90	0.04	0.12	0.21	0.03	-0.06	-0.13
Rb	0.41	0.78	0.03	0.18	0.09	0.02	0.11
Sr	0.54	0.08	0.09	0.35	0.03	0.23	0.28
Zr	-0.17	0.85	-0.13	-0.02	0.00	-0.10	-0.16
Cr	-0.27	-0.17	0.03	-0.18	-0.63	-0.00	0.30
Ni	0.45	0.02	0.53	0.34	-0.16	0.11	0.22
As	-0.06	-0.00	0.09	0.10	-0.19	0.75	-0.19
Se	0.22	0.18	0.17	0.68	0.06	-0.21	0.06
RH	-0.83	-0.05	0.01	0.27	-0.06	-0.23	-0.00

Variance explained by each factor						
FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4	FACTOR 5	FACTOR 6	FACTOR 7
7.69	3.86	3.47	2.91	1.68	1.68	1.28

At Paradise, Si was used to represent factor 1, K for factor 2, Pb for factor 3 (Zn is loaded higher in factor 3 but because Pb was used at Tahoma Woods it is used at Paradise also), Cu for factor 5, As for factor 6, and Na for factor 7. Se and ECHT are both weakly loaded into factor 4 and both were included separately as variables.

Stepwise regressions were carried out using the above species as independent variables. Ammonium sulfate, ammonium nitrate, b_{abs}, organic mass, and light absorbing carbon (LAC) were dependent variables. A number of variables added to the regression model were negative. A negative variable is suggestive of collinearities between it and other variables. Therefore, all negative variables were removed from the final regression model.

Tables 8-5 through 8-8 present the results for Tahoma Woods while Tables 8-9 through 8-12 present the analysis for Paradise. In each table the variable parameter estimate, standard error, and F are presented. As part of each table the order in which the variable was entered the partial r^2 and model r^2 are also listed. For easier examination these results are summarized in Table 8-13. Each variable used in the regression models is listed along with the order in which they were added to the model, the partial r^2, and model r^2. Also presented in Table 8-13, is the average fraction of the aerosol species (dependent variable) associated with each independent variable.

Interpretation of these results should be used in a semi-quantitative way. Even though variables used in the regression models were selected on the basis of a factor analysis and should not be excessively collinear, each of the variables is associated with more than one source. The analysis is meant to give some insight into the source types associated with secondary species at the two receptor sites.

8.2.1 The Tahoma Woods Data Set

When interpreting Table 8-13 the reader should refer to the source profiles presented in Appendix 5. At Tahoma Woods the r^2 associated with the sulfate model is 0.42 while all other models have r^2 that are 0.80 or greater. The first variable added to the sulfate model is Br, the second is Si and the third is Se. Apportionment of sulfur to these three species yields 33%, 19%, and 12%, respectively. Bromine is associated with transportation and with agricultural and wood burning. However, fine K is emitted by agricultural or slash burning and it is not related to sulfur. Therefore, sulfur associated with bromine may be primarily associated with transportation. On the other hand, Pb is not linked to sulfur but is usually thought of as being a transportation tracer. It may be that Br is representative of both transportation and burning and more highly correlated with sulfur than either Pb or K.

Si is usually associated with soil. However, burning and coal-fired power plants also emit significant amounts of Si. Most emissions associated with Se are from coal-fired power plants and a large fraction of Se is expected to be emitted from the Centralia Power Plant. However, examination of the source profiles in Appendix 5 shows that Se is also emitted from other sources such as kilns and recovery furnaces.

Table 8-5. Tahoma Woods: Results of a stepwise ordinary least square regression analysis with sulfur as the dependent variable and Si, Br, and Se as independent variables. Also presented in the table is the order in which the variables were added to the regression model and the partial r^2 associated with each variable.

Sulfur			$r^2 = 0.42$	
Variable	Estimate	Std Error	Sum of Squares	F
INTERCEPT	0.86	0.19	25.73	20.66
Si	0.01	0.00	13.16	10.56
Br	0.45	0.15	11.74	9.43
Se	1.55	0.71	5.96	4.79

Summary of Stepwise Procedure

Step	Variable	# In	Partial r^2	Model r^2
1	Br	1	0.348	0.35
2	Si	2	0.056	0.40
3	Se	3	0.017	0.42

Table 8-6. Tahoma Woods: Results of a stepwise ordinary least square regression analysis with ammonium nitrate as the dependent variable and Si, Se, Na, K, and ECHT as independent variables. Also presented in the table is the order in which the variables were added to the regression model and the partial r^2 associated with each variable.

Nitrate			$r^2 = 0.82$	
Variable	Estimate	Std Error	Sum of Squares	F
INTERCEPT	-0.12	0.04	0.30	10.86
Si	0.0022	0.0003	1.74	62.42
Se	0.59	0.11	0.82	29.45
Na	4.34	0.25	8.46	304.41
K	0.00065	0.00027	0.16	5.89
ECHT	0.26	0.15	0.08	2.88

Summary of Stepwise Procedure

Step	Variable	# In	Partial r^2	Model r^2
1	Na	1	0.443	0.44
2	Si	2	0.320	0.76
3	Se	3	0.048	0.81
4	K	4	0.006	0.82
5	ECHT	5	0.004	0.82

Table 8-7. Tahoma Woods: Results of a stepwise ordinary least square regression analysis with organic carbon as the dependent variable and Si, Se, Pb, and Br as independent variables. Also presented in the table is the order in which the variables were added to the regression model and the partial r^2 associated with each variable.

Organic Carbon			r^2 = 0.80	
Variable	Estimate	Std Error	Sum of Squares	F
INTERCEPT	0.19	0.18	1.20	1.11
Si	0.01	0.00	35.21	32.58
Se	1.09	0.70	2.64	2.44
Pb	0.28	0.05	32.57	30.14
Br	0.88	0.15	35.15	32.53

Summary of Stepwise Procedure

Step	Variable	# In	Partial r^2	Model r^2
1	Br	1	0.675	0.68
2	Pb	2	0.069	0.74
3	Si	3	0.050	0.79
4	Se	4	0.003	0.80

Table 8-8. Tahoma Woods: Results of a stepwise ordinary least square regression analysis with light absorbing carbon as the dependent variable and Si, Se, K, pb, and Br as independent variables. Also presented in the table is the order in which the variables were added to the regression model and the partial r^2 associated with each variable.

Light Absorbing Carbon			r^2 = 0.86	
Variable	Estimate	Std Error	Sum of Squares	F
INTERCEPT	0.07	0.03	0.14	5.04
Si	0.0019	0.0003	1.05	36.54
Se	0.23	0.11	0.12	4.23
K	0.0005	0.0003	0.09	3.12
Pb	0.09	0.01	3.81	133.27
Br	0.09	0.03	0.35	12.12

Summary of Stepwise Procedure

Step	Variable	# In	Partial r^2	Model r^2
1	Pb	1	0.731	0.73
2	Si	2	0.107	0.84
3	Br	3	0.016	0.85
4	Se	4	0.004	0.86
5	K	5	0.003	0.86

Table 8-9. Paradise: Results of a stepwise ordinary least square regression analysis with sulfur as the dependent variable and Se, Cu, and ECHT as independent variables. Also presented in the table is the order in which the variables were added to the regression model and the partial r^2 associated with each variable.

Sulfur			$r^2 = 0.52$	
Variable	Estimate	Std Error	Sum of Squares	F
INTERCEPT	0.02	0.27	0.01	0.01
Se	7.07	1.45	25.37	23.94
Cu	0.38	0.18	4.96	4.68
ECHT	3.95	1.11	13.47	12.71

Summary of Stepwise Procedure

Step	Variable	# In	Partial r^2	Model r^2
1	Se	1	0.363	0.36
2	ECHT	2	0.118	0.48
3	Cu	3	0.036	0.52

Table 8-10. Paradise: Results of a stepwise ordinary least square regression analysis with ammonium nitrate as the dependent variable and K, SE, Na, As, and ECHT as independent variables. Also presented in the table is the order in which the variables were added to the regression model and the partial r^2 associated with each variable.

Nitrate			$r^2 = 0.65$	
Variable	Estimate	Std Error	Sum	F
INTERCEPT	-0.04	0.03	0.02	1.64
K	0.0012	0.0002	0.53	38.09
Se	0.52	0.17	0.13	9.29
Na	1.65	0.57	0.12	8.34
As	0.23	0.07	0.15	10.55
ECHT	0.44	0.13	0.16	11.74

Summary of Stepwise Procedure

Step	Variable	# In	Partial r^2	Model r^2
1	K	1	0.28	0.28
2	ECHT	2	0.20	0.47
3	Se	3	0.075	0.55
4	As	4	0.052	0.60
5	Na	5	0.048	0.65

Table 8-11. Paradise: Results of a stepwise ordinary least square regression analysis with organic carbon as the dependent variable and Si, Se, Pb, and Br as independent variables. Also presented in the table is the order in which the variables were added to the regression model and the partial r^2 associated with each variable.

Organic Carbon			r^2 = 0.79	
Variable	Estimate	Std Error	Sum of Squares	F
INTERCEPT	0.39	0.18	2.73	5.00
Si	0.006	0.002	7.14	13.09
K	0.003	0.002	2.66	4.89
Pb	0.38	0.11	6.59	12.09
Br	0.63	0.19	6.03	11.07
As	0.91	0.44	2.34	4.30

Summary of Stepwise Procedure

Step	Variable	# In	Partial r^2	Model r^2
1	Br	1	0.670	0.67
2	Pb	2	0.068	0.74
3	Si	3	0.030	0.77
4	As	4	0.015	0.78
5	K	5	0.012	0.79

Table 8-12. Paradise: Results of a stepwise ordinary least square regression analysis with light absorbing carbon as the dependent variable and Si, K, Pb, Cu, and As as independent variables. Also presented in the table is the order in which the variables were added to the regression model and the partial r^2 associated with each variable.

Light Absorbing Carbon			r^2 = 0.77	
Variable	Estimate	Std Error	Sum of Squares	F
INTERCEPT	0.09	0.028	0.09	10.31
Si	0.0011	0.0002	0.22	27.11
K	0.0013	0.0002	0.14	41.51
Pb	0.076	0.017	0.17	19.10
Cu	0.047	0.021	0.04	5.16
As	0.18	0.071	0.03	6.64

Summary of Stepwise Procedure

Step	Variable	# In	Partial r^2	Model r^2
1	Si	1	0.445	0.45
2	K	2	0.150	0.60
3	Pb	3	0.109	0.71
4	As	4	0.022	0.73
5	Cu	5	0.019	0.75

The first variable to be added to the nitrate model is Na and the second is Si. Together these two variables form a model with an r^2 of 0.76. Adding Se, K and ECHT increases the model r^2 to 0.82. Na accounts for 37% of the nitrate while Si accounts for 28%, and Se for 19%. Nitrates are expected to be formed from NO_x emitters. NO_x emitters, which are also known as NO emitters, are cement kilns and the Kraft recovery furnace (pulp and paper).

Examination of other source profiles suggests that combustion sources emitting significant amounts of Na are slash or agricultural burns. Coal-fired power plants emit a significant fraction of NO_x and it is not surprising that Se is related to nitrates. Likewise, if the source of Si is either coal-fired power plants or burning activity, then one would expect to see a correlation between it and nitrates. The lack of correlation between nitrates and Br or Pb is surprising. Apparently, nitrates at Tahoma Woods are not from urban or transportation type emissions.

As with sulfate, Br is the first variable to be added to the organic model. Pb is the second variable added. Br and Pb together strongly suggest transportation and burning as the sources of organic aerosol. On the other hand, LAC is more closely tied to Pb emissions suggesting a transportation source. Br accounts for the second largest fraction of LAC. Si is also linked to carbon emissions. As pointed out, significant amounts of silicon are emitted by fire-related activity and coal-fired boilers. However, it is not expected that significant amounts of organics are emitted by coal burning activity.

8.2.2 The Paradise Data Set

Not surprisingly, there are obvious similarities between Paradise and Tahoma Woods. But there are also some significant differences. For the Paradise data set Se is responsible for most of the explained variance in the sulfur data set, while ECHT is second. Together these two variables account for 87% of the measured sulfur.

As in the Tahoma Woods data set Na is linked to most of the nitrates with Se, ECHT and K also being significant contributors. The close association of nitrates with Na suggests pulp and paper mill or cement kiln contributions to nitrates, while ECHT and K both suggest burning activity to nitrate levels. Se is suggestive of coal-fired boilers.

There is a significant difference in the relationship between OCM and LAC and tracer material between Tahoma Woods and Paradise. Like Tahoma Woods the link between OCM, Br, and Pb is strong. However, unlike Tahoma Woods, K is correlated with organics at Paradise. Furthermore, at Paradise LAC is strongly associated with K while at Tahoma Woods it is not. Carbon is more strongly tied to urban and transportation emissions at Tahoma Woods, while at Paradise there is a clear association between burning and carbon.

8.3 SUMMARY

There are some obvious surprises in the relationship between the dependent and independent variables. Even though the SO_2 emission inventory presented in Chapter 1 suggested Centralia Power Plant as the single largest SO_2 emitter, it doesn't seem to be the largest contributor to sulfates at Tahoma Woods. At Paradise it may be a large contributor but so are other sources. If all the Se were from Centralia Power Plant, and it probably is not, then the regressions suggest that at Tahoma Woods only about 10% of the sulfur could be attributed to the power plant, while at Paradise it's contribution could be between 30% and 40%.

Furthermore, the lack of any relationship between Na and sulfur tends to rule out the ocean as a significant contributor to ambient sulfur concentrations. Apparently transportation, agricultural and wood burning, and coal-fired power plants all contribute to a fraction of measured sulfur.

Another unanticipated relationship is the strong link between transportation activity and organic and light absorbing carbon levels. Organic aerosols are not only associated with agricultural or wood burning, but also, to a large degree, with transportation activities.

Finally, there is evidence that nitrates are associated not only with transportation and fire related activities, but also, to a large degree, with pulp and paper mill activity or with cement kilns.

Table 8-13. Summary of the regression analysis for Tahoma Woods and Paradise. The partial r^2 are presented along with the percent contribution to the independent variable associated with each independent variable. For instance the amount of sulfur mass associated with Br is derived by multiplying the Br regression coefficient by the average Br concentration. The percent sulfur identified with Br is then calculated by dividing the "Bromine sulfur" by the total predicted sulfur.

TAHOMA WOODS		Si	Br	Se	Na	K	ECHT	Pb
Sulfur	r^2	0.06	0.35	0.02				
	%	19	33	12				
NO_3	r^2	0.32		0.05	0.44	0.01	<0.01	
	%	16		11	21	3	6	
OCM	r^2	0.05	0.68	<0.01				0.07
	%	21	45	6				23
LAC	r^2	0.11	0.02	<0.01		<0.01		0.73
	%	20	23	6		4		36

PARADISE		Si	Br	Se	Na	K	ECHT	Pb	Cu	As
Sulfur	r^2			0.36			0.12		0.04	
	%			37			50		10	
NO_3	r^2			0.08	0.05	0.28	0.20			0.05
	%			13	41	12	26			8
OCM	r^2	0.03	0.67			0.01		0.07		0.02
	%	22	32			6		20		5
LAC	r^2	0.45				0.15		0.11	0.02	0.02
	%	23				15		28	5	6

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