

**DEPOSITION HISTORY OF ATMOSPHERIC CHEMICALS AT TERRESTRIAL SINKS  
IN NEW YORK STATE**

**FINAL REPORT**

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## 1. Introduction

The introduction of airborne pollutants into ecosystems has become a recent concern with the acid rain issue, particularly in the northeastern United States and Canada. Atmospheric radiotracers, such as natural  $^{210}\text{Pb}$  are transported with other particulate matter in the atmosphere and can be used to determine the historical sequence of trace chemical deposition in various ecosystems. To fully understand how an ecosystem responds to changes in anthropogenic emissions, a reasonably accurate estimate of the historical record of regional chemical deposition is essential.

This project addressed the Hudson River Foundation's goal of determining the history of pollutant inputs to the Hudson River system. We applied proven  $^{210}\text{Pb}$  dating and trace analysis techniques (Schell, 1987) to study pollutant deposition in the Hudson River system by analyzing cores collected from the Black Rock Forest area (near West Point) and the Tivoli South Bay and Stockport Flats freshwater marshes. The Black Rock Forest bog component of this study provides information on the atmospheric chemical deposition on terrestrial ecosystems at highlands above the Hudson River. The marshland areas include both atmospheric and riverine inputs to the sediments. This component of the study addresses the Foundation's interest in the role of wetlands in the Hudson River ecosystem. These results provide information on the deposition and relative importance of airborne pollutants into the Hudson River ecosystem over the past 200 years.

### 1.1 Statement of Research Goals and Objectives

The principal goal of this study was to establish the deposition history of anthropogenic chemicals in the Hudson River ecosystem. This final report addresses these questions:

- (1) Is  $^{210}\text{Pb}$  dating applicable to the bog and wetland areas under study?
- (2) How do freshwater marshland and mountaintop areas compare as sinks for the deposition of airborne pollutants?

## 2. Results and Discussion

Sampling protocols and analytical methodology were described in earlier reports (see Tobin and Schell, 1988a, 1988b), and are summarized in Appendix 1. Elemental concentrations (C, H, N, total CHN, Na, Mg, Al, P, S, K, Ca, V, Fe, Cu, As, Cd, Pb, in  $\mu\text{g g}^{-1}$ ) for the Black Rock Forest, Tivoli South Bays, and Stockport Flats sampling areas are presented in Appendix 2. Using the bulk sedimentation rate profiles obtained from the "CRS/MV" (Tobin and Schell, 1987)  $^{210}\text{Pb}$  date estimates, concentrations were converted to elemental deposition rates ( $\mu\text{g cm}^{-2} \text{yr}^{-1}$ ), also given in Appendix 2. (The deposition rate profiles for Pb, Cd, and Cu were discussed in Tobin and Schell, 1989). In addition, enrichment factors calculated by normalizing individual deposition rates to the product of the observed deposition rate for Aluminum and the soil elemental abundance ratio (natural concentration of element/natural concentration of Al, from Valković (1975)), are included in Appendix 2. Appendix 3 is an atlas of deposition and enrichment factor profiles for the three locations that comprises the bulk of this report.

### 2.1 Intra-site comparison of deposition rates and enrichment factors

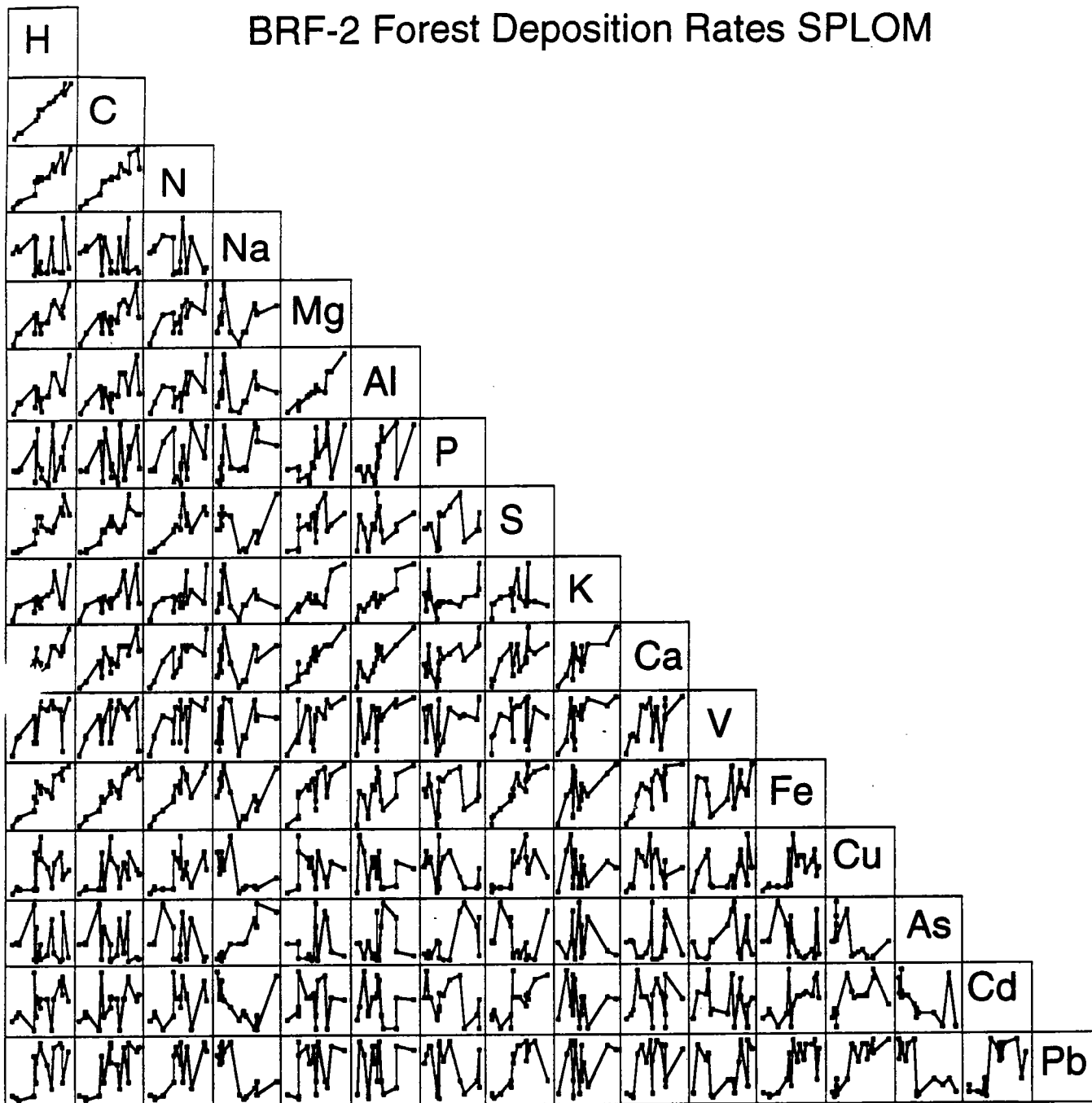
#### 2.1.1 Black Rock Forest Bog.

SPLOM (Scatterplot Matrix, Cleveland, (1985)) plots of elemental deposition rate and enrichment factor data for the Black Rock Forest site (BRF) are presented in Figures 1 and 2, respectively. The analogous Pearson Correlation Matrices are given in Tables 1 and 2. Referring to Figure 1 and Table 1, the deposition rates for H, C, N are highly correlated, ( $> 0.9$ ) in accordance with their origin as organic (plant) matter deposited in the sediment. To test the hypothesis that foliage is the primary collector of airborne particulate material deposited in wetland sediments, we examined the correlations between C and suspected pollutant elements S, V, Cu, As, Cd, and Pb. Of these, S and Pb have moderately high Pearson correlation coefficients (0.85 and 0.67), and V, Cu, and Cd somewhat lower, ranging from 0.4 to 0.48. Arsenic exhibits a low negative correlation with C (-0.2). Correlation coefficients between Pb and these selected elements range from -0.7 (As), 0.3 (V), 0.6 (Cd), 0.7 (S), to 0.9 (Cu).

Referring to Figure 2 and Table 2, enrichment factors for C, N are also highly correlated. Compared to the deposition rate data, the correlations between C and S (0.9), Pb (0.8), Cu (0.7), and Cd (0.7) are higher, with V (0.4) remaining the same.

Figure 1.

### BRF-2 Forest Deposition Rates SPLOM



Again, As exhibits a low negative correlation with C (-0.2). Correlation coefficients between Pb enrichment factors and these selected elements are similar to the deposition profiles, ranging from -0.5 (As), 0.5 (V), 0.6 (Cd), 0.7 (S), to 0.9 (Cu).

Table 1. Pearson Correlation Matrix for Black Rock Forest Elemental Deposition Rates (16 Observations)

	H									
H	1.000	C								
C	0.987	1.000	N							
N	0.928	0.921	1.000	Na						
Na	-0.167	-0.240	-0.323	1.000	Mg					
Mg	0.822	0.788	0.779	0.068	1.000	Al				
Al	0.679	0.653	0.680	0.003	0.954	1.000	P			
P	0.332	0.284	0.356	0.580	0.619	0.618	1.000	S		
S	0.849	0.848	0.792	-0.129	0.554	0.308	0.157	1.000	K	
K	0.596	0.579	0.612	-0.193	0.858	0.923	0.380	0.238	1.000	
Ca	0.862	0.848	0.822	0.094	0.938	0.846	0.668	0.667	0.735	
V	0.547	0.477	0.595	0.048	0.611	0.570	0.385	0.363	0.643	
Fe	0.933	0.932	0.895	-0.289	0.752	0.577	0.164	0.925	0.552	
Cu	0.381	0.404	0.505	-0.647	0.021	-0.106	-0.410	0.592	0.054	
As	-0.109	-0.187	-0.269	0.933	0.136	0.100	0.581	-0.164	-0.086	
Cd	0.474	0.459	0.440	-0.389	0.115	-0.084	-0.362	0.707	-0.061	
Pb	0.621	0.666	0.704	-0.747	0.283	0.181	-0.288	0.674	0.322	
		Ca								
Ca	1.000	1.000	V							
V	0.566	0.475	1.000	Fe						
Fe	0.776	0.475	0.551	1.000	Cu					
Cu	0.108	0.308	-0.28	-0.582	1.000	As				
As	0.153	0.189	0.646	0.642	-0.488	1.000	Cd			
Cd	0.14	-0.049	0.646	0.642	-0.488	0.620	1.000	Pb		
Pb	0.322	0.326	0.736	0.874	-0.684	0.620	0.620	1.000		

Figure 2.

### BRF-2 Forest Enrichment Factors SPLOM

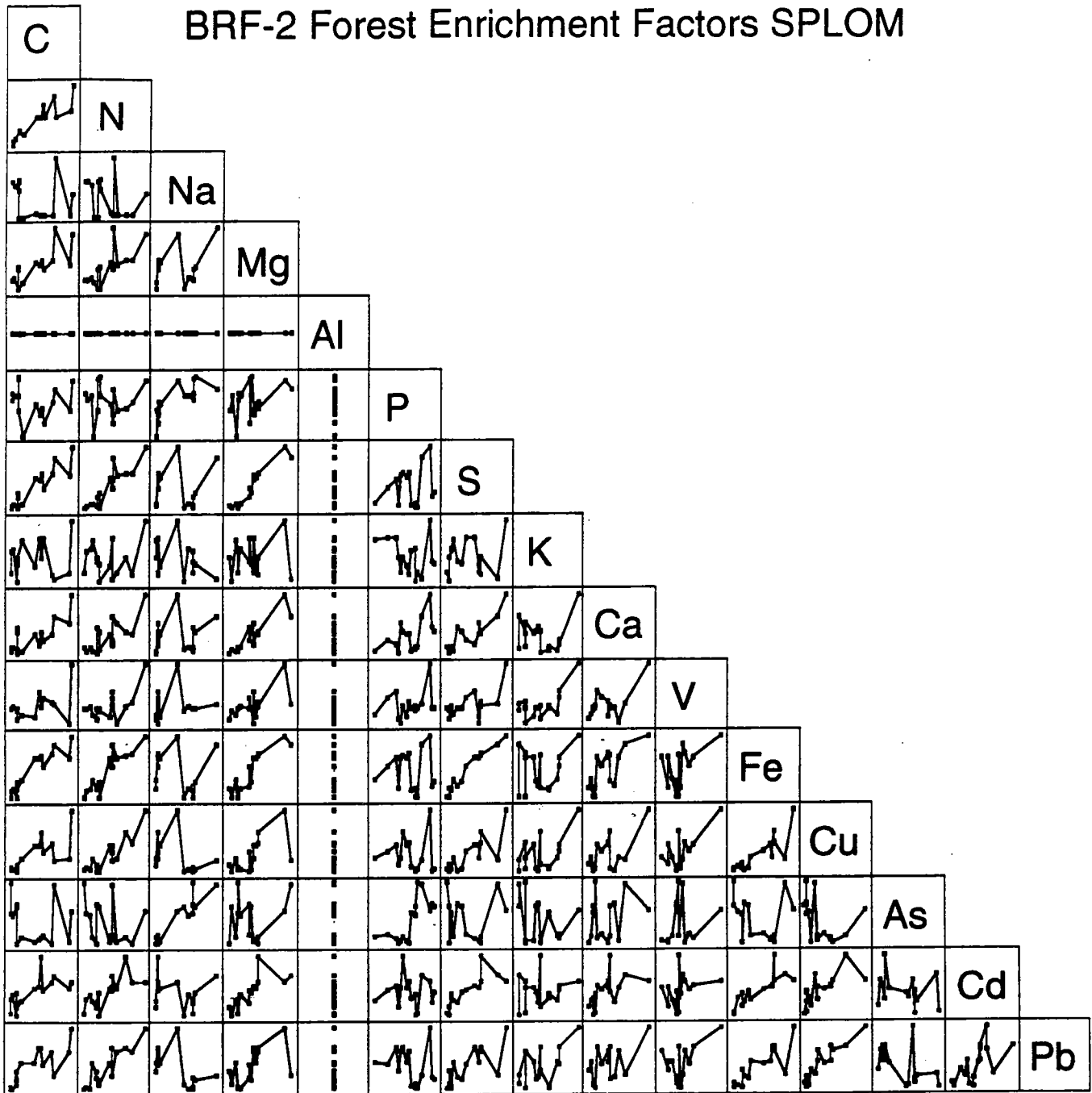


Table 2. Pearson Correlation Matrix for Black Rock Forest Elemental Enrichment Factors (16 Observations)

	C								
C	1.000	N							
N	0.894	1.000	Na						
Na	-0.26	-0.344	1.000	Mg					
Mg	0.773	0.721	0.261	1.000	Al				
Al	.	.	.	.	1.000	P			
P	-0.033	0.057	0.753	0.364	.	1.000	S		
S	0.904	0.887	-0.037	0.943	.	0.197	1.000	K	
K	0.138	0.218	-0.301	0.105	.	-0.234	0.161	1.000	
Ca	0.776	0.752	0.207	0.882	.	0.511	0.872	0.159	
V	0.427	0.573	0.111	0.561	.	0.287	0.548	0.634	
Fe	0.918	0.9	-0.23	0.874	.	-0.019	0.973	0.233	
Cu	0.728	0.876	-0.425	0.615	.	-0.08	0.784	0.527	
As	-0.246	-0.329	0.933	0.215	.	0.695	-0.07	-0.262	
Cd	0.654	0.714	-0.188	0.715	.	-0.038	0.783	0.158	
Pb	0.810	0.886	-0.599	0.536	.	-0.226	0.754	0.473	

	Ca							
Ca	1.000	V						
V	0.564	1.000	Fe					
Fe	0.765	0.5	1.000	Cu				
Cu	0.633	0.686	0.822	1.000	As			
As	0.207	0.2	-0.262	-0.349	1.000	Cd		
Cd	0.538	0.312	0.82	0.683	-0.271	1.000	Pb	
Pb	0.587	0.524	0.832	0.924	-0.539	0.63	1.000	

### 2.1.2 Stockport Flats Marsh.

SPLM plots of elemental deposition rate and enrichment factor data for the Stockport Flats Marsh site (STO) are presented in Figures 3 and 4, respectively. The analogous Pearson Correlation Matrices are given in Tables 3 and 4. Referring to Figure 3 and Table 3, the deposition rates for H,C,N are highly correlated, (> 0.9) in agreement with the Black Rock Forest site. Again, we examined the correlations between C and suspected pollutant elements S, V, Cu, As, Cd, and Pb. In contrast to the BRF location, S, Cu, V, and As exhibit moderately high Pearson correlation coefficients (0.86, 0.86, 0.81, 0.72), with Pb (0.58) and Cd (0.42) somewhat lower.



Correlation coefficients between Pb and these elements are: 0.7 (S), 0.7 (V), 0.7 (Cu), 0.7 (As), 0.4 (Cd). These values are much more consistent than those obtained at the BRF site.

In Figure 4 and Table 4, enrichment factors for C,N are also highly correlated (> 0.9). Compared to the deposition rate data (and the BRF results), the correlations between C and S (0.5), V (0.3), Cu (0.3), As (0.4), Cd (0.3) and Pb (0.3), are uniformly lower. Correlation coefficients between Pb enrichment factors and these selected elements are much lower than the deposition rate counterparts (both STO and BRF), ranging from 0.22 (Cd), 0.23 (Cu), 0.4 (As), 0.56 (S), to 0.63 (V).

Table 3. Pearson Correlation Matrix for Stockport Flats Elemental Deposition Rates (First 13 Observations)

	H									
H	1.000	C								
C	0.982	1.000	N							
N	0.918	0.903	1.000	Na						
Na	0.767	0.692	0.740	1.000	Mg					
Mg	0.864	0.813	0.699	0.875	1.000	Al				
Al	0.740	0.701	0.568	0.796	0.908	1.000	P			
P	0.894	0.840	0.794	0.919	0.980	0.872	1.000	S		
S	0.890	0.856	0.763	0.885	0.969	0.876	0.981	1.000	K	
K	0.814	0.769	0.674	0.904	0.958	0.895	0.932	0.927	1	
Ca	0.891	0.834	0.707	0.859	0.961	0.870	0.951	0.960	0.911	
V	0.855	0.808	0.712	0.896	0.994	0.911	0.978	0.971	0.977	
Fe	0.626	0.656	0.716	0.520	0.518	0.437	0.591	0.542	0.561	
Cu	0.881	0.855	0.769	0.882	0.929	0.855	0.939	0.969	0.94	
As	0.783	0.724	0.618	0.880	0.903	0.840	0.906	0.904	0.852	
Cd	0.440	0.415	0.395	0.391	0.395	0.327	0.459	0.554	0.364	
Pb	0.569	0.579	0.551	0.689	0.674	0.776	0.715	0.744	0.648	
	Ca									
Ca	1.000	V								
V	0.946	1.000	Fe							
Fe	0.443	0.552	1.000	Cu						
Cu	0.944	0.946	0.571	1.000	As					
As	0.947	0.891	0.363	0.874	1.000	Cd				
Cd	0.494	0.401	0.226	0.547	0.377	1.000	Pb			
Pb	0.608	0.698	0.426	0.673	0.667	0.433	1.000			





Table 4. Pearson Correlation Matrix for Stockport Flats Elemental Enrichment Factors (First 13 Observations)

	C								
C	1.000								
N	0.894	1.000							
Na	-0.26	-0.344	1.000						
Mg	0.773	0.721	0.261	1.000					
Al	.	.	.	.	1.000				
P	-0.033	0.057	0.753	0.364	.	1.000			
S	0.904	0.887	-0.037	0.943	.	0.197	1.000		
K	0.138	0.218	-0.301	0.105	.	-0.234	0.161	1.000	
Ca	0.776	0.752	0.207	0.882	.	0.511	0.872	0.159	
V	0.427	0.573	0.111	0.561	.	0.287	0.548	0.634	
Fe	0.918	0.9	-0.23	0.874	.	-0.019	0.973	0.233	
Cu	0.728	0.876	-0.425	0.615	.	-0.08	0.784	0.527	
As	-0.246	-0.329	0.933	0.215	.	0.695	-0.07	-0.262	
Cd	0.654	0.714	-0.188	0.715	.	-0.038	0.783	0.158	
Pb	0.810	0.886	-0.599	0.536	.	-0.226	0.754	0.473	

	Ca							
Ca	1.000							
V	0.510	1.000						
Fe	-0.009	0.394	1.000					
Cu	0.721	0.816	0.295	1.000				
As	0.216	0.154	-0.279	0.079	1.000			
Cd	0.181	0.374	-0.069	0.331	0.344	1.000		
Pb	0.117	0.634	0.158	0.232	0.397	0.223	1.000	

### 2.1.3 Tivoli South Bays Marsh.

SPLoM plots of elemental deposition rate and enrichment factor data for the Tivoli South Bays Marsh (TSB) are presented in Figures 5 and 6, with analogous Pearson Correlation Matrices in Tables 5 and 6. Figure 5 and Table 5 show that the deposition rates for H,C,N are not as highly correlated (H 0.84, N 0.42 vs. C), in contrast to the Black Rock Forest and Stockport Flats sites. In contrast to the BRF and STO locations, S, V, and Cd exhibit lower Pearson correlation coefficients vs. C (0.6, 0.3, 0.3), with Pb (0.01), As (-0.07), and Cu (0.06) showing no correlation. Correlation coefficients between Pb and these elements are: 0.7 (S), -0.7 (V), -0.2 (Cu), 0.9 (As),

0.8 (Cd). These values also differ markedly from those obtained at the BRF and STO sites.

In Figure 6 and Table 6, enrichment factors for C,N do not correlate well (0.22). Compared to the deposition rate data (and the STO and BRF results), the correlations between C and: S (0.27), V (0.22), Cu (0.11), As (0.26), Cd (0.08) and Pb (0.14), are all much lower. Correlation coefficients between Pb enrichment factors and these selected elements differ markedly from their deposition rate and enrichment factor counterparts (both STO and BRF), ranging from -0.8 (V), -0.3 (Cu), 0.77 (S), 0.84 (Cd), to 0.89 (As).

Table 5. Pearson Correlation Matrix for Tivoli South Bays Elemental Deposition Rates (First 12 Observations)

	H									
H	1.000	C								
C	0.841	1.000	N							
N	0.582	0.417	1.000	Na						
Na	-0.268	-0.264	-0.279	1.000	Mg					
Mg	0.511	0.515	0.343	0.492	1.000	Al				
Al	0.551	0.530	0.512	0.247	0.930	1.000	P			
P	0.546	0.498	0.354	0.351	0.892	0.786	1.000	S		
S	0.443	0.590	0.242	0.509	0.950	0.840	0.798	1.000	K	
K	0.254	0.308	0.089	0.593	0.885	0.764	0.798	0.879	1.000	
Ca	0.467	0.573	0.238	0.511	0.953	0.817	0.901	0.961	0.867	
V	0.337	0.287	0.484	-0.722	-0.214	0.080	-0.306	-0.269	-0.551	
Fe	0.675	0.700	0.385	0.304	0.965	0.917	0.878	0.932	0.796	
Cu	-0.014	0.063	-0.175	0.037	0.073	0.171	-0.128	0.061	0.020	
As	-0.197	-0.074	-0.323	0.920	0.552	0.272	0.477	0.625	0.733	
Cd	0.051	0.275	-0.273	0.728	0.657	0.401	0.619	0.747	0.753	
Pb	-0.093	0.014	-0.238	0.835	0.607	0.317	0.613	0.647	0.636	
	Ca									
Ca	1.000	V								
V	-0.318	1.000	Fe							
Fe	0.929	-0.067	1.000	Cu						
Cu	0.091	0.268	0.048	1.000	As					
As	0.622	-0.856	0.401	-0.112	1.000	Cd				
Cd	0.761	-0.699	0.590	-0.051	0.902	1.000	Pb			
Pb	0.698	-0.706	0.501	-0.204	0.887	0.841	1.000			





Table 6. Pearson Correlation Matrix for Tivoli South Bays Elemental Enrichment Factors (First 12 Observations)

	C										
C	1.000	N									
N	0.224	1.000	Na								
Na	-0.442	-0.477	1.000	Mg							
Mg	0.083	-0.400	0.798	1.000	Al						
Al	.	.	.	.	1.000	P					
P	0.240	-0.060	0.312	0.712	.	1.000	S				
S	0.270	-0.384	0.635	0.883	.	0.541	1.000	K			
K	-0.168	-0.565	0.696	0.772	.	0.558	0.755	1.000			
Ca	0.285	-0.348	0.620	0.915	.	0.76	0.9	0.722			
V	0.222	0.507	-0.769	-0.840	.	-0.675	-0.721	-0.966			
Fe	0.603	-0.226	0.299	0.791	.	0.72	0.796	0.487			
Cu	-0.114	-0.332	-0.030	-0.340	.	-0.553	-0.316	-0.255			
As	-0.258	-0.538	0.932	0.881	.	0.468	0.778	0.845			
Cd	0.077	-0.561	0.726	0.837	.	0.542	0.754	0.701			
Pb	-0.140	-0.439	0.826	0.916	.	0.62	0.774	0.688			

	Ca								
Ca	1.000	V							
V	-0.763	1.000	Fe						
Fe	0.798	-0.500	1.000	Cu					
Cu	-0.225	0.312	-0.444	1.000	As				
As	0.767	-0.899	0.455	-0.161	1.000	Cd			
Cd	0.823	-0.772	0.587	-0.078	0.885	1.000	Pb		
Pb	0.834	-0.791	0.593	-0.298	0.892	0.835	1.000		

## 2.2 Inter-site comparison of deposition rates and enrichment factors

### 2.2.1 Deposition Rate Comparisons

SPLM plots comparing individual elemental deposition rates for V, Fe, Cu, As, Cd, and Pb from the Black Rock Forest (BRF), Stockport Flats (STO) and Tivoli South Bays (TSB) sites are presented in Figure 7. The analogous Pearson Correlation Matrices are given in Table 7. (V and Fe are representative of "normal" sediment constituents, with low enrichment factors, and Cu, As, Cd, and Pb representative of the airborne pollutants). Since the time increment per sediment section varies from core



to core, smoothed profiles of the actual deposition data were interpolated against a constant time increment of 10 years so that the sites could be directly compared. The maximum cumulative time before present was set to 135 years prior to the date at the top of the core (late 1985 or early 1986).

Of the selected elements, the deposition profiles for Pb have the highest inter-site correlations ( $\geq 0.73$ ) with Cu ( $\geq 0.68$ ) and Cd ( $\geq 0.41$ ) showing reasonable correlation. The iron profiles for the high sediment rate (silt) river marshes are strongly correlated (0.76) and that these sites correlate poorly with the low sediment rate, organic-rich BRF bog site (0.06). Likewise, As profiles from STO and TSB are reasonably correlated (0.35). Finally, there are moderate negative correlations between STO and TIV for V deposition, and positive correlation between BRF and TSB.

Figure 7.

### Inter-Site Comparisons: Deposition Profiles

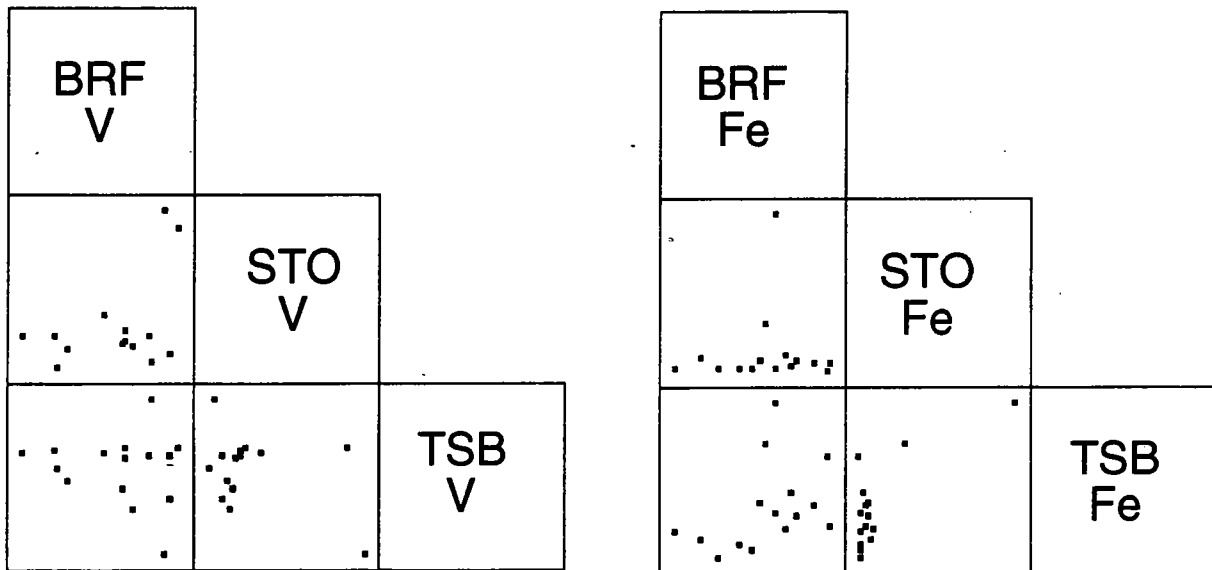


Figure 7 cont'd.

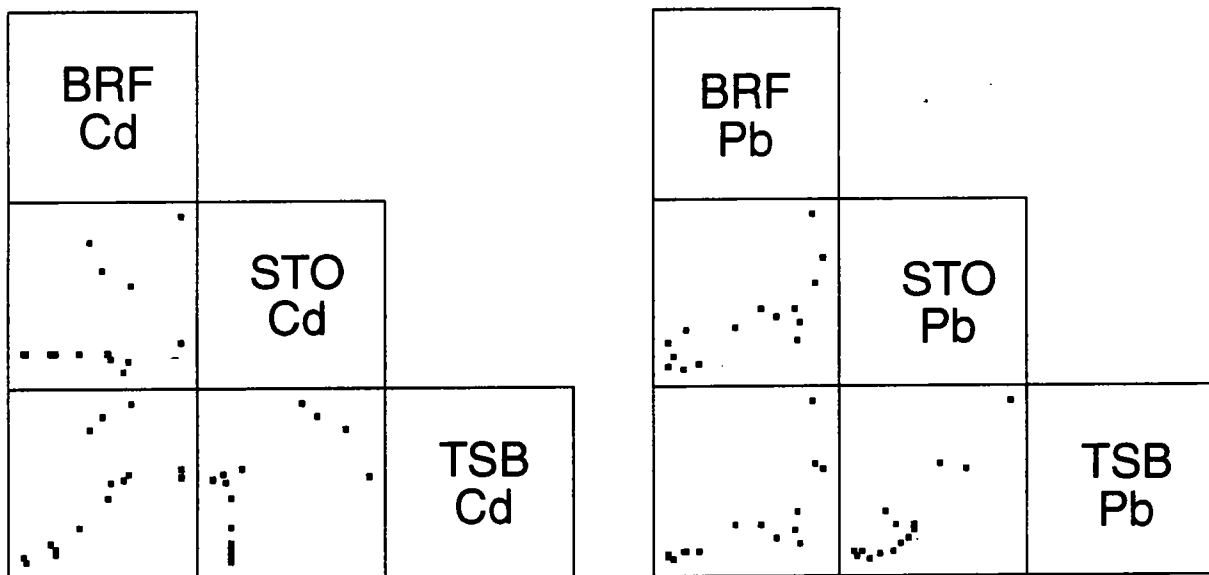
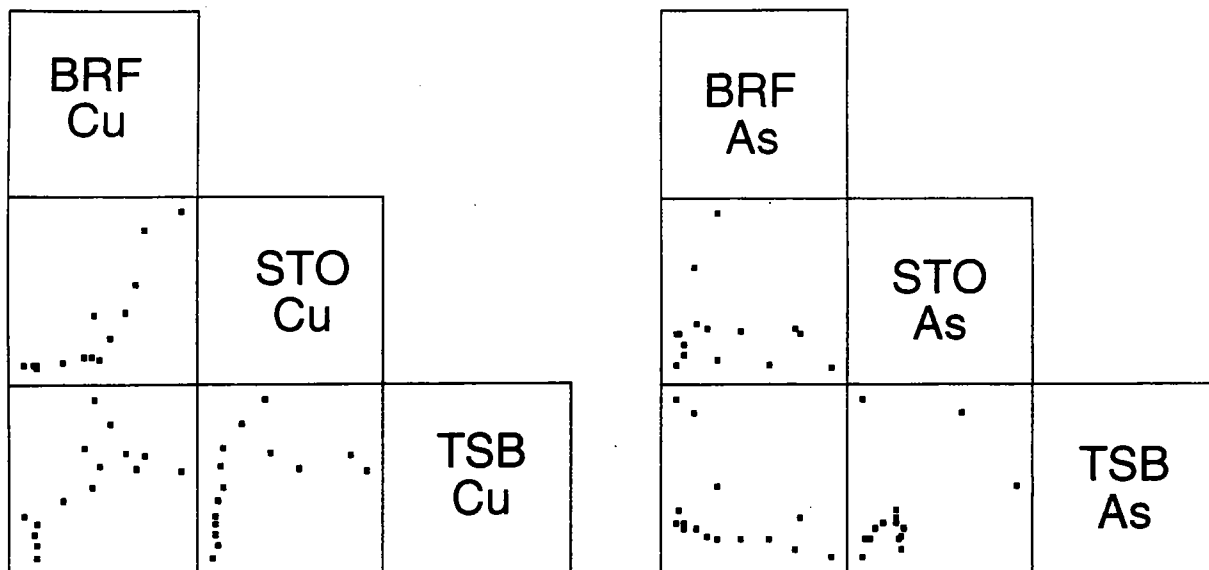


Table 7. Pearson Correlation Matrix for Elemental Deposition Rates  
(15 Observations)

V	BRF	STO	TSB	Fe	BRF	STO	TSB
BRF	1.000			BRF	1.000		
STO	0.361	1.000		STO	0.055	1.000	
TSB	-0.150	-0.396	1.000	TSB	0.406	0.755	1.000
Cu	BRF	STO	TSB	As	BRF	STO	TSB
BRF	1.000			BRF	1.000		
STO	0.868	1.000		STO	-0.157	1.000	
TSB	0.684	0.441	1.000	TSB	-0.464	0.347	1.000
Cd	BRF	STO	TSB	Pb	BRF	STO	TSB
BRF	1.000			BRF	1.000		
STO	0.407	1.000		STO	0.769	1.000	
TSB	0.682	0.613	1.000	TSB	0.731	0.924	1.000

### 2.2.2 Enrichment Factor Comparisons

SPLOM plots comparing individual elemental enrichment factors for V, Fe, Cu, As, Cd, and Pb from the (BRF), (STO), and (TSB) sites are presented in Figure 8, with the respective Pearson Correlation Matrices in Table 8. As with the deposition data, smoothed profiles of the actual enrichment factors were interpolated against a constant time increment of 10 years up to a maximum of 135 years prior to the date at the top of the core (late 1985 or early 1986).

Table 8. Pearson Correlation Matrix for Elemental Enrichment Factors  
(15 Observations)

V	BRF	STO	TSB	Fe	BRF	STO	TSB
BRF	1.000			BRF	1.000		
STO	0.698	1.000		STO	0.320	1.000	
TSB	0.475	-0.810	1.000	TSB	0.903	0.459	1.000
Cu	BRF	STO	TSB	As	BRF	STO	TSB
BRF	1.000			BRF	1.000		
STO	0.871	1.000		STO	-0.177	1.000	
TSB	0.321	0.284	1.000	TSB	-0.409	0.446	1.000

Table 8 cont'd

Cd	BRF	STO	TSB	Pb	BRF	STO	TSB
BRF	1.000			BRF	1.000		
STO	0.767	1.000		STO	0.536	1.000	
TSB	0.611	0.289	1.000	TSB	0.812	0.447	1.000

Figure 8.

## Inter-Site Comparisons: Enrichment Factor Profiles

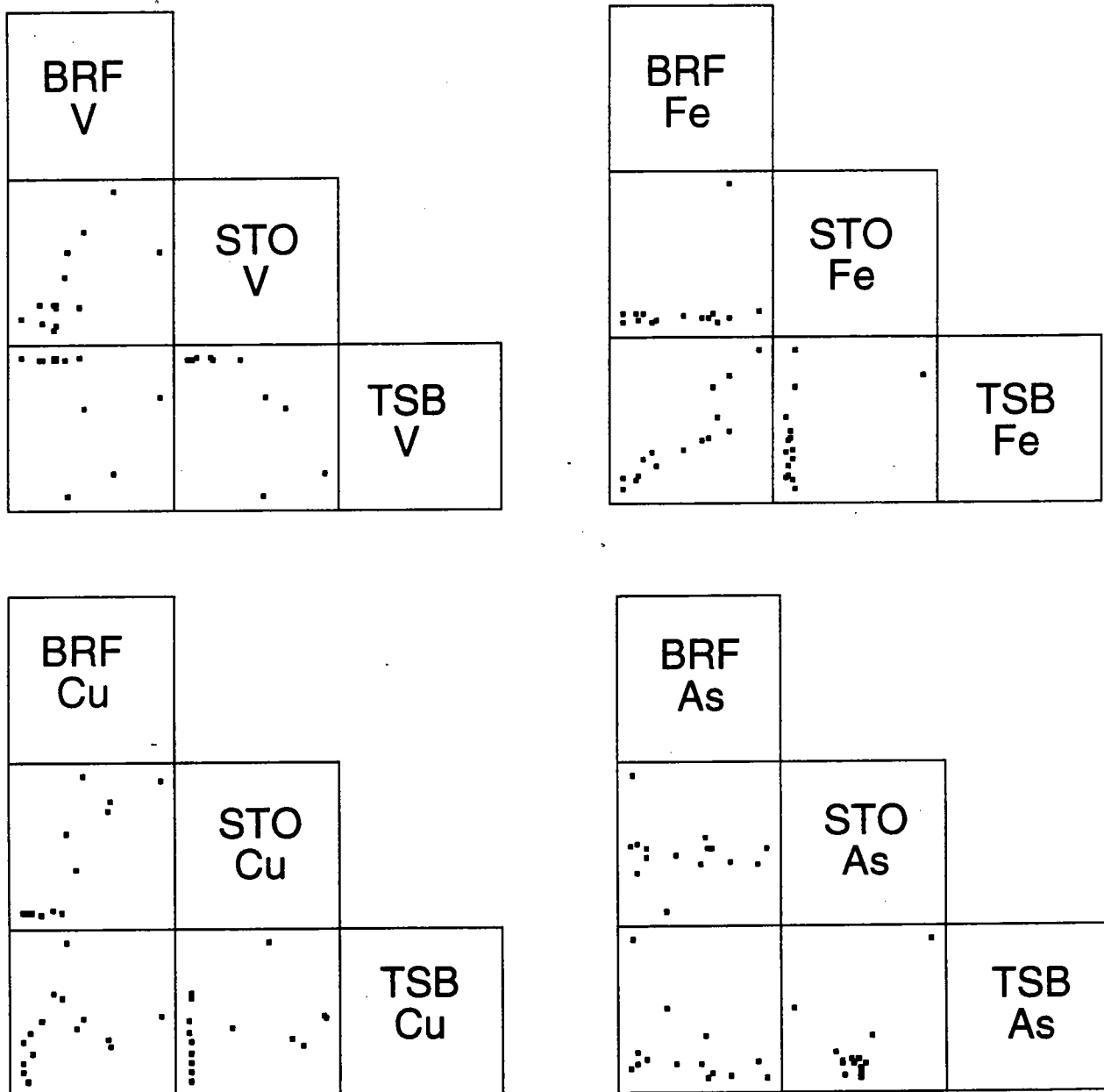
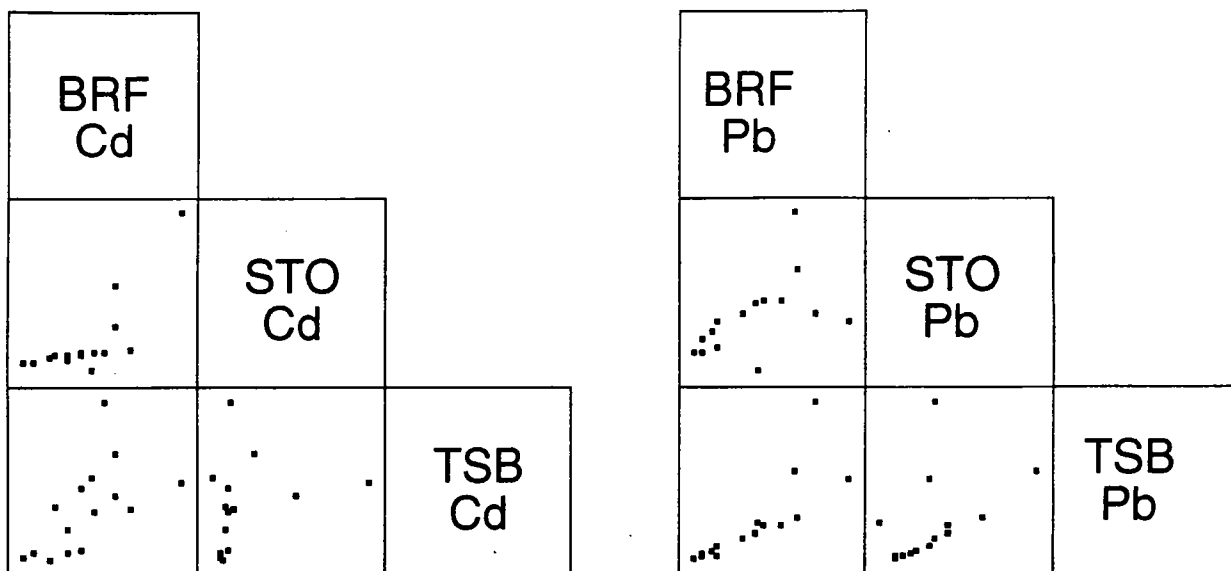


Figure 8 cont'd



Enrichment factor profiles for Pb ( $\geq 0.45$ ) Cu ( $\geq 0.29$ ) and Cd ( $\geq 0.29$ ) and V ( $\geq 0.47$ ) show good to fair correlation (strong negative correlation between TSB and STO for V). Interestingly, for these elements, enrichment factors from BRF correlate better with each of the river marsh sites than these sites do with each other, in contrast to the deposition data. The iron ("normal" soil constituent) profiles for the high sediment rate (silt) TSB river marsh also strongly correlate with the low sediment rate, organic-rich BRF bog site BRF (0.9) and less well with TSB marsh (0.45). However, arsenic profiles from STO and TSB are better correlated (0.35).

### 2.3 Discussion of Correlation Analyses

Intra-site comparisons reveal a unique set of correlations for each site, with only Pb and S giving consistently high correlation coefficients among the suspected airborne pollutant elements. The intra-site correlations between Pb and C, Cd, Cu, As, and V vary, with somewhat higher correlations at the BRF and TSB sites compared to STO. This is not surprising, since each site "records" the deposition chronology at a different rate. For example, referring to Appendices 2 and 3, 5 cm of sediment accumulation corresponds to nearly 50 years of deposition at the low sedimentation rate BRF site, and only 15-20 years at the higher sedimentation rate STO, TSB river marsh locations. In addition, these potential airborne pollutant elements arise from chronologically independent sources (Rod, 1989), there is no *a priori* reason that any of these "airborne pollutant" elements should correlate closely at a given site. Nevertheless, when compared across similar cumulative time intervals, the inter-site correlations for each individual element are consistently stronger for the "pollutant" elements Pb, Cu, Cd, As, and S. Thus, the

sediments at these three sampling locations do reflect at least a qualitative historical record of regional pollutant deposition.

Again referring to Appendix 3, the *magnitude* of the enrichment factors at each location for C, As, Cd, Cu, and S are comparably elevated (ie maximum values exceeding 5), while V is not (maxima  $\leq 1.2$ ). Since V is not present in abnormally large quantities at any location, we conclude that V is not an airborne (combustion product) pollutant. It should also be noted that the remaining elements (Mg, Al, P, K, Ca, Fe) with the exception of Na, also have fairly flat deposition profiles and low ( $\sim 1.0$ ) enrichment factors, and tend to follow the trend bulk sedimentation rates. Thus, these elements are representative of "normal" inorganic soil constituents.

## 2.4 Summary of Research

In this project we determined the chronology of organic productivity of the Black Rock Forest, Stockport Flats, and Tivoli South Bay sites through C,H,N elemental analysis. Elemental analysis for C,H, N, Pb, Cd, Cu, As, Fe, V, S, P, Al, Na, Ca, Mg, K were also determined. Monte Carlo simulations of the complex sedimentation processes operative in the Hudson River wetlands were performed to provide a rigorous assessment of the CRS/MV  $^{210}\text{Pb}$  dating model. The results of the present study have led to the presentation of 3 papers at international meetings (Tobin and Schell, 1988a,1988b).

In this final report, an atlas of deposition rate and enrichment factor profiles are presented for the entire elemental database that we have amassed. We also examined the correlations between the various airborne pollutants and baseline elements that were measured, both intra-site and inter-site. These explorations show that  $^{210}\text{Pb}$  dating is definitely applicable to river marshland areas and that these wetlands do preserve at least a qualitative historical record of regional pollutant deposition. It is hoped that this database, in conjunction with complementary studies of PCB's and other contaminants, will provide additional insight on both the quantities and sources of the various pollutants deposited in the Hudson River ecosystem.

### 3. References

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## Appendix 1. Sampling Protocol and Analytical Methods

### 1. Field Sampling Protocol

Wetland sampling locations in this work were the Black Rock Forest bog (41°23' N, 74°02' W) near West Point, and Hudson River marshlands at Stockport Flats (42°17' N, 73°49' W ) river mile 120, and Tivoli South Bay (42°02' N, 73°55' W ) river mile 95, (Schell et al, 1987). The Stockport sampling site was located approximately 0.5 km from the railroad on the river side and the Tivoli site was 0.8 km from the railroad on the inland side. Sediment cores were taken by driving a 10-cm diameter polyvinyl chloride tube vertically into a suitable ground site away from tree roots and hummocks. A minimum of three cores from each sampling site were collected. The cores were cut into 0.5-, 1.0-, or 2.0-cm sections, weighed, dried at 70°C and homogenized. Duplicate cores were frozen promptly and stored until used. Aliquots of each layer were taken for the various radiochemical and elemental analyses. To avoid contamination, samples were stored in acid-washed polyethylene bags during collection and after sectioning.

### 2. Analytical Procedures

#### 2.1 Assay of $^{210}\text{Pb}$ in Sediments

Standard radiochemical techniques were used to analyze for  $^{210}\text{Pb}$ . This data was used to construct a chronology for the sediment layers, following the constant rate of supply (CRS) interpretation and our "CRS/MV" enhanced treatment described below. In the laboratory, the wet and dry weights were determined and 2- to 3-g aliquots were spiked with 10.0 to 50.0 dpm of  $^{208}\text{Po}$  (chemical yield tracer), leached and heated with concentrated  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$  and  $\text{HCl}$  for at least four hours, and centrifuged twice. The leachate was then evaporated to dryness and the residue converted completely to chlorides by repeatedly adding  $\text{HCl}$  and evaporating to dryness. The residue was dissolved in approximately 120 ml of 0.3 M  $\text{HCl}$ , and ascorbic acid added to complex iron in solution. The polonium isotopes plated spontaneously at 65 degrees C onto a silver disk (one side coated with an insulating varnish, "RedGipt") suspended in the solution. The disks were rinsed, dried, and alpha-particle counted using Si surface-barrier detectors and pulse-height analysis for  $^{208}\text{Po}$  and  $^{210}\text{Po}$ . The  $^{210}\text{Po}$  activity concentration was assumed to be in secular equilibrium with the parent  $^{210}\text{Pb}$  concentration in sediment because of its short half life (138 days). The supported  $^{210}\text{Pb}$  concentration was determined by measuring  $^{226}\text{Ra}$  concentrations in each core section, or by peeling the outer 3-mm layers of each core section, combining the outer



layers, and gamma counting of  $^{214}\text{Bi}$  using Ge(Li) detectors and pulse-height analysis; the inner portion of each section is used for the  $^{210}\text{Po}$  analysis. The Ge(Li) detector efficiency was determined by counting a known concentration of  $^{226}\text{Ra}$  and other NBS-traceable standards in the same geometry and density configuration as the sediment sample.

## 2.2 The CRS/MV model for stratigraphic dating

Goldberg (1963) suggested two approaches to the stratigraphic dating of glaciers. Assuming a constant nuclide deposition rate, the cumulative activity over time  $t$  at depth  $x$  is

$$A_c(t) = \int_0^t \alpha e^{-\lambda t} dt = A_\Sigma (1 - e^{-\lambda t}) \quad (1)$$

where  $\alpha$  = nuclide deposition rate

$\lambda$  = nuclide decay constant

and  $A_\Sigma = \alpha/\lambda$

If the sedimentation rate is also constant, the activity at any depth  $x$  is simply

$$A(x) = A_0 e^{-\lambda t} \quad (2)$$

where  $A_0$  = measured activity at the surface. Eq.(2) is the formal basis of the constant initial concentration (CIC) model.

For the general case, rearrange Eq. (1) to solve for  $t$ :

$$t = \frac{\ln\left(\frac{A_\Sigma}{A_\Sigma - A_c(t)}\right)}{\lambda} \quad (3)$$

where  $A_\Sigma - A_c(t)$  is the cumulative activity at depth  $x$ . Eq. 3 is the formal basis of the constant rate of supply (CRS) model.

In accord with the "decay curve" character of Eq.(3), the relative uncertainty increases as the magnitude of  $A_\Sigma - A_c(t)$  decreases. Thus, the uncertainty of the CRS dating estimate increases with depth. In order to obtain a minimum variance dating estimate, we can apply our *a priori* knowledge of the underlying radioactive decay systematics according to the following development. Again rearranging Eq. (1)

$$A_{\Sigma} - A_c(t) = A_{\Sigma} e^{-\lambda t} \quad (4)$$

$$\text{let } A_{\Sigma} e^{-bx} = A_{\Sigma} e^{-\lambda t} \quad (5)$$

where linear depth  $x$  serves as an incremental dummy argument, and  $b$  is the analogous decay constant with units of  $x^{-1}$ . The optimal value of  $b$  is obtained by a nonlinear least squares fit to:

$$A_{\Sigma} - A_c(t) = A_{\Sigma} e^{-bx} \quad (6)$$

From Eq. 5, the time-estimate at any depth  $x$  is:

$$t(x) = \frac{bx}{\lambda} \quad (7)$$

While the dating error introduced by the CRS/MV treatment also tends to increase with depth, the magnitude of the errors are a factor of two to three smaller than those introduced by application of the CRS treatment given by Eq. 3.

### 2.3 C,H,N Elemental Analysis

Sediment core sections were assayed for total carbon, hydrogen, and nitrogen with a Perkin-Elmer 240B elemental analyzer provided for our use by Dr. Robert Streeter at the Bituminous Coal Research National Laboratory, Pittsburgh, PA. Aliquot weights ( $\leq 3$  mg) were determined to  $\pm 1$   $\mu\text{g}$  accuracy with a Cahn 26 Electrobalance. Spectroscopic grade (.9999% purity) acetanilide ( $\text{C}_6\text{H}_5\text{NH} \cdot \text{COCH}_3$ ) was used as a calibration standard.

### 2.4 Sample Preparation for Atomic Absorption and Plasma Emission Spectrometry

100 - 1000 mg aliquots of sediment were placed in 20 ml of 8N  $\text{HNO}_3$  to which 0.5 ml of  $\text{H}_2\text{O}_2$  is added. The samples were heated to boiling, and refluxed for a period of two to four hours. The strongly oxidizing reflux medium effectively destroyed any metal-organic chelate systems. The filtered solutions were volumetrically diluted for atomic absorption and/or plasma emission analysis.

## 2.5 Determination of element concentrations by ICP/AES and Furnace AAS

ICP/AES (inductively coupled argon plasma/atomic emission spectroscopy) quantitative methods were used to determine the concentrations of 23 elements in the Hudson River core samples. In addition, Furnace AAS (atomic absorption spectroscopy) quantitative methods were also used for the determination of Pb, Cd, Cu, and V.

### Apparatus

Bausch & Lomb (Applied Research Laboratories) ARL Model S34000 ICP/AES (inductively coupled argon plasma/atomic emission) spectrometer and Perkin Elmer 4000 AAS and Model 400 graphite furnace attachment were used in this study.

### Reagents

Throughout all analytical work, deionized distilled water was used. "ULTREX" distilled hydrochloric and nitric acids were used.

### Sample Preparation

Aliquots of sediment (~ 100 mg) were placed in 20 ml of 8N HNO<sub>3</sub> to which 0.5 ml of H<sub>2</sub>O<sub>2</sub> was added. The samples were heated to boiling, and refluxed for a period of two to four hours. The strongly oxidizing reflux medium effectively destroys any metal-organic chelate systems. The filtered solutions were gravimetrically diluted to approx. 25 ml for ICP/AES analysis. For AAS samples, the filtered solutions were volumetrically diluted to 50.00 ml.

### Calibration Standards

Initially, qualitative ICP/AES scans (40 elements) were made of the acid-digested sediment extracts to determine if any species were present in unusually high concentrations. Based on the scans, calibration standards spanning the observed concentrations were prepared by serial dilution of 10 ppm stock solutions prepared from 1000 ppm Fisher or Baker Certified Standards.

Mixed standards were prepared in 10 ml volumetric flasks by adding 0.0, 0.5, or 2.0 ml of the appropriate 10 ppm stock solutions and diluting volumetrically. A 200 ppm Al standard was also prepared to obtain a continuum emission background to correct for interferences.

Furnace AAS (Pb, Cd, Cu, and V) "low level" 0.0, 5,10,20,50 ppb and "high level" standards 0.0, 0.5,1.0,5.0,10.0 ppm were prepared by serial dilution of Fisher or Baker Primary Standard solutions.

From these data, calibration curves were obtained as used to determine aliquot elemental concentrations. Appropriate dilution factors were then applied to determine the corresponding concentrations in the original sediment sample.

#### Quality Control

For all samples analyzed by ICP/AES and AAS:

- a) Reagent blanks were processed and analyzed
- b) 10% of all samples were analyzed in duplicate
- c) Several samples were analyzed by standard addition  
(a duplicate aliquot of sample was spiked with a known quantity of standard) for comparison to the calibration curve results
- d) After each 5 samples, a standard solution was analyzed to verify that the instrument calibration remained constant
- e) Several of the Pb samples and spikes were analyzed on both instruments to verify cross calibrations

Very good precision and accuracy were obtained on analyzed samples and standards. In most cases, results and intercomparisons varied by less than  $\pm 10\%$  of the amount of each metal present. Standard addition results were also within  $\pm 10\%$ .

**Appendix 2. Deposition and Enrichment Factor Data for Black Rock Forest, Stockport Flats, and Tivoli South Bays Locations.**

BRF-2 core elemental analysis March 1988 to October 1989

section	midpt depth (cm)	2.6529 1986.70 1986.70 $\Delta t$ incr. $\Delta t$	22.35 8.42	Core slice dry wt. g	91.524 sediment d Pb g/cm <sup>2</sup> -yr $\mu$ g/g sample	natural abundance Pb		10 $\mu$ g/g		natural abundance S		850 $\mu$ g/g	
						ratio/ nat. Al	91.524 cm <sup>2</sup>	Pb deposition $\mu$ g/cm <sup>2</sup> -yr factor	Pb enrichment $\mu$ g/g sample	ratio/ nat. Al	0.00014025	S deposition $\mu$ g/cm <sup>2</sup> -yr factor	S enrichment $\mu$ g/g sample
0-2	1	1978.28	8.42	13.844	0.018	94.41	1.70	39.03	4838.04	86.86	23.53		
2-3	2.5	1965.64	8.42	14.134	0.018	86.56	1.59	27.54	4290.20	78.64	16.06		
3-4	3.5	1957.21	8.42	17.739	0.023	73.05	1.68	25.68	4221.33	97.12	17.46		
4-5	4.5	1948.79	8.42	13.645	0.018	75.67	1.34	27.64	4102.14	72.59	17.63		
5-6	5.5	1940.36	8.42	18.901	0.025	28.36	0.70	11.13	4627.48	113.43	21.36		
6-7	6.5	1931.94	8.42	17.241	0.022	53.58	1.20	19.47	3937.73	88.05	16.83		
7-8	7.5	1923.52	8.42	18.636	0.024	64.95	1.57	24.88	3777.35	91.30	17.02		
8-9	8.5	1915.09	8.42	15.833	0.021	53.84	1.11	18.20	3546.81	72.83	14.11		
9-10	9.5	1906.67	8.42	18.844	0.024	64.87	1.59	18.68	3203.67	78.29	10.85		
10-11	10.5	1898.24	8.42	22.143	0.029	50.70	1.46	14.13	3108.03	89.26	10.19		
11-12	11.5	1889.82	8.42	10.69	0.014	17.23	0.24	4.58	3445.18	47.76	10.78		
12-13	12.5	1881.39	8.42	9.0623	0.012	31.16	0.37	9.12	3859.39	45.36	13.28		
13-14	13.5	1872.97	8.42	10.748	0.014	22.55	0.31	5.93	3329.32	46.41	10.30		
14-15	14.5	1864.54	8.42	15.32	0.020	33.37	0.66	9.84	3471.83	68.98	12.04		
15-16	15.5	1856.12	8.42	16.905	0.022	24.01	0.53	6.29	3185.29	69.84	9.82		
16-17	16.5	1847.69	8.42	16.698	0.022	15.02	0.33	4.69	2592.88	56.15	9.53		
17-18	17.5	1839.27	8.42	20.7	0.027								
18-19	18.5	1830.84	8.42	26.29	0.034								
19-20	19.5	1822.42	8.42	28.577	0.037	32.40	1.20	11.32	1638.16	60.71	6.73		
20-21	20.5	1813.99	8.42	26.616	0.035								
21-22	21.5	1805.57	8.42	21.83	0.028								
23-24	23.5	1788.72	8.42	19.879	0.026	22.55	0.58	4.62	1789.27	46.13	4.31		
31-32	31.5	1721.32	8.42	27.544	0.036	20.03	0.72	5.14	3609.44	128.94	10.90		
46-47	46.5	1594.95	8.42	50.09	0.065				3458.77	224.69			
52-53	52.5	1544.41	8.42	39.09	0.051				5589.01	283.34			
60-61	60.5	1477.01	8.42	23.22	0.030	16.41	0.49	5.59	7835.46	235.96	31.38		

sample midpt depth (cm)	natural abundance P		800 µg/g		natural abundance Al		71300 µg/g		natural abundance Na		6300 µg/g	
	ratio/ nat. Al	ratio/ nat. Al	0.0112202	µg/cm <sup>2</sup> -yr factor	ratio/ nat. Al	ratio/ nat. Al	1	µg/cm <sup>2</sup> -yr factor	ratio/ nat. Al	ratio/ nat. Al	0.08835905	µg/cm <sup>2</sup> -yr factor
	P µg/g sample	P µg/cm <sup>2</sup> -yr factor	P enrichment Al µg/g sample	Al deposition µg/cm <sup>2</sup> -yr factor	Al enrichment Na µg/g sample	Al deposition µg/cm <sup>2</sup> -yr factor	Al enrichment Na µg/g sample	Na deposition µg/cm <sup>2</sup> -yr factor	Na enrichment µg/cm <sup>2</sup> -yr factor	Na deposition µg/cm <sup>2</sup> -yr factor	Na enrichment µg/cm <sup>2</sup> -yr factor	Na deposition µg/cm <sup>2</sup> -yr factor
1.00	1100.03	19.75	5.69	17245.01	309.63	1.00	605.14	10.87	0.40	10.87	0.40	
2.50	934.50	17.13	3.72	22410.94	410.81		257.96	4.73	0.13	4.73	0.13	
3.50	995.42	22.90	4.37	20281.75	466.60		231.30	5.32	0.13	5.32	0.13	
4.50	887.00	15.70	4.05	19517.29	345.39		191.63	3.39	0.11	3.39	0.11	
5.50	1065.27	26.11	5.22	18173.42	445.49		1464.77	35.91	0.91	35.91	0.91	
6.50	940.84	21.04	4.27	19625.67	438.83		264.40	5.91	0.15	5.91	0.15	
7.50	826.42	19.97	3.96	18611.22	449.82		193.34	4.67	0.12	4.67	0.12	
8.50	752.71	15.46	3.18	21090.13	433.07		208.73	4.29	0.11	4.29	0.11	
9.50	689.66	16.85	2.48	24762.47	605.17		233.98	5.72	0.11	5.72	0.11	
10.50	1112.07	31.94	3.87	25591.10	734.92		232.42	6.67	0.10	6.67	0.10	
11.50	1435.28	19.90	4.77	26810.09	371.70		1236.06	17.14	0.52	17.14	0.52	
12.50	1630.91	19.17	5.96	24373.23	286.46		1336.52	15.71	0.62	15.71	0.62	
13.50	1376.26	19.18	4.53	27104.85	377.82		1368.59	19.08	0.57	19.08	0.57	
14.50	1564.36	31.08	5.76	24185.64	480.54		1259.31	25.02	0.59	25.02	0.59	
15.50	1462.06	32.05	4.79	27215.69	596.69		1110.98	24.36	0.46	24.36	0.46	
16.50	1252.50	27.12	4.89	22827.36	494.35		1176.42	25.48	0.58	25.48	0.58	
17.50												
18.50												
19.50	1066.04	39.51	4.66	20407.08	756.33		1128.11	41.81	0.63	41.81	0.63	
20.50												
21.50												
23.50	1495.39	38.55	3.83	34822.33	897.77		1168.93	30.14	0.38	30.14	0.38	
31.50	953.47	34.06	3.06	27778.70	992.32		1259.81	45.00	0.51	45.00	0.51	
46.50	616.63	40.06					766.27	49.78		49.78		
52.50	864.74	43.84					684.75	34.71		34.71		
60.50	373.73	11.25	1.59	20945.66	630.77		1003.66	30.22		30.22	0.54	

NOTE: 3-4, 7-8 through 10-11, and 46-47,52-53 cm Al are lower limits

