DEDICATION

This thesis is dedicated to my brother Kalamazad, who died in a tragic accident on 11th February, 1976. Kalamazad, 4 years my senior, was my mathematics teacher for 2 years and his inspiration has certainly made me a better mathematics student which is reflected largely in this thesis.

Kalamazad was not only a great teacher, but he also earned the distinction of being one of the top engineers in Guyana. Had he not such an untimely death, he would have made, I am sure, an outstanding contribution to engineering.

It seems fitting therefore to dedicate this thesis as a small tribute to my brother whose tragic loss will be felt for years to come.
SPECTRAL ANALYSIS

OF

ATMOSPHERIC POLLUTANTS

IN THE

UPPER GREAT LAKES REGION
SPECTRAL ANALYSIS
OF
ATMOSPHERIC POLLUTANTS
IN THE
UPPER GREAT LAKES REGION

By

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ABSTRACT

Chemical data from atmospheric precipitation in the Upper Great Lakes region were collected on a monthly basis by various organizations from late 1972 to late 1975. The data for pairs of chemical parameters are regarded as simultaneously recorded time series and are analyzed by spectral analysis to bring out periodic components present in both time series and also to reflect the correlation and phase difference between the pairs of time series.

The precipitation data have four major bands of periodicities: (1) a yearly cycle representing high and low atmospheric loadings in the summer and winter respectively with regards to Fe, PART, SO₄ and P; (2) a 6 monthly period reflecting the four seasons of the year and affecting Fe, PART, P and pH; (3) a 9 monthly period for the heavy metals (Cu, Ni, Cd, Pb and Zn); and (4) 2 to 5 cycles/month periodicities caused by atmospheric turbulence and affecting all the parameters.

The mining-smelting industry at Sudbury has been identified as a major point source of atmospheric emissions of acid, sulfate and the heavy metals, with the exception of iron. This is evident in view of the facts that the spectral intensities at the major periodicities decrease away from the mining-smelting centre; the strikingly high correlation and practically inphase relationship between Cu and Ni, and the 9 monthly period for the heavy metals which is associated with the industry.
ACKNOWLEDGEMENTS

The writer would like to express his gratitude to Dr. H. D. Grundy for suggesting the topic for this project and for his supervision and intellectual inspiration provided throughout. Dr. Grundy has been particularly helpful in providing the author with valuable references, and also by devoting his time to entertain frequent discussions -- all of which contributed to a better understanding of the problem and for which the author is extremely grateful.

I would also like to express my greatest thanks to my wife Jackie for her patience and understanding during the writing of this thesis and also for her continual help with its preparation.
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1. INTRODUCTION

1.1 Statement of Problem

An international network of stations is set up in the Upper Great Lakes region to collect chemical data from atmospheric precipitation. Samples of precipitation are collected on a monthly interval and the concentration of various chemical parameters are determined. The large amount of data ranging from late 1973 to late 1975 is particularly suited for computer manipulations and is therefore analyzed by spectral analysis.

The aim of the present study is to analyze the data (time series) for any periodic components. Furthermore, to see if any loading parameters are correlated and what are their possible sources of origin. If a model is suggested as a result of this analysis, then it can be used to make predictions. That is, the estimation of future values $x(t + T)$ of the time series in some future range $0 \leq T < T'$ from some values of the series up to and including time $t$.

1.2 Outline of Analysis

The obvious method of analysis of periodic data is the classical Fourier analysis. The precise use of the technique in this study is to approximate non-periodic functions by sine and cosine functions. The approximation becomes better as the number of points increases and becomes exact if the number of points is infinite.
To analyze for cross correlation between two series involves statistical analysis. Thus statistical questions, to be discussed later, do arise from the fact that it is necessary to estimate the accuracy of the various functions obtained from finite amounts of data.

Consequently two very important approaches are considered, the statistical analysis of time series and the method of Fourier analysis. These two approaches constitute spectral analysis.

The main advantage of spectral analysis is that large amounts of data are digested into a few graphical spectral presentations, the main features of which can be readily interpreted and which disclose persistent periodicities in the data, if present.

The power spectrum shows the frequency distribution of the energy (variance) of a time series over a defined frequency range. Peaks in particular frequency bands of the spectrum indicate higher contents of energy in those bands than in neighbouring ones. The positions of the peaks give the periodicities.

To disclose relationships between loading parameters, they must be analyzed in pairs. The pairs are regarded as simultaneously recorded time series. Cross spectral analysis of such series contains two different types of information. The first is the squared coherency spectrum which effectively measures the correlation between the two series at each frequency, and the second is the phase spectrum which measures the phase difference between the two series at each frequency.

Energy distribution with frequency is not a continuous distribution, but is a "histogram" made up of estimates of successive small sub-divisions of the frequency range. The number of such sub-divisions is
called the number of "lags". It determines the statistical reliability of the results obtained and the frequency resolution. The resolution increases as the number of lags $L$ increases. However, the number of degrees of freedom ($\frac{2N}{L}$ where $N$ is the number of points in the time series) and hence the statistical reliability, decreases as $L$ increases (i.e. the confidence limits widen as $L$ increases).

When large amounts of data are analyzed, for example 10,000 points, it is not possible to look at the data and the spectra consistently and the number of lags becomes crucial. However, with an average of 40 points displayed graphically together with the spectra, interpretation can be consistent and less emphasis can be placed on the number of lags. Thus in the present work the number of lags is set equal to $N/2$ to give an adequate amount of resolution to disclose gross features.

The data used in this study were collected on a monthly interval and thus the maximum frequency $f_n$ is 0.5 cycles/month. If there is appreciable energy in the time series corresponding to frequencies greater than $f_n$, then this energy can generate spurious additions and peaks in the range 0 to $f_n$, which in severe cases can completely mask the true spectrum. For the present data, a period of less than two months is unlikely. In any event, it would be very costly to sample, say, every $\frac{1}{2}$ month to see a $\frac{1}{6}$ monthly period, if present.

Fourier analysis requires a continuous series. In most cases the data are complete but in the few cases where data are missing for less than 3 months then such gaps are filled by the value of the month immediately preceding the gap.
Spectral analysis is applicable to stationary time series. Hence any trends present in the data must be removed. Atmospheric loading is presumably due to industries and therefore broad trends are expected which reflect the gradual growth of the economy. Such trends are rather difficult to remove if the data are not well understood. At the present time, the best one can do is to assume a linear trend and remove it by a least squares fit to all the data and subtraction to obtain the residuals which are used in the analysis. Negative residuals do not have physical meaning for the data and are set equal to zero.
2. METHODS

2.1 Mathematical Development

Spectral analysis brings together two very important theoretical approaches, the statistical analysis of time series and the methods of Fourier analysis. The role of Fourier analysis in applied mathematics and engineering is well documented. The analytic techniques are particularly important in three applications: (a) for studying periodic solutions to physical problems described by differential equations; (b) as an operational device for solving differential equations; (c) for approximating non-periodic functions.

The present study is concerned primarily with the latter case. Before going into the analysis in some details, it is necessary to define a few basic terms.

A function is said to be periodic of period \( T \), if for all \( t \),

\[
f(t) = f(t + T).
\]  

(2.1.1)

The function between time \( t \) and \( t + T \) can be of any shape whatsoever. A particularly simple shape is the cosine function,

\[
f(t) = A \cos 2\pi f_t, \quad -\infty < t < \infty,
\]  

(2.1.2)

which has a period \( T = 1 \), since

\[
A \cos 2\pi f_t = A \cos 2\pi f_{t+\left(\frac{1}{T}\right)}.
\]  

(2.1.3)

Furthermore, a function \( f(t) \) is said to be a (real) harmonic with frequency \( w \) and amplitude \( A \), where \( A \) and \( w \) are positive constants,
if it is of the form

\[ f(t) = A \cos wt \]

or

\[ f(t) = A \sin wt. \]  

(2.1.4)

A harmonic with frequency, \( w \), has period

\[ T = \frac{2\pi}{w}, \]  

(2.1.5)

and since it is a harmonic, it must satisfy

\[ T = k\frac{2\pi}{w} \text{ for some integer } k=1,2,..., \]  

(2.1.6)

since

\[ \cos (w(t+e)) = \cos wt \Rightarrow e=k\frac{2\pi}{w}. \]  

(2.1.7)

The frequency, \( w \), represents the number of complete cycles in \( 2\pi \) units of time and is therefore called the angular frequency, to distinguish it from the true frequency, \( f \), measured in cycles per unit time. The true frequency \( f \) of a harmonic with angular frequency \( w \) is given by

\[ f = \frac{w}{2\pi} = \frac{1}{T}. \]  

(2.1.8)

For completeness, we may define zero frequency by a constant function

\[ f(t) = A, \]  

(2.1.9)

which may be regarded as the value of the harmonic function \( A \cos wt \) with \( w = 0 \).

2.2 Fourier Analysis

It is possible to represent any non-periodic functions using any class of periodic functions. In Fourier analysis, the periodic functions used are sine and cosine functions. They have the important properties that an approximation consisting of a given number of terms
achieves the minimum mean square error between the signal and the approximation, and also they are orthogonal, so the coefficients may be determined independently of one another.

Consider a signal which is specified only at discrete times, and suppose it is required to be expanded in terms of periodic functions. The discrete signal can be regarded as having been derived from a continuous signal $S(t)$ of duration $T$ by sampling the values of the signal at spacing $\Delta$, as shown in Figure 2.2.1. This produces $N = T/\Delta$ sample values $S_r$, where

$$S_r = S(t=r\Delta). \quad (2.2.1)$$

![Figure 2.2.1: A discrete signal obtained by sampling a continuous signal.](image)

For convenience it is assumed that $N$ is even and equal to $2n$ so that $r$ may run through the integers $-n, \ldots, 0, 1, \ldots, n - 1$.

Note that periodic functions which pass through the sample values may be chosen in an infinite number of ways. For example, the
finite Fourier series

\[ S(t) = A_0 + 2 \sum_{m = 1}^{n-1} \left( A_m \cos 2\pi mf_1 t + B_m \sin 2\pi mf_1 t \right) + A_n \cos 2\pi nf_1 t \]  

(2.2.2)

contains \( N \) constants, the \( A_m \) and \( B_m \), which can be determined so that the discrete and continuous values coincide at the points \( t = r\Delta \), that is, \( S(t) = S_r \). Thus the function \( S(t) \) provides an approximation to the original continuous function \( S(t) \) in the interval \( -T/2 \leq t < T/2 \).

On substituting \( t = r\Delta \) in (2.2.2) and setting \( S(r\Delta) = S_r \), a set of \( N \) equations for the \( N \) unknown constants is obtained. The equations are

\[ S_r = A_0 + 2 \sum_{m = 1}^{n-1} \left( A_m \cos 2\pi mf_1 r\Delta + B_m \sin 2\pi mf_1 r\Delta \right) + A_n \cos 2\pi nf_1 r\Delta, \]

\( (r = -n, \ldots, 0, 1, \ldots, n - 1) \).  

(2.2.3)

Choosing \( f_1 = 1/N\Delta \) simplifies the solution of equation (2.2.3), because then the sines and cosines are orthogonal. The frequency \( f_1 = 1/N\Delta \) is called the fundamental frequency of the signal \( S(t) \), and it corresponds to a period \( T_1 \) equal to the length of the record,

\[ f_1 = \frac{1}{N\Delta}; \quad T_1 = N\Delta. \]  

(2.2.4)

The function \( S(t) \) is composed of a sum of sine and cosine functions whose frequencies are multiples or harmonics of the fundamental \( f_1 \). Note that \( (N = 2n) \) the

2nd harmonic: \( f_2 = \frac{2}{N\Delta}; \quad T_2 = \frac{N\Delta}{2}; \quad f_2 = 2f_1 \)

and

\[ \text{nth harmonic: } f_n = \frac{n}{N\Delta} = \frac{N/2}{N\Delta} = \frac{1}{2\Delta}, \quad T_n = 2\Delta, \quad f_n = nf_1 \]  

(2.2.5)
The highest frequency $f_n$ present is $1/2\Delta$, which corresponds to a Period of 2 sampling intervals. The parameter $f_n$ is called the "Nyquist frequency". If the number of points $N$ is odd, say $2n - 1$, (2.2.2) can be solved by similar reasoning, the only difference being that the $A_n$ term vanishes. Furthermore, it can be shown that $A_0$ is the mean or average value of $S_r$ if $N$ is either even or odd.

To solve (2.1.3) for the constants, the $A_m$ and $B_m$, the discrete Fourier transform of the series of $N$ terms would require approximately $N^2$ operations. This is very expensive to operate when large number of data points are involved. However, a recent innovation in spectral analysis is the fast Fourier transform (FFT).

2.3 Fast Fourier Transform

The FFT is an algorithm for computing discrete Fourier transforms much more quickly than the direct method given above, but at the same time retaining accuracy. For a series of $N$ terms, the FFT requires only $2N\log_2 N$ operations compared to $N^2$ operations required for the direct method. Thus savings in computer time is very large if one is interested in the Fourier analysis of long series.

The relevance of the FFT to spectral analysis is that it is now faster to compute the power spectrum directly using an FFT, then smooth the spectrum rather than compute the autocorrelation function, smooth with a lag window and finally transform.

Description of the Fast Fourier Transform

Suppose it is required to find the Fourier transform
\[ X_m, m = 0, 1, \ldots, N - 1, \] of the series \[ x_t, t = 1, 2, \ldots, N, \] where \( N \) is even.

The series can be partitioned into two series \( y_t \) and \( z_t \), where

\[
y_t = x_{2t-1},
\]
\[
z_t = x_{2t}, \quad t = 1, 2, \ldots, N/2.
\] (2.3.1)

The series \( y_t, z_t \) each consist of \( N/2 \) values and hence have Fourier transforms

\[
y_m^{(N/2)} = \frac{2}{N} \sum_{t=1}^{N/2} y_t e^{-j(4\pi tm/N)},
\]

and

\[
z_m^{(N/2)} = \frac{2}{N} \sum_{t=1}^{N/2} z_t e^{-j(4\pi tm/N)},
\] (2.3.2)

where the superscript on the transform denotes the number of terms in the series and the transform. But \( X_m^{(N)} \) and \( Y_m^{(N/2)}, Z_m^{(N/2)} \) are related. In fact,

\[
X_m^{(N)} = e^{j(2\pi m/N)} \frac{1}{2} y_m^{(N/2)} + \frac{1}{2} z_m^{(N/2)}
\]

and

\[
X_m^{(N)} + Z_m^{(N/2)} = -e^{j(2\pi m/N)} \frac{1}{2} y_m^{(N/2)} + \frac{1}{2} z_m^{(N/2)}, \quad 0 \leq m \leq \frac{N}{2} - 1.
\] (2.3.3)

Therefore, the Fourier transform for the series \( x_t \) is easily obtained from the Fourier series of the half-series \( y_t \) and \( z_t \). Likewise, if \( N/2 \) is even, the series \( y_t \) and \( z_t \) are partitioned into two series \( y_t', z_t', \) and \( y_t'', z_t'' \) respectively, and an appropriate version of (2.3.3)
is used to construct the transforms $Y^{(N/2)}_m$ and $Z^{(N/2)}_m$ from the transforms of the series of length $N/4$.

For series of length $N = 2^k$, the procedure is followed until partitions of only one term are obtained, for which the Fourier transform equals the term itself. In practice, $N$ is not an exact power of 2, thus sufficient zeros must be appended to the data to make $N$ an exact power of 2. This procedure does not alter the accuracy of the answers in anyway.

2.4 Power Spectrum

The power spectrum is the Fourier transform of the autocovariance function (acvf). The spectrum shows how the variance (energy) is distributed with frequency for a time series over a defined frequency range. Subject to statistical considerations, peaks in particular frequency bands of the power spectrum indicate higher contents of energy in those bands than in neighbouring ones.

The variance or average power of a discrete signal $x(t)$ observed at times $t = -n\Delta, -(n - 1)\Delta, \ldots, (n - 1)\Delta$, can be decomposed into contributions at a finite number of harmonics of the fundamental frequency $f_1 = 1/N\Delta \ (N = 2n)$ according to

$$s_T^2 = \frac{1}{N} \sum_{t=-n}^{n-1} x_t^2 = \sum_{m=-n}^{n-1} |X_m|^2,$$

(2.4.1)

$X_m$ is called the complex amplitude at the harmonic frequency $f_m$ and measures the amplitudes of the sine and cosine terms at frequency $f_m$ in $x(t)$. $X_m$ is given by
The contribution of $|X_m|^2$ to the average power of frequency $f_m$ is called the intensity at this frequency.

The power spectrum $C_{xx}(f)$ is the Fourier transform of the acvf $y_{xx}(k)$,

$$C_{xx}(f) = \Delta \sum_{k=-\infty}^{\infty} y_{xx}(k) e^{-j2\pi kf} , \quad -\frac{1}{2\Delta} < f < \frac{1}{2\Delta} , \quad k = 0, \pm 1, \pm 2, \ldots \quad (2.4.3)$$

$C_{xx}(f)$ shows how the variance of the $X(t)$ process is distributed over frequency and is non-negative for all $f$. The spectrum is usually plotted on a logarithmic scale which shows more detail in the spectrum over a wider amplitude range. Another reason why the log. scale is a sensible choice is that only proportional changes in power is important. Furthermore, if confidence intervals is to be represented on the plot, then on a log. scale it is simply a constant interval about the spectral estimate.

**2.5 Cross Spectrum**

Cross spectral analysis of two simultaneously recorded time series provides information on the relationships between them, in the form of estimates of coherences and phase differences, as functions of frequency.

The acvf has a Fourier transform called the cross spectrum. This spectrum is a complex quantity which may be written as the product of a real function called the cross amplitude spectrum and a complex function called the phase spectrum. However, a more useful quantity than the
cross amplitude spectrum is the **coherency square spectrum**. The latter is dimensionless.

**2.6 Phase and Cross Amplitude Spectra**

Suppose that $x_1(t)$ and $x_2(t)$ are arbitrary real signals with Fourier transforms $X_1(f)$ and $X_2(f)$ respectively. These Fourier transforms give the amplitude and phase distribution of the signals, i.e.

$$X_i(f) = A_i(f) e^{j\Phi_i(f)}, \ i = 1, 2. \quad (2.6.1)$$

The cross spectrum can be written as

$$C_{12}(f) = A_{12}(f) e^{j\Phi_{12}(f)}. \quad (2.6.2)$$

The covariance between the two series $x_1(t)$ and $x_2(t)$ may be described by the **phase spectrum** $F_{12}(f)$,

$$F_{12}(f) = F_2(f) - F_1(f) \quad (2.6.3)$$

and the **cross amplitude spectrum**

$$A_{12}(f) = A_1(f)A_2(f)/T. \quad (2.6.4)$$

The phase spectrum $F_{12}(f)$ shows whether the frequency components in one series lead or lag the components at the same frequency in the other series. Similarly, the cross amplitude spectrum $A_{12}(f)$ shows whether the amplitude of the components at a particular frequency in one series is associated with a large or small amplitude at the same frequency in the other series.
2.7 Co- and Quadrature Spectra

Since (2.6.2) is a complex quantity, it can be written as a sum of a real and imaginary part, that is,

\[ C_{12}(f) = L_{12}(f) - jQ_{12}(f), \]

where

\[ L_{12}(f) = A_{12}(f) \cos F_{12}(f), \quad Q_{12}(f) = -A_{12}(f) \sin F_{12}(f), \quad (2.7.1) \]

and

\[ A_{12}^2(f) = L_{12}^2(f) + Q_{12}^2(f), \quad F_{12}(f) = \arctan \frac{Q_{12}(f)}{L_{12}(f)}. \]

\( L_{12}(f) \) is called the co-spectrum and it measures the variance between the in-phase components of the two series. \( Q_{12}(f) \) is called the quadrature spectrum and it measures the out of phase components of the two series.

2.8 Squared Coherency Spectrum

The squared coherency is defined as

\[ K_{12}^2(f) = \frac{L_{12}^2(f)}{C_{11}(f)C_{22}(f)} \quad (2.8.1) \]

where \( C_{11}(f) \) and \( C_{22}(f) \) are the power spectra of series 1 and series 2 respectively. A plot of \( K_{12}^2(f) \) versus \( f \) is called the squared coherency spectrum. It resembles the ordinary correlation coefficient. In fact, the coherency plays the role of the correlation coefficient defined at each frequency \( f \). A value near to unity indicates that the two series correlate closely, in terms of variance contribution, at a particular
frequency interval, while a value near to zero indicates little correlation between the two series at that frequency interval.

The coherency spectrum is useful in practice because it provides non-dimensional measure of the correlation between the two time series as a function of frequency. Thus it should be preferred to the cross amplitude spectrum, which depends on the scale of measurement of $x_1(t)$ and $x_2(t)$.

Consequently the cross correlation properties of two time series can be described by the squared coherency spectrum and the phase spectrum. The main uses of the co- and quadrature spectrum are in their estimation of the above two spectra.

2.9 Smoothed Cross Spectral Estimators

The estimators of the sample cross spectra have the undesirable properties that their variances are dominated by a constant term which does not tend to zero as the record length increases. Hence cross spectral estimators must be smooth using a spectral (lag) window. The lag window Hanning is used to smooth the data analyzed in this present study. Hanning is defined as

$$D(u) = \begin{cases} \frac{1}{2}(1 + \cos \frac{\pi u}{T_m}) & \text{for } |u| < T_m, \\ 0 & \text{for } |u| > T_m, \end{cases}$$

(2.9.1)

where $T_m$ is the maximum lag desired to be used. Note that $D(u)$ is an even function of $u$ and is regarded as a window of variable transmission which modifies the values of the autocovariance function at different lags.
2.10 Description of Computer Program (Fortran)

The program is presented in Appendix A. Except for the main program OFF and subroutine PLOTT, the program was obtained from Fee (1969) and little or no alteration was made to it.

The program is simple to understand. The major steps of operation of the program are as follows:

1. PROGRAM OFF: This is the main program which reads the data of two time series and their identification from tape. The two series represent data collected within the same period of time. The number of data points N is also noted.

2. SUBROUTINE FOUR: DELTAT (the time interval between observations), NUMBER (the number of time series to be analysed) and LAGS (the number of spectral estimates to be made) are set equal to 1, 2, and N/2 respectively. This subroutine also labels the output.

3. SUBROUTINE INPUT: The trend in the data is removed by a least squares fit to the data and subtraction to obtain the residuals. Negative residuals are set equal to zero. Finally, zeros are appended to the end of the data to make N an exact power of 2 (N = 2^k) as required for the fast Fourier transform.

4. SUBROUTINE FOURT: The time series is Fourier transformed to obtain the Fourier coefficients (a_{1k} + jb_{1k}, k = 0, \ldots, N).

Steps (3) and (4) are repeated for the second time series to obtain a_{2k} + jb_{2k}. Since two series are analysed, SUBROUTINE SPEC1 is inactive. However, it has been retained for generalization.

5. SUBROUTINE SPEK2: The real and imaginary Fourier coefficients are squared and summed over the number of lags L and normalized
by the number of terms squared,

\[ \sum_{k=1}^{L} \frac{(a_k^2 + b_k^2)}{(L - i + 1)} \]

to obtain the raw spectral estimates of both series.

The raw cross spectrum is obtained by taking the sum of the cross products of the real and imaginary parts of the transformed series,

\[ \sum_{k=1}^{L} (a_{1k} \times a_{2k}) + (b_{1k} \times b_{2k}) / (L - i + 1). \]

(6) The raw estimates are smoothed by Hanning (SUBROUTINE HANN) before estimation of the phase and coherency squared spectra.

(7) PHASE = \arctan \frac{(Quadrature spectrum_{k} \text{ smoothed})}{(Co-spectrum_{k} \text{ smoothed})} where k refers to the k\text{th} lag.

(8) \text{COHERENCE}_{k} = \frac{(Co-spectrum_{k})^2 + (Quadrature spectrum_{k})^2}{(Spectrum(1)_{k} \times spectrum(2)_{k})}

(9) SUBROUTINE PLOTT: This subroutine produces a series of plots of the data and spectra.

a) Raw data of series 1 (and trend) vs. time;

b) Series 1 (trend removed) vs. time;

c) Same as a) and b) for series 2;

d) Power spectrum for both series 1 and 2;

e) Phase spectrum;

f) Squared coherency spectrum.

2.11 Testing of Computer Program

The program is tested on simple periodic functions, namely the
sine and cosine functions. The values for the functions are estimated at ninety-six equally spaced sampling intervals on the domain 0 to $8\pi$. A linear least squares fit of all the points is also estimated.

The power spectra for the trigonometric functions are estimated for various lags, which include the lag to be used for the precipitation data of the Upper Great Lakes region. The expected results were obtained. They are discussed in Section 3.3.1.
3. RESULTS

3.1 Station Locations

Figure 3.1.1 shows the distribution of the monthly stations in the Upper Great Lakes (U.G.L.) region. Table 3.1.1 gives the latitude and longitude of the stations.

TABLE 3.1.1: Station locations

<table>
<thead>
<tr>
<th>No.</th>
<th>Station</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Skead</td>
<td>46.658N</td>
<td>80.752W</td>
</tr>
<tr>
<td>3</td>
<td>Killarney</td>
<td>45.990N</td>
<td>81.447W</td>
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<tr>
<td>4</td>
<td>Gore Bay</td>
<td>45.881N</td>
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<tr>
<td>5</td>
<td>Jamot</td>
<td>46.105N</td>
<td>80.625W</td>
</tr>
<tr>
<td>6</td>
<td>Windy Lake</td>
<td>46.615N</td>
<td>81.458W</td>
</tr>
<tr>
<td>8</td>
<td>Mount Lake</td>
<td>46.680N</td>
<td>82.725W</td>
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<tr>
<td>9</td>
<td>Gogama</td>
<td>47.675N</td>
<td>81.727W</td>
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<td>47.067N</td>
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<td>Espanola</td>
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<td>81.768W</td>
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<td>47.833N</td>
<td>83.400W</td>
</tr>
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<tr>
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<td>Kapuskasing</td>
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<td>Longitude</td>
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<td>Manitoulin Buoy</td>
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<td>Wawa Tower</td>
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<tr>
<td>110</td>
<td>Gore Bay Airport r</td>
<td>45.881N</td>
<td>82.570W</td>
</tr>
<tr>
<td>140</td>
<td>Gore Bay Airport s</td>
<td>45.881N</td>
<td>82.570W</td>
</tr>
<tr>
<td>112</td>
<td>Thunder Bay Airport r</td>
<td>48.373N</td>
<td>89.320W</td>
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<td>141</td>
<td>Thunder Bay Airport s</td>
<td>48.373N</td>
<td>89.320W</td>
</tr>
<tr>
<td>113</td>
<td>Wiarton Airport r</td>
<td>44.650N</td>
<td>81.233W</td>
</tr>
<tr>
<td>142</td>
<td>Wiarton Airport s</td>
<td>44.650N</td>
<td>81.233W</td>
</tr>
<tr>
<td>120</td>
<td>Sarnia Airport r</td>
<td>42.983N</td>
<td>82.283W</td>
</tr>
<tr>
<td>143</td>
<td>Sarnia Airport s</td>
<td>42.983N</td>
<td>82.283W</td>
</tr>
<tr>
<td>130</td>
<td>Caribou Island r</td>
<td>47.367N</td>
<td>85.833W</td>
</tr>
<tr>
<td>144</td>
<td>Caribou Island s</td>
<td>47.367N</td>
<td>85.833W</td>
</tr>
<tr>
<td>131</td>
<td>Copper Harbour r</td>
<td>47.469N</td>
<td>87.867W</td>
</tr>
<tr>
<td>145</td>
<td>Copper Harbour s</td>
<td>47.469N</td>
<td>87.867W</td>
</tr>
<tr>
<td>132</td>
<td>Isle Royale r</td>
<td>47.896N</td>
<td>89.216W</td>
</tr>
<tr>
<td>146</td>
<td>Isle Royale s</td>
<td>47.896N</td>
<td>89.216W</td>
</tr>
<tr>
<td>No.</td>
<td>Station</td>
<td>Latitude</td>
<td>Longitude</td>
</tr>
<tr>
<td>-----</td>
<td>--------------------------------------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>133</td>
<td>Ney Provincial Park r</td>
<td>48.750N</td>
<td>86.567W</td>
</tr>
<tr>
<td>147</td>
<td>Ney Provincial Park s</td>
<td>48.750N</td>
<td>86.567W</td>
</tr>
<tr>
<td>134</td>
<td>Pinery Provincial Park r</td>
<td>43.233N</td>
<td>81.800W</td>
</tr>
<tr>
<td>148</td>
<td>Pinery Provincial Park s</td>
<td>43.233N</td>
<td>81.800W</td>
</tr>
<tr>
<td>135</td>
<td>Inverhuron Park r</td>
<td>44.300N</td>
<td>81.567W</td>
</tr>
<tr>
<td>149</td>
<td>Inverhuron Park s</td>
<td>44.300N</td>
<td>81.567W</td>
</tr>
<tr>
<td>137</td>
<td>Kilbear Provincial Park r</td>
<td>45.350N</td>
<td>80.200W</td>
</tr>
<tr>
<td>138</td>
<td>Southampton Buoy</td>
<td>44.325N</td>
<td>81.650W</td>
</tr>
<tr>
<td>150</td>
<td>Kilbear Provincial Park s</td>
<td>45.350N</td>
<td>80.200W</td>
</tr>
<tr>
<td>201</td>
<td>Porcupine Mountains State Park</td>
<td>46.818N</td>
<td>89.644W</td>
</tr>
<tr>
<td>202</td>
<td>Isle Royale</td>
<td>47.896N</td>
<td>89.216W</td>
</tr>
<tr>
<td>203</td>
<td>Fort Wilkins State Park</td>
<td>47.497N</td>
<td>87.867W</td>
</tr>
<tr>
<td>204</td>
<td>Baraga State Park</td>
<td>46.760N</td>
<td>88.506W</td>
</tr>
<tr>
<td>205</td>
<td>Pictured Rocks</td>
<td>46.664N</td>
<td>86.006W</td>
</tr>
<tr>
<td>206</td>
<td>Tahquamenon Falls</td>
<td>46.543N</td>
<td>75.035W</td>
</tr>
<tr>
<td>207</td>
<td>Mackinac Island State Park</td>
<td>45.858N</td>
<td>84.617W</td>
</tr>
<tr>
<td>208</td>
<td>U.S. Coast Guard Station Alpena</td>
<td>45.034N</td>
<td>83.239W</td>
</tr>
<tr>
<td>209</td>
<td>U.S. Coast Guard Station Tawas Point</td>
<td>44.254N</td>
<td>83.447W</td>
</tr>
<tr>
<td>210</td>
<td>Albert Sleeper State Park</td>
<td>43.977N</td>
<td>83.211W</td>
</tr>
<tr>
<td>211</td>
<td>Port Sanilac</td>
<td>43.429N</td>
<td>82.552W</td>
</tr>
<tr>
<td>212</td>
<td>Bayfield</td>
<td>46.786N</td>
<td>90.865W</td>
</tr>
<tr>
<td>213</td>
<td>Tawas Buoy</td>
<td>44.225N</td>
<td>83.422W</td>
</tr>
<tr>
<td>214</td>
<td>Grand Marais</td>
<td>47.735N</td>
<td>90.334W</td>
</tr>
<tr>
<td>215</td>
<td>Benton Harbor</td>
<td>42.150N</td>
<td>93.384W</td>
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<tr>
<td>216</td>
<td>Silver Lake</td>
<td>43.608N</td>
<td>86.521W</td>
</tr>
<tr>
<td>217</td>
<td>Beaver Island</td>
<td>45.681N</td>
<td>85.508W</td>
</tr>
<tr>
<td>218</td>
<td>Two Harbors</td>
<td>47.002N</td>
<td>91.652W</td>
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<tr>
<td>219</td>
<td>Alpena Buoy</td>
<td>45.167N</td>
<td>83.217W</td>
</tr>
<tr>
<td>301</td>
<td>Mount Forest - wet</td>
<td>43.164N</td>
<td>80.750W</td>
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<tr>
<td>302</td>
<td>Armstrong - wet</td>
<td>50.283N</td>
<td>88.090W</td>
</tr>
<tr>
<td>303</td>
<td>Woodbridge - wet</td>
<td>43.795N</td>
<td>79.552W</td>
</tr>
</tbody>
</table>
Figure 3.1.1: Precipitation chemistry stations and wind directions in the Upper Great Lakes region.
3.2 Codes and Units of Parameters Considered in this Study

Table 3.2.1 shows the parameters used in this study. Not all the parameters listed in this table were used in the six areas considered. Those used in the various areas are given in Appendix B.

TABLE 3.2.1: Codes and units of parameters

<table>
<thead>
<tr>
<th>Name</th>
<th>Code</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd T</td>
<td>101</td>
<td>Total cadmium</td>
<td>micro-g/l</td>
</tr>
<tr>
<td>Cu F</td>
<td>106</td>
<td>Filtered copper</td>
<td>micro-g/l</td>
</tr>
<tr>
<td>Cu T</td>
<td>107</td>
<td>Total copper</td>
<td>micro-g/l</td>
</tr>
<tr>
<td>Fe T</td>
<td>110</td>
<td>Total iron</td>
<td>micro-g/l</td>
</tr>
<tr>
<td>Pb T</td>
<td>113</td>
<td>Total lead</td>
<td>micro-g/l</td>
</tr>
<tr>
<td>Ni T</td>
<td>116</td>
<td>Total nickel</td>
<td>micro-g/l</td>
</tr>
<tr>
<td>Zn F</td>
<td>118</td>
<td>Filtered zinc</td>
<td>micro-g/l</td>
</tr>
<tr>
<td>Zn T</td>
<td>119</td>
<td>Total zinc</td>
<td>micro-g/l</td>
</tr>
<tr>
<td>SP CON</td>
<td>122</td>
<td>Specific conductivity</td>
<td>umho/cm</td>
</tr>
<tr>
<td>pH</td>
<td>123</td>
<td>Hydrogen ion concentration</td>
<td></td>
</tr>
<tr>
<td>SO₄</td>
<td>127</td>
<td>Sulphate</td>
<td>mg/l</td>
</tr>
<tr>
<td>T PART</td>
<td>128</td>
<td>Total particulate weight</td>
<td>g/l</td>
</tr>
<tr>
<td>P T</td>
<td>240</td>
<td>Total phosphorus</td>
<td>micro-g/l</td>
</tr>
</tbody>
</table>

3.3 Data and Spectra

3.3.1 Sine and cosine functions

Figures 3.3.1 and 3.3.2 show the data and trends for the sine and cosine functions respectively. Note that the trends are not straight lines of zero slopes and zero intercepts. This is due to termination errors which result since a finite number of points are used. Figures 3.3.3 and 3.3.4 show the functions after the trends are removed. As expected, small trends result due to the least squares fit.
Figure 3.3.1: Sine function and trend for the domain 0 to 8\pi
(24 sampling intervals = 2\pi)
Figure 3.3.2: Cosine function and trend for the domain 0 to $8\pi$
(24 sampling intervals = $2\pi$)
Figure 3.3.3: Sine function of Figure 3.3.1 after trend removed
Figure 3.3.4: Cosine function of Figure 3.3.2 after trend removed
The effects of various lags on the power spectrum are shown in Figures 3.3.5 through 3.3.10. The peaks in the spectra indicate the periodicity. The peaks are very close to \(2\pi\), which corresponds to 24 sampling intervals. In the spectra, the peak positions are given in terms of lags which has to be converted to sampling intervals.

Figures 3.3.5 and 3.3.6, for which the lags equal 32, show essentially pure spectra. As the lags increase the resolution increases (peaks are sharper) but the spectra become contaminated with "ripples" and the statistical reliability decreases.

To illustrate the fact that any obvious trends in the data must be removed before analysis, a linear trend is added to the sine function (Figure 3.3.11). The power spectrum is shown in Figure 3.3.12. The peak is more or less "washed-out". Hence it is absolutely necessary to remove any trends from the data before using the Fourier analysis.

The phase and squared coherency spectra were not plotted for the trigonometric functions, but the values obtained agree quite well with the expected results. The correlation at the \(2\pi\) periodicity is 0.99 and the phase difference is 90.0 degrees.

### 3.3.2 Errors

The peaks in the power spectra do not occur exactly at 24 sampling intervals. Table 3.3.1 gives the periodicity for the various lags and the cross correlation properties. From the spectra, it can be seen that if smooth curves are to be drawn through the points then the periodicity would be very close to the lower values given in the Table. Even though there is some variation in the periodicity, the correlation and phase are quite consistent and very accurate.
Figure 3.3.5: Power spectrum for data of Figure 3.3.3, lags = 32
Figure 3.3.6: Power spectrum for data of Figure 3.3.4, lags = 32
Figure 3.3.7: Power spectrum for data of Figure 3.3.3, lags = 48
Figure 3.3.8: Power spectrum for data of Figure 3.3.4, lags = 48
Figure 3.3.9: Power spectrum for data of Figure 3.3.3, lags = 64
Figure 3.3.10: Power spectrum for data of Figure 3.3.4, lags = 64

FOR \( Y = \cos(X) \)
Figure 3.3.11: Data for linear trend added to the sine function
Figure 3.3.12: Power spectrum for data of Figure 3.3.11, lags = 48
TABLE 3.3.1:

Periodic and cross-correlation properties for the trigonometric functions. (24 sampling intervals = 2π).

<table>
<thead>
<tr>
<th>Period (sampling intervals)</th>
<th>sin x and cos x</th>
<th>Correlation</th>
<th>Phase (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>21.3 - 32.0</td>
<td>.99</td>
<td>90.0</td>
</tr>
<tr>
<td>48</td>
<td>24.0 - 32.0</td>
<td>.99</td>
<td>90.0</td>
</tr>
<tr>
<td>64</td>
<td>25.6 - 32.0</td>
<td>.99</td>
<td>90.0</td>
</tr>
</tbody>
</table>

The reason why the periodicity does not occur at exactly 24 sampling intervals is due mainly to the finite amount of points used. The least squares fit is not quite adequate and leads to a small error. Furthermore, there is no definite way to determine the number of lags to be used. However, one must compromise between resolution and statistical reliability. Finally, another source of error is the graphing of the spectra which consist of straight line segments rather than smooth curves.

3.3.3 Precipitation data and spectra

The data for the parameters studied can be displayed in two forms. The first consists of the raw data and trend. The resulting data after the trend is removed is the second form. Note that negative residuals are set equal to zero. The second form is used in the actual analysis. Due to space limitation, only the raw data and trend are given in this work, since they contain more information. However, the second form of data can easily be visualized if one considers the trend line as the time-axis. The data are given in Appendix B.

Three types of data are studied. The first consists of the individual stations 12, 2, 3, and 4. The second consists of data which is
the average over eleven stations (2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13). This will be referred to as the Sudbury area. The third type is the data which is the average of the Upper Great Lakes area. This consists of the stations listed in Table 3.1.1.

The Figures to follow are the spectra of pairs of data sets representing two simultaneously recorded time series. The figures show the parameters, the length of the data and locations. The parameters considered here are listed in Table 3.3.2. Spectra for other parameters are given in Appendix B.

**TABLE 3.3.2: Parameters, locations and length of data.**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Area</th>
<th>Time Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu T &amp; Ni T</td>
<td>Station 12</td>
<td>7210-7511</td>
</tr>
<tr>
<td>Cu T &amp; Ni T</td>
<td>Station 2</td>
<td>7206-7511</td>
</tr>
<tr>
<td>Cu T &amp; Ni T</td>
<td>Station 3</td>
<td>7211-7511</td>
</tr>
<tr>
<td>Cu T &amp; Ni T</td>
<td>Station 4</td>
<td>7204-7511</td>
</tr>
<tr>
<td>Cu T &amp; Ni T</td>
<td>Sudbury area</td>
<td>7208-7511</td>
</tr>
<tr>
<td>Cu T &amp; Ni T</td>
<td>U.G.L. area</td>
<td>7201-7511</td>
</tr>
<tr>
<td>Cd T &amp; Ni T</td>
<td>Station 12</td>
<td>7210-7511</td>
</tr>
<tr>
<td>Cd T &amp; Ni T</td>
<td>Station 2</td>
<td>7206-7510</td>
</tr>
<tr>
<td>Cd T &amp; Ni T</td>
<td>Station 3</td>
<td>7211-7511</td>
</tr>
<tr>
<td>Cd T &amp; Ni T</td>
<td>Station 4</td>
<td>7204-7507</td>
</tr>
<tr>
<td>Cd T &amp; Ni T</td>
<td>Sudbury area</td>
<td>7208-7511</td>
</tr>
<tr>
<td>Cd T &amp; Ni T</td>
<td>U.G.L. area</td>
<td>7201-7511</td>
</tr>
<tr>
<td>Zn T &amp; Zn F</td>
<td>Sudbury area</td>
<td>7204-7511</td>
</tr>
<tr>
<td>Zn T &amp; Zn F</td>
<td>U.G.L. area</td>
<td>7204-7511</td>
</tr>
<tr>
<td>Cu T &amp; Cu F</td>
<td>Sudbury area</td>
<td>7204-7511</td>
</tr>
<tr>
<td>Cu T &amp; Cu F</td>
<td>U.G.L. area</td>
<td>7204-7511</td>
</tr>
<tr>
<td>pH &amp; T PART</td>
<td>Station 12</td>
<td>7206-7511</td>
</tr>
<tr>
<td>pH &amp; T PART</td>
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<td>7206-7511</td>
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<tr>
<td>pH &amp; T PART</td>
<td>U.G.L. area</td>
<td>7204-7511</td>
</tr>
</tbody>
</table>
Figure 3-3.18: Phase spectrum for Cu T & Mi T, station 2 (7206-7511)

PHASE SPECTRUM

PHASE

180
150
120
90
60
30
0
-30
-60
-90
-120
-150
-180

0.00
0.053
0.105
0.158
0.211
0.263
0.316
0.368
0.421
0.474

FREQUENCY (CYCLES/MONTH)
PERIOD (MONTHS)
Figure 3.3.19: Power spectrum for Cu T & Ni T, station 3 (721-7511)

RELATIVE SPECTRAL INTENSITIES

FREQUENCY (CYCLES/MONTH)

PERIOD (MONTHS)
Figure 3.3.20: Coherency spectrum for Cu T & Ni T, station 3 (7211-7511)

SQUARED COHERENCY SPECTRUM

COHERENCE

0.00 0.10 0.20 0.30 0.40 0.50 0.60 0.70 0.80 0.90 1.00

FREQUENCY (CYCLES/MONTH)

PERIOD (MONTHS)
Figure 3.3.21: Phase spectrum for Cu, T, & N, station 3 (7211-7511)

Phase Spectrum

Phase

Frequency (cycles/month)
Period (months)

36.00 5.20 111 167 5.14 222 4.00 278 3.27 333 2.77 389 2.40 444 2.00 500
SQUARED COHERENCY SPECTRUM

COHERENCE

FREQUENCY (CYCLES/MONTH)

PERIOD/MONTHS

49
Figure 3.25. Power spectrum for Cu T & Ni T, Sudbury area (7208-7511)

RELATIVE SPECTRAL INTENSITIES

FREQUENCY (CYCLES/MONTH)

PERIOD (MONTHS)

X 116 NI T MICRO-GM/L
+
107 CU T MICRO-GM/L
SQUARED COHERENCY SPECTRUM

COHERENCE

FREQUENCY (CYCLES/MONTH) PERIOD (MONTHS)

0.00 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50
40.00 63.33 8.00 5.71 4.44 3.64 3.08 2.67 2.35

Figure 3.3.26: Coherency spectrum for Cu, T & Mt, Sudbury area (7208-7511)
Figure 3.3.27: Phase spectrum for Cu T & Ni T, Sudbury area (7208-7311)

Phase Spectrum

Frequency (Cycles/Month)
Period (Months)

Phase

-180
-150
-120
-90
-60
-30
0
30
60
90
120
150
180

40.00 13.33 8.00 5.71 4.44 3.33 2.67 2.35 2.08 2.00 1.71 1.50 1.33 1.00 0.80 0.67 0.50

400 450 400 350 300 250 200 150 100 50
Figure 3.28: Power spectrum for Cu T & Ni T, U.G.I. area (7200±5±11)

RELATIVE SPECTRAL INTENSITIES

FREQUENCY (CYCLES/MONTH)
PERIOD (MONTHS)

X 116 Ni T MICRO-GM/L
+ 107 Cu T MICRO-GM/L

4.695
4.572
4.325
4.078
3.832
4.828
4.680
4.388
4.087
3.791

0.043
0.087
0.130
0.174
0.217
0.261
0.304
0.348
0.391
0.435
0.479
0.50
SQUARED COHERENCY SPECTRUM

Figure 3.3.29: Coherency spectrum for Cu T & Ni T, U.G.I. area (2201-3511)
Figure 3.3.20: Phase spectrum for Cu, T & Ni, T, U.G.I. area (7/20/73-11/20/74)
Figure 3.3.22: Coherence spectrum for Od T. M1 T., station 12 (720-751)
Figure 3.3.33: Phase spectrum for Ga T & Nt T, station 12 (7210-7511)
SQUARED COHERENCY SPECTRUM

Figure 3.35: Coherence spectrum for 03 T & N, T, station 2 (7205-7511)

COHERENCE

FREQUENCY (CYCLES/MONTH) PERIOD (MONTHS)
Figure 3.36: Phase spectrum for Cdt & Mt station 2 (7206-7311)
Figure 3.39: Phase spectrum for Cd T & M T. station 3 (72-1-75II)
Figure 3.3.41: Coherence spectrum for Oil T & Mt T station 4 (7204-7507)

Squared Coherence Spectrum

Coherence

0.00 0.10 0.20 0.30 0.40 0.50 0.60 0.70 0.80 0.90 1.00

Frequency (cycles/month)

Period (months)
Figure 3.42: Phase spectrum for Ca T & Mi T, station 4 (7204-7507)
Figure 3.34: Power spectrum for 063, F, and NL, Essex area (7208-7511)
RELATIVE SPECTRAL INTENSITIES

FREQUENCY (CYCLES/MONTH)

PERIOD (MONTHS)

0.00 0.46 1.86 2.27 2.61 2.97 3.30 3.67 3.94 4.20 4.57 4.89

Figure 3.34: Power spectrum for DM I & II, U.G.L. area (1954-1974)
Figure 3.3: Coherency spectrum for Ca T & Mt T, U.G.L. area (1920-75).
Figure 3.3-31: Phase spectrum for Zn T & Zn F, Sudbury area (7204-7511)
SQUARED COHERENCY SPECTRUM

Figure 3.3, 53: Coherency spectrum for Zn T & Zn F, U G I I area (1204-2511)
Figure 3.3.55: Power spectrum for Cu T & Cu F, Sudbury area (7204-7511)

RELATIVE SPECTRAL INTENSITIES

X 106 Cu F MICRO-GM/L
+
107 Cu T MICRO-GM/L

FREQUENCY (CYCLES/MONTH)
PERIOD (MONTHS)
Figure 3.56, Coherency spectrum for Cu I & Cu F, Sudbury area (7204-7211).
SQUARED COHERENCY SPECTRUM

Figure 3.3.59: Coherence spectrum for Cu & Cu P. U.G.L. area (7204-7511)
Figure 3.60: Phase spectrum for CuT & CuP, U.C.I. area (7704-7911)
SQUARED COHERENCY SPECTRUM

Figure 3.62: Coherence spectrum for DH & T PRT, station 12 (7206-751)
PHASE SPECTRUM

Figure 3.3.03: Phase spectrum for pH & T PART station 12 (7206-7511)
SQUARED COHERENCY SPECTRUM

Figure 3.36: Coherence spectrum for pH & T PART, station 2 (7206-7511)
Figure 3.3.1, Phase spectrum for pH & T PART, station 2 (7206-7511)
SQUARED COHERENCY SPECTRUM

Figure 3.3.68: Coherency spectrum for PH & T PART, U.G.I. area (7204-7511)
3.4 Errors for Precipitation Data

Section 3.3.2 discusses the errors involved in the spectral analysis with regards to the trigonometric functions. The same comments hold for the precipitation data. In addition, the precipitation data length is much shorter. On the average, about forty points are analyzed, which is less than half of that used for the trigonometric functions. This will introduce quite a bit of errors in the periodicities in particular. The writer has no control over this in that the data available are limited. However, as the record length increases the errors should decrease.

In an innocent example as the sine function, the trend could not be removed properly. Thus, for the rather fluctuating precipitation data, the trend removal is quite likely to be unreliable. It is extremely difficult to remove trends associated with the economy and at the moment it is the best one can do until the data are better understood. Only then methods other than the least squares fit can be used to remove the trends.

For a few data sets, gaps occur in the time series. If the duration is less than three months then the gaps are filled by substituting the result from the preceding month. Linear interpolation might have been better but since this is an initial investigation and greater errors occur for other reasons it was judged worthless of the effort.

It was assumed that chemical analyses are reliable to an extent. However, Kramer,(1975) observed variations among the different laboratories doing the analyses. This would certainly lead to some errors in the averaging procedure. It may be better to use data from one laboratory where the analysis is systematic to avoid random errors.
In view of the above remarks, a spectral analysis at this time is somewhat premature but should be very powerful as the record length of the time series increases and the data become better understood. Then confidence intervals can also be computed for the spectral estimates.
4. INTERPRETATION AND DISCUSSION

4.1 Choice of Pairs of Parameters

First and foremost, pairs of parameters are selected which are expected to have a high degree of correlation between them. The choice is guided by a knowledge of their chemistry and also from the similarity of the ratio of each parameter in rain to snow for 1973-74 period (Kramer, 1975). If these ratios for two parameters are close together, then presumably their chemical cycles are similar and a high degree of correlation may be expected. The choice is restricted somewhat by the length of the data which was recorded for each parameter.

The computer program is designed to compute spectral properties for two simultaneously recorded time series which by definition spans the same period of time. The length of the data is different for each parameter considered in this study. Therefore an appropriate truncation must be made to each pair of data set considered in order to obtain the data collected for both sets within the same period of time.

Furthermore, some parameters are studied only for their periodic components. For such parameters all the available data are used. However each of these parameters must be run against a dummy parameter which has data of equal or longer length than that of the parameter of interest. The pH data is the longest and is often used as a dummy parameter.

Emphasis in this work is placed on the heavy metals (Cd, Cu, Ni, Fe, Pb, Zn) due to their industrial association, particularly in view of
the levels of atmospheric pollutants presently being emitted from the
smoke stacks at Sudbury (Kramer, 1975) which act as a point source.
Furthermore, the data for these metals are more or less complete.

The periodic patterns of parameters other than the heavy metals
are also considered and compared to those of the heavy metals. Such
parameters are pH, $\text{SO}_4^-$, SP CON, PART and P. These parameters are
certainly related to industries, however, a substantial proportion of
airborne phosphorus is thought to be associated with agriculture.

4.2 Periodicities

The periodic components of the precipitation data can be resolved
from the power spectrum in that the "peaks" in the spectrum occur at
persistent periodicities. The intensities of the peaks indicate the
persistence of each periodic component. Therefore, in each power spectrum,
the intensities at periodicities can be arbitrarily classified as strong
(s), medium (m), or weak (w) to reflect the relative importance of each
periodic component. It should be noted that the intensities are in log
units, thus the values for the intensities appear to be similar, but in
fact they are quite different. The weak periodicities in the power spect­
rum may be due to termination errors, but this is difficult to establish
at the present time. Furthermore, since the data for the parameters are
somewhat limited from the point of view of spectral analysis, only the
pattern of periodicities associated with the various parameters at
different locations, is important.

Figures 4.2.1(a) to 4.2.1(c) show the periodicities associated
with the various parameters at different locations. The solid, dashed
Figure 4.2.1(a): Periodicities of Parameters
Figure 4.2.1(b): Periodicities of Parameters

---Pb T---  Zn T  ---Fe T---  ---T PART---

Period in Months

SUD UGL  S2  S12  S3  S4  SUD UGL  S2  S12  S3  S4  SUD UGL  S2  S12  UGL
Figure 4.2.1(c): Periodicities of Parameters

<table>
<thead>
<tr>
<th>SP CON</th>
<th>PT</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>19</td>
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<tr>
<td>19</td>
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<tr>
<td>21</td>
<td>26</td>
</tr>
<tr>
<td>21</td>
<td>19</td>
</tr>
</tbody>
</table>

Period in Months

- pH
- SO4
- SP CON
- PT

S2  S12  S3  S4  SUD  UGL
S2  S12  S3  S4  SUD  UGL
SUD  UGL  S2  S12  UGL
and dotted lines represent strong, medium and weak periodicities respectively, with respect to the peak intensities in each power spectrum. The error bars shown in the figures result from the fact that if a smooth curve is drawn through three points then an error is associated with the positions of the maximum or the minimum. However, more than this error occurs in the present analysis and thus the error bars are taken as the two points on either side of the "maximum" point.

From the figures, definite patterns can be seen for the periodicities. The heavy metals, in particular Cu, Ni, Cd, Pb and Zn, generally show two frequency bands of periodicities. The first is a period of 9 cycles/month and the second is a period or periods in the range of 2 to 5 cycles/month.

Iron is the only heavy metal that, though it shows the lower periodicities, does not show the 9 monthly period as associated with the other heavy metals. However, it does show 12 monthly and 6 monthly periodicities. The particulates (T PART) have periodicities that are the same as for iron. This is due to the fact that most of the particulates consist of iron.

The other parameters also show periodicities ranging from 2 to 5 cycles/month. In addition, pH shows a 6 monthly period and SO₄ shows a 12 monthly period.

Phosphorus shows, in addition to the low periodicities, both 6 and 12 monthly periods. Since phosphorus is generally associated with agriculture, a 12 monthly period is expected. This represents high phosphorus concentration in summer and low in winter. The 6 monthly period may reflect the four seasons of the year.
The origin of the high periodicities for the other parameters is not well understood but the periodicities must be real due to the high intensities observed in the power spectra. For Fe and PART, the 6 monthly period may reflect the four seasons while some yearly cycle must be responsible for the 12 monthly period. Whatever this cycle is, it may also explain the 12 monthly period of SO$_4$. The yearly cycle may be seasonal, representing high concentration of the parameters in summer and low in winter. The 6 monthly period is less clear and the data for the parameters showing this period fluctuates throughout the year. It is quite likely therefore, that the four seasons may be responsible for this periodicity.

The 9 monthly period for the heavy metals is even more difficult to explain in view of the fact that not many natural cycles of this duration are known. However, since most of the metals are associated with industries, this periodicity is most likely reflecting some strong periodic components involved with industries.

Furthermore, all the parameters considered in this study show a high frequency component of periodicities ranging from 2 to 5 cycles/month. Thus there must be some universal phenomenon affecting all the parameters. A study of the spectrum of the vertical velocity field of atmospheric turbulence (Lumley and Panofsky, 1964) indicates that peak in the spectrum moves towards lower frequencies with increased solar radiation. This suggests that there are two different causes for the fluctuations in atmospheric turbulence, a high frequency component due to frictional forces and a low-frequency component due to heat convection caused by solar radiation. The precipitation data are certainly affected
by atmospheric turbulence, thus the high frequency periodicities may
very well be due to frictional forces associated with turbulence.

Periodicity is due to "natural" phenomena and in some way it may
also reflect the origin and/or behaviour of the precipitation data. This
study shows clearly that Fe is the only heavy metal that does not follow
the pattern of the other heavy metals, and therefore cannot be as strongly
linked to the smoke stacks at Copper Cliff as are the other heavy metals.
This is further supported by correlation and phase studies discussed in
the next section.

4.3 Correlation and Phase Relationships

The squared coherency and phase spectra give the correlation and
phase relationships of any two parameters. A high coherence indicates that
the two parameters are correlated at that frequency band and the phase
spectrum gives the phase difference between the two series as a function
of frequency.

4.3.1 Cu T and Ni T

The spectra for Cu and Ni are given in Figures 3.3.13 through
3.3.30. Table 4.3.1 summarizes the periodicities, peak intensities, cor-
relation and phase relationships.

The correlation between Cu and Ni is in general very good for the
major periodicities. At station 12, the correlation is somewhat low thus
reflecting the questionable data for Ni (Fig. B.1.5). Data are judged to
be unreliable if anomalous values occur for a few months. In such cases
the least squares fit and trend removal are impractical. For the other
five spectra where the data are better the correlation is quite good.
Figure 4.3.1: Precipitation chemistry stations and wind directions in the Upper Great Lakes region
Figure 4.3.2: Precipitation chemistry stations in the Sudbury area. The spatial relationship of stations 12, 2, 3, and 4 to Copper Cliff should be noted. These four stations lie in the path of the predominant northeastward wind direction (Fig. 4.3.1)
The strong correlation between Cu and Ni implies that the two elements undergo a chemically similar cycle from their points of emission. These elements probably form similar complexes of nearly equal stability. Thus it may be possible to predict the behaviour of one element from the other.

In general, the phase difference between the two parameters are very small at the frequency bands of major periodicities. This inphase relationship is seen for the four individual stations as well as the Sudbury and U,G,L. areas. This would imply a common source of origin for Cu and Ni. Furthermore, this source must be a point source of loading that is little affected from other sources, as required for the inphase relationship.

A trend exists for the intensities of the peaks at the frequency bands of periodicities for the six areas. From the tables which give the intensities in log units, it can be seen that the intensities decrease in a general way from the individual stations to the U,G,L. region, that is 12 > 2 > 3 > 4 > Sudbury area > U.G.L. area, at least for Cu. The Ni data show a similar trend, but to a lesser degree.

In view of the location of the stations, this trend will point to INCO's 1250-foot smoke stacks at Copper Cliff as the source of emission of Cu and Ni. It should be noted that stations 12 and 2 are northwest of the smoke stacks with the former being closer, while stations 4 and 3 are south-east of the smoke stacks with the latter being closer. The variation of the intensities among these four individual stations reflects the predominant northeastward wind direction and further evidence for the smoke stack being the source of emission of Cu and Ni. Thus, even if
TABLE 4.3.1: Cross-correlation properties between Cu T and Ni T

<table>
<thead>
<tr>
<th>STATION 12</th>
<th>STATION 2</th>
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<tr>
<td>INTENSITIES (Log. Units)</td>
<td>INTENSITIES (Log. Units)</td>
</tr>
<tr>
<td>T</td>
<td>Cu T</td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
</tr>
<tr>
<td>12.7</td>
<td>5.67(m)</td>
</tr>
<tr>
<td>9.5</td>
<td>----</td>
</tr>
<tr>
<td>6.3</td>
<td>5.80(s)</td>
</tr>
<tr>
<td>4.2</td>
<td>----</td>
</tr>
<tr>
<td>2.7</td>
<td>5.26(w)</td>
</tr>
<tr>
<td>2.0</td>
<td>----</td>
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</tbody>
</table>

<table>
<thead>
<tr>
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<th>STATION 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTENSITIES (Log. Units)</td>
<td>INTENSITIES (Log. Units)</td>
</tr>
<tr>
<td>T</td>
<td>Cu T</td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
</tr>
<tr>
<td>9.0</td>
<td>?4.50(s)</td>
</tr>
<tr>
<td>7.2</td>
<td>----</td>
</tr>
<tr>
<td>4.5</td>
<td>----</td>
</tr>
<tr>
<td>4.0</td>
<td>3.99(s)</td>
</tr>
<tr>
<td>2.6</td>
<td>----</td>
</tr>
<tr>
<td>2.3</td>
<td>4.04(s)</td>
</tr>
<tr>
<td>2.0</td>
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<th>U.G.L.</th>
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<td>INTENSITIES (Log. Units)</td>
<td>INTENSITIES (Log. Units)</td>
</tr>
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<td>Cu T</td>
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<tr>
<td>-----</td>
<td>------</td>
</tr>
<tr>
<td>6.7</td>
<td>4.53(s)</td>
</tr>
<tr>
<td>4.4</td>
<td>----</td>
</tr>
<tr>
<td>2.9</td>
<td>4.39(s)</td>
</tr>
<tr>
<td>2.7</td>
<td>----</td>
</tr>
<tr>
<td>2.1</td>
<td>4.38(s)</td>
</tr>
<tr>
<td>3.1</td>
<td>4.08(w)</td>
</tr>
<tr>
<td>2.4</td>
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</tr>
<tr>
<td>2.2</td>
<td>4.27(m)</td>
</tr>
</tbody>
</table>

T = Period (months); r = Correlation; φ = Phase (degrees)

* Ni T data unreliable to a certain extent.
there is loading of Cu and Ni to the atmosphere from sources other than Copper Cliff, the latter dominates the loading cycle for the U.G.L. region.

4.3.2 Ni(T) - Cd (T)

A sympathetic relationship exists between Cd and Ni at station 12 since they are highly correlated throughout the frequency range and also remarkably inphase (Figs. 3.3.31 to 3.3.33). The probable source of Cd and Ni is the effluent from Copper Cliff since station 12 is located in the immediate vicinity.

The above relationship is not seen in any of the other areas analyzed. The results are shown in Figures 3.3.34 to 3.3.48. This inconsistency may be explained by considering the molecular weight of Ni and Cd. The latter is about twice as heavy as the former and it would not be expected therefore, to be dispersed from the smoke stack as far as the Ni. Thus any similarity that exists near the smoke stack will not be the same at any great distance from it.

Total cadmium

The peak intensities at periodicities in the power spectrum for Cd T shows a general trend among the areas studied. Table 4.3.2 shows the intensities of the frequency bands of the periodicities.

The intensities for station 12 are greater than that for station 2, while those for station 3 are greater than that for station 4 in a general way. Furthermore, the intensities for these individual stations are greater than that for the Sudbury area. (The data for Cd T for the U.G.L. region is somewhat questionable, Fig. B.6.1). In view of the station locations, the intensities increase towards Copper Cliff and this points to the smoke stacks as the source of emission of Cd.
<table>
<thead>
<tr>
<th>PERIOD (months)</th>
<th>STATION 12</th>
<th>STATION 2</th>
<th>STATION 3</th>
<th>STATION 4</th>
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<tbody>
<tr>
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<td>PERIOD (months)</td>
<td>INTENSITIES (Log. Units)</td>
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<tr>
<td></td>
<td>Cd T</td>
<td></td>
<td>Cd T</td>
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<td>9.0</td>
<td>1.68(s)</td>
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<td>6.3</td>
<td>1.56(s)</td>
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<td>1.49(w)</td>
<td>4.8</td>
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<td>2.8</td>
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<td>3.5</td>
<td>1.48(s)</td>
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<td>1.51(m)</td>
<td>2.1</td>
<td>1.10(w)</td>
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<td>1.50(m)</td>
<td>2.02(s)</td>
<td>1.56(s)</td>
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<td>4.5</td>
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<td>3.0</td>
<td>1.53(s)</td>
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<td>2.6</td>
<td>2.4</td>
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<td>2.4</td>
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<td></td>
<td></td>
<td>1.98(m)</td>
<td>1.67(s)</td>
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<td>2.4</td>
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<td>1.50(s)</td>
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<td>1.53(s)</td>
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<td>1.67(s)</td>
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<td></td>
<td>1.50(s)</td>
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<td></td>
<td></td>
<td>1.43(m)</td>
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<td></td>
<td>1.29(w)</td>
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<td>1.15(w)</td>
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<tr>
<td></td>
<td></td>
<td>1.01(w)</td>
<td></td>
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</tbody>
</table>

*Cd T data for U.G.L. area unreliable.
4.3.3 Zn T - Zn F

Striking relationships exist between the total and filtered zinc for the Sudbury and U.G.L. areas. An exceedingly high correlation is seen for the total and filtered zinc and they are practically inphase at all frequencies. These relationships are demonstrated quite well in Figures 3.3.49 to 3.3.54 and imply that the chemistry for the total and filtered zinc are quite similar, and in fact the behaviour of one can be predicted for the other. Consequently, from the point of view of chemical analysis all one needs to do is to analyze one form of zinc and infer the trend for the other.

4.3.4 Cu T and Cu F

The Sudbury and U.G.L. areas are analyzed for the total and filtered Cu. The former shows moderately strong correlation and low phase difference at the frequency bands of the periodicities. A similar relationship is seen for the U.G.L. area but to a lesser degree. Figures 3.3.55 through 3.3.60 show the spectra for the total and filtered copper.

The relationship between total and filtered Cu is not as strong as that of the two forms of zinc. Thus the total and filtered copper have slightly different chemical cycles. However, Cu T and Zn T have a similar behaviour since they have similar periodicities.

4.3.5 pH and T PART

A local relationship exists between pH and T PART. Station 12 shows high correlation and inphase properties for pH and T PART throughout the frequency range of the spectra (Figs. 3.3.61 to 3.3.63). A similar
trend is seen at station 2, but to a lesser degree (Figs. 3.3.64 to 3.3.66). However, no such relationship exists for the U.G.L. region as can be seen from Figures 3.3.67 to 3.3.69.

The spectral intensities at periodicities for the parameters decrease in a general way from station 12 to station 2 and are lowest for the U.G.L. region. Thus the pH and T PART show some association with the smoke stack.

The restriction of these parameters to the Sudbury area is expected since particulates are quite heavy and "rains" near its source of origin. Furthermore, on a regional scale as the U.G.L., the pH is buffered by carbonates, etc. and no association between pH and T PART exists on such a scale.

The association between pH and T PART locally is probably due to the surface chemistry of the particulates which have considerable surface area. Presumably, the hydrogen ions attach themselves to the surface of the particulates by electrostatic forces and they are dispersed together as a unit.

4.3.6 pH, SO₄, SP CON

It is a common thought that pH should be related to SO₄ in some way since the latter may be responsible for the low pH in the U.G.L. area. Therefore an intensive analysis is made to investigate the relationship, if any. Four individual stations (12, 2, 3, 4) and also the Sudbury and U.G.L. areas are analyzed and the results are given in Appendix B.

Generally, no relationship is found to exist between the two parameters. This would indicate that the chemistry between the two ions
TABLE 4.3.3: Cross-correlation properties between pH and SO₄

<table>
<thead>
<tr>
<th>STATION 12</th>
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</tr>
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<tbody>
<tr>
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<tr>
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<tr>
<td><strong>T</strong></td>
<td><strong>pH</strong></td>
</tr>
<tr>
<td>14.0</td>
<td>---</td>
</tr>
<tr>
<td>6.0</td>
<td>1.50(s)</td>
</tr>
<tr>
<td>4.7</td>
<td>---</td>
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<td>3.2</td>
<td>---</td>
</tr>
<tr>
<td>3.0</td>
<td>1.36(s)</td>
</tr>
<tr>
<td>2.6</td>
<td>---</td>
</tr>
<tr>
<td>2.0</td>
<td>1.31(s)</td>
</tr>
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</table>

<table>
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<tr>
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<th>STATION 4</th>
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<tbody>
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<td></td>
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<tr>
<td><strong>(Log. Units)</strong></td>
<td><strong>r</strong></td>
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<tr>
<td><strong>T</strong></td>
<td><strong>pH</strong></td>
</tr>
<tr>
<td>14.0</td>
<td>1.43(s)</td>
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<tr>
<td>7.0</td>
<td>1.26(w)</td>
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<td>1.23(w)</td>
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<td>1.32(m)</td>
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<tr>
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<td>1.30(m)</td>
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<th>SUDBURY</th>
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<td><strong>INTENSITIES</strong></td>
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<td><strong>(Log. Units)</strong></td>
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<td><strong>T</strong></td>
<td><strong>pH</strong></td>
</tr>
<tr>
<td>10.4</td>
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<td>-.06(s)</td>
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<td>-.03(s)</td>
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<tr>
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<td>-.11(w)</td>
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T = Period (months); r = Correlation; ø = Phase (degrees)
is not very simple or that other factors are involved, for example, many sources of the ions may be interfering.

The spectral intensities for the individual stations decrease in a general way from the smoke stack at Copper Cliff. The lowest intensities are associated with the U.G.L. area. This trend can be seen from Table 4.3.3.

Generally, hydrogen ions are considerably more mobile than most of the other ions in solution. Thus it may be related to the superconductivity of the solution. Consequently, pH and SP CON are analyzed for the Sudbury and the U.G.L. areas and the results are given in Appendix B. In general, the correlation is low and they are out of phase. Perhaps, the super conductivity is due to ions other than the hydrogen ions. In fact this is brought out in the light that pH is associated with particulates.

4.3.7 FeT and ZnT

These two elements are analyzed for four individual stations (12, 2, 3, 4). The spectra are given in Figures B.7.25 to B.7.36. Table 4.3.4 summarizes the frequency bands of periodicities, correlation and phase relationships.

Stations 12 and 2 show little correlation and out of phase relationships between Fe and Zn. However, stations 3 and 4 are quite the opposite as the correlation is high and they are generally inphase. This relationship is strongest for station 4. Furthermore, the spectral intensities do not show any trend among the four stations and the correlation is high for the leeward stations (3, 4) with respect to the smoke stack. This suggests that the loading of these elements are not from the smoke stack but from some other source which is probably close to station 4.
TABLE 4.3.4: Cross-correlation properties between Fe T and Zn T

<table>
<thead>
<tr>
<th>STATION 12</th>
<th>STATION 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>INTENSITIES</td>
</tr>
<tr>
<td></td>
<td>(Log. Units)</td>
</tr>
<tr>
<td>T</td>
<td>Fe T</td>
</tr>
<tr>
<td>8.4</td>
<td>---</td>
</tr>
<tr>
<td>6.0</td>
<td>7.30(m)</td>
</tr>
<tr>
<td>4.2</td>
<td>---</td>
</tr>
<tr>
<td>3.8</td>
<td>7.22(m)</td>
</tr>
<tr>
<td>3.0</td>
<td>7.39(s)</td>
</tr>
<tr>
<td>2.6</td>
<td>---</td>
</tr>
<tr>
<td>2.5</td>
<td>7.17(w)</td>
</tr>
<tr>
<td>2.1</td>
<td>7.31(m)</td>
</tr>
<tr>
<td>2.0</td>
<td>---</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>STATION 3</th>
<th>STATION 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>INTENSITIES</td>
</tr>
<tr>
<td></td>
<td>(Log. Units)</td>
</tr>
<tr>
<td>T</td>
<td>Fe T</td>
</tr>
<tr>
<td>8.4</td>
<td>5.43(m)</td>
</tr>
<tr>
<td>5.3</td>
<td>---</td>
</tr>
<tr>
<td>4.2</td>
<td>5.68(s)</td>
</tr>
<tr>
<td>2.8</td>
<td>5.70(s)</td>
</tr>
<tr>
<td>2.5</td>
<td>6.33(s)</td>
</tr>
<tr>
<td>2.1</td>
<td>5.41(m)</td>
</tr>
<tr>
<td>2.3</td>
<td>5.88(w)</td>
</tr>
</tbody>
</table>
4.4 Summary

1. All the parameters considered in this study have periodicities in the range 2 to 5 cycles/month. In addition to these periodicities, they also have higher periodicities which are as follows:
   (a) 9 cycles/month for Cu, Ni, Cd, Pb, and Zn;
   (b) 12 cycles/month for Fe, PART, P, and SO₄;
   (c) 6 cycles/month for pH, Fe, PART, and P.

2. The yearly cycle corresponds to high and low atmospheric loadings in the summer and winter respectively; the 6 monthly period reflects the four seasons of the year; the 9 monthly period is possibly associated with the smelting and mining industry at Sudbury and the 2 to 5 cycles/month periodicities are due to atmospheric turbulence.

3. Good correlation and low phase difference are found between the following parameters:
   (a) Cu T and Ni T at stations 12, 2, 3, 4, Sudbury and U.G.L. areas;
   (b) Cd T and Ni T at station 12;
   (c) Zn T and Zn F for Sudbury area and U.G.L. areas;
   (d) Cu T and Cu F for Sudbury area; and
   (e) pH and PART at stations 12 and 2.

4. The mining and smelting industry at Sudbury has been established by this work as a major point source of atmospheric emissions of acid, sulfate and the heavy metals, with the exception of iron. This phenomena is well-substantiated by (i) the pattern of the heavy metal periodicities; (ii) the general correlation and phase relationships given in 3. above and (iii) the general decrease in spectral intensities at major periodicities, away from the mining-smelting centre.
5. Semkin and Kramer (1976) found that the Sudbury-area lakes effectively act as a sink for heavy metals that have been introduced via atmospheric precipitation. Their evidence for this phenomena has been well-substantiated by observing heavy metal trends in both lake sediment and atmospheric fall-out. This conclusion has been arrived at since their results indicate (i) similar metal ratios in both media; (ii) increasing concentration gradients for the trace elements in sediments and atmospheric precipitation toward the mining-smelting centre; and (iii) significant correlation of the sediment parameters, suggesting a point source emission of heavy metals.
REFERENCES


APPENDIX A

SPECTRAL ANALYSIS PROGRAM
COMPUTER PROGRAM

PROGRAM OFF( INPUT, OUTPUT, TAPE1, TAPE2, TAPE3, PUNCH, 
$ TAPE5= INPUT, TAPE6=OUTPUT )
DIMENSION ICD0 (260), FLC (260), VAL (260)
DIMENSION SAT1 (2*45), SAT2 (2*45)
DIMENSION IXX (163)
COMMON / VAI/ NAM (260), INO (216), ZNAME (200), ND
COMMON / PLY / NVIS (455), FACTOR, AINTER
NNO=2
VAL1=NV2=0
NIX=0
VALX=-1.0
VALY=-1.0
NTEST=7111
NO=0
II=1C+1C
DO 45 I=1, ND
IXX (I) = 1.0
45 FORMAT (215)
999 READ (1) NTAG, NSET, ICOM
IF (NTAG.EQ.99) GO TO 26
NTAG=NTAG/110
IF (NNTAG .LT. NTEST) GO TO 20
IF (NTX .EQ. 6) GO TO 10
98 IF (NTAG-NTX) 1, 20, 3
1 IF (I2-13) 26, 2, 99
2 I2=1
II=I1+1
GO TO 26
10 II=NTAG / I6
I2=NTAG - I1*10
NTX=II*1CC + I2
11 IF (NTAG-NTX) 31, 12, 99
12 VAL2=VAL + J
13 IF (J) 27, 10
26 DO 21 I=1, NSET
FAC (1) I = NIV, (ICD0 (J), FLC (J), VAL (J), J=1, NV)
21 CONTINUE
IF (I1TAG .LT. NTEST) GO TO 265
DO 25 J=1, NV
IF (FC (J).NE.1H) GO TO 25
DO 22 I=1, NO
IF (F (J) - I1COD0 (J)) 42, 43, 44
43 IXX (I) = 1.0
GO TO 44
42 CONTINUE
44 CONTINUE
IF (ICD0 (J) - ICD1) 23, 22, 23
VAL1=VAL1+VAL (J)
IC1=IC1+1
GO TO 26
23 IF (ICD (J) - ICD2) 25, 24, 25
24 VAL2=VAL2+VAL2
IC2=IC2+1
25 CONTINUE
254 IF (ICOM) 399, 999, 255
255 DO 256 I=1, ICOM
FAC (25)
256 CONTINUE
GO TO 999
PRINT 122,NTAG,IXX
FORMAT(1X,IX,1X,103A1)
GO 41
1=1,ND
IXX(I)=11
IF(IX1)=51,51,56
50 VAL1=0
VAL1=VAL1/FLOAT(IC1)
GO TO 52
51 VAL1=VAL1+1
52 VALX=VAL1
IF(IC2)54,54,53
53 VAL2=3
VAL2=VAL2/FLOAT(IC2)
GO TO 55
54 VAL1=VAL1+1
55 VAL2=VAL2+1
IF(VA12)56,56,56
56 VAL1=10-VAL1+1
GO TO 57
57 NTX=11*10G+12
NNO=NNO+1
VO=1G+1
NNTS(1.0)=NTX
DAT1(1.N0)=VAl1
DAT2(N0)=VAL2
IF(NNTS.EQ.99)30 TO 99
GO TO 11
31 IC1=IC2=1
GO TO 1
99 PRINT 111,NO
FORMAT(1X,11),2(1F,16.2)
C USE CN. AS SCALE.
CALL PL0T(0.,-20.,-20.)
CALL LETF1(116.,5,50.,1.,1.,1000.)
CALL PLOT(2.,2.,3.)
CALL FOUR(N,N0,DAT1,DAT2,ICD1,ICD2)
STOP
END

SUBROUTINE FOUR (N,DAT1,DAT2,ICD1,ICD2)
DIMENSION DAT(2,1),DAT2(2,1)
DELTA1=1.0
NUMSEF=2
LAGS=N/2
2 FORMAT(F5.2,I5,I5,A13,2F5.3,I35)
IF(LAGS.GT.25)GO TO 9
CALL INPUT(DAT1,DELTA1,NWORK,ICD1)
IF(N.EQ.0)GO TO 9
BW=FLOAT(NWORK)/(2.*FLOAT(LAGS))
WRITE(5,3)N,LAT,BW,DELTA1
IF(NUMSSEF.EQ.2)4,5,11
4 CALL SPEC1(DAT1,NWORK/2,DELTA,DATS,LATS,BW)
GO TO 33
5 CALL SPEC2(DAT1,DAT2,N,DELTA1,LATS,BW,ICD2,ICD1)
GO TO 33
9 WRITE(5,10)
GO TO 33
11 WRITE(5,12)
123

SUBROUTINE INPUT (DATA, N, DELTAT, WORK, ICO)
DIMENSION DATA (2, I) , Ni (I) , WORK (201)
DIMENSION A (5) , B (2) , X (100) , Y (100)
COMMON / 1X / NIS (465) , FACTOR , INTER , TIME
C......
IF (ICO .NE. 123) GO TO 13
DO 14 I = 1 , N
DATA (1, I) = A LOG (DATA (1, I))
CONTINUE
14 DO 1 1 = 1 , N
Y (1) = DATA (1, I)
X (1) = FLOAT (I - 1)
1 CONTINUE
CALL LESSQ (A, 3 , X, Y, 1, N)
INTER = FLOAT (1)
SLOPE = FLOAT (2)
FACTOR = SLOPE + DELTAT
DO 10 I = 1 , N
WRITE (5, 11) DATA (1, I)
10 CONTINUE
11 FORMAT (10. 2)
PRINT 12 , ICO , N
12 FORMAT (210)
CALL PLOT (DATA, N, ICO)
DO 3 I = 1 , N
3 DATA (1, I) = DATA (1, I) - INTER - FACTOR * FLOAT (I)
PRINT ICO , INTER , FACTOR
100 FORMAT (1X , * INTERCEPT = * , F10.5 , * FACTOR = * , F10.5)
DO 2 I = 1 , N
IF (DATA (1, I) .LT. 0. 0) DATA (1, I) = 0. 0
2 CONTINUE
101 FORMAT (1X , F10.2)
CALL PLOT (DATA, N, ICO)
WORK = 2
IF (NWORK - N) G37, 3
GOTO 4
4 N1 = N + 1
DO 5 I = N1 , NWORK
DATA (1, I) = C
5 DATA (2, I) = C
DO 6 I = 1 , NWORK
DATA (2, I) = 0. 0
6 NN (I) = NWORK
CALL FOJRT (DATA, NY, 1, - 1, 3, WORK)
RETURN
END

SUBROUTINE HANN (A, LAGS)
DIMENSION A (1)
T1 = A (1)
A (1) = (C. 5 * (T1 + A (2)))
K = LAGS - 1
DO 1 I = 2 , K

\[ T_2 = A(I) \]
\[ A(I) = 3.5 \times T_2 + 0.25 \times (T_1 + A(I+1)) \]
\[ T_1 = T_2 \]
\[ A(LAGS) = (0.5 \times (T_1 + A(LAGS))) \]
\[ \text{RETURN} \]
\[ \text{END} \]

SUBROUTINE SPEC1(DATA, N, DELTAT, NDIM, BW)
DIMENSION DATA(2, 435), WORK(24)
FACTOR = 0.5 / (FLOAT(NDIM) * DELTAT)
WRITE(6, 1)
1 FORMAT(1HC4, 45X, 1LAGS, 7X, CR=CO, 7X, PERIOD, 2X, $*LOG10 (SPECTRUM)/*)
\[ \leq C \]
\[ P = 0.0 \]
DO 10 T = 1, LAGS
WORK(I) = 0.0
J = K + 1
IF (J - 1) 13, 13, 2
3 = BW / 2.0 + 1
\[ \leq IFIX(P) \]
GO TO 4
2
\[ \geq = P + 3 \]
IF (P - N) 14, 14, 3
\[ \leq = IFIX(P + 0.5) \]
GO TO 4
3
DO 4 L = J, K
WORK(I) = WORK(I) + DATA(1, L) * DATA(1, L) * DATA(2, L)
4 WORK(I) = WORK(I) / FLOAT(K - J + 1)
CALL HANN(WORK, LASS)
DO 4 I = 1, LAGS
WORK(I) = ALOG10(WORK(I))
DO 4 I = 1, LAGS
FRQ = FLOAT(I - 1) * FACTOR
IF (I - 1) 15, 15, 8
PERIOD = 999, 9999
GO TO 9
9 PERIOD = 1.0 / FRQ
J = I - 1
WRITE(6, 11) J, FRQ, PERIOD, WORK(I)
11 FORMAT(-3X, I = 3(*X, FS, L))
WRITE(6, 12) (WORK(I), I = 1, LAGS)
12 FORMAT(1EC8, 4)
\[ \text{RETURN} \]
\[ \text{END} \]

SUBROUTINE SPEC2(DATA1, DATA2, N, DELTAT, NDIM, BW, ICO2, ICO1)
DIMENSION DATA1(2, 435), DATA2(2, 1)
DIMENSION COSP(200), QUASP(200), SPECT1(200), SPECT2(200)
DIMENSION SPECTO(2, 435)
DIMENSION spectro(2, 435)
CALL NATOR/VECTOR(50), YCOHER(50)
CALL INPUT(DATA2, N, DELTAT, NDIM, ICO2)
FACTOR = 0.5 / (FLOAT(NDIM) * DELTAT)
N = 1, WORK / 2 + 1
LAGS = NDIM + 1
\[ \leq \]
\[ \geq = 0.3 \]
DO 5 I = 1, LAGS
COSP(1) = 0.0
QUASP(I) = 0.0
SPECT1(I) = 0.0
SPECT2(I) = L.1
J = K+1
IF (J-1) .11, 14, 1
P = 3W/2, J+1
< = IFIX(P)
0 TO 3
P = P+3
IF (P-K) 13, 13, 2
< = IFIX(P+4.5)
0 TO 3
K = N
0 L = J, K
COSP(I) = COSP(I) + DATA1(1, L) * DATA2(1, L)
QUASP(I) = QUASP(I) + DATA1(1, L) * DATA2(2, L)
SPECT1(I) = SPECT1(I) + DATA1(1, L) * DATA1(1, L)
SPECT2(I) = SPECT2(1) + DATA2(1, L) * DATA2(2, L)
4
IF (K-J+1) 35, 35, 35
FACT = K
0 TO 3
FACT = 1.0 / FLOAT(K-J+1)
CONTINUE
IF (I) = FACT
QUASP(I) = QUASP(I) * FACT
SPECT1(I) = SPECT1(I) * FACT
SPECT2(I) = SPECT2(I) * FACT
5
CONTINUE
CALL HANN(SPECT1, LAGS)
CALL HANN(SPECT2, LAGS)
CALL HANN(COSP, LAGS)
WRITE(5, 20)
20 FORMAT(1H1)
WRITE(5, 3)
JO 13 = 1, LAGS
PHASE = ATAN2(QUASP(I), COSP(I)) * 57.29578
YPHASE = PHASE
SPECT1(I) = ALOG10(SPECT1(I))
SPECT2(I) = ALOG10(SPECT2(I))
FREQ = FLOAT(I-1) * FACT
J = I-1
IF (I-1) 12, 12, 7
PEIOD = 999.999
0 TO 6
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abd
8 8
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100
101 CONTINUE
C ALL FLOT(SPCZ,LAGS,ICD2)
C RETURN
END

SUBROUTINE FOURT(DATA,NN,NDIM,ISIGN,IFORM,WORK)
DIMENSION DATA(1),NN(1),IFACT(32),WORK(1)

CMTLF = 0.7071E57212
TWOPI = 6.283185307
IF (KDIM = 1) 926,1,1
1
NTOT = 2
DO 2 IDIM=1,NDIM
2 NT=NTOT*(IDIM)
ISAVE = NTOT
NP1 = 2
DO 91 IDIM=1,NDIM
N=M*(IDIM)
NP2=NP1*N
IF (I-1) 920,920,5
M=N
NTWO=NP1
IF = 1
DIV=2
10 IQUOT=M/DIV
IREM=M*IDIV-IQUOT
IF (IQUOT-IDIV) 50,11,11
11 IF (IREM) 26,12,20
12 NTWO=NTWO+NTWO
IFACT(IF) = IDIV
IF = IF+1
M = IQUOT
GO TO 10
20 IDIV=3
INON2 = IF
30 IQUOT=M/DIV
IREM=M-IDIV*1QUOT
IF (IQUOT-IDIV) 60,31,31
31 IF (IREM) 40,32,40
32 IFACT(IF) = IDIV
IF = IF+1
M = IQUOT
GO TO 30
40 IDIV=IDIV+2
GO TO 30
50 INON2 = IF
51 NTWO=NTWO+NTWO
GO TO 70
60 IFACT(IF) = M
70 ICASE = 1
IFMIN = 1
I1KG = NP1
IF (IDIM = 1) 71,100,100
71 IF (IF0M) 72,73,73
72 IF (IDIM = 1) 71,100,100
73 ICASE = 2
I1KG = NP2*(1+NP2REV/2)
GO TO 110
74 IF (NTWO-NP1) 75,75,76
75 ICASE = 3
GO TO 110
76 ICASE = 4
IFMIN=2
NTWO=NTWO/2
V=W/2
NP2=NP2/2
NTOT=NTOT/2
I = 3
DO 80 J=2,NTOT
DATA(J)=DATA(I)
80 I=I+2
100 IF(I,NTHO-NP2) 200,110,110
110 NP2HF=W/2
J=1
DO 120 I2=1,NP2,NP1
IF(J-I2) 122,135,135
120 I3=I2+NP1-2
DO 125 I3=I2+NP1-2
DATA(I3)=DATA(I3)
DATA(I3+1)=DATA(I3+1)
DATA(I3+1)=DATA(I3+1)
DATA(I3+1)=DATA(I3+1)
125 M=NP2HF
130 IF(J-M) 150,150,145
145 J=J-M
M=W/2
150 IF(M-NP1) 150,150,140
160 J=J+M
GO TO 130
200 N0RKK=2*N
DO 27C I3=1,NP1,2
DO 27C I3=1,NTOT,NP2
J = I3
DO 266 I3=1,NWORK,2
IF(I3) 210,210,210
WORK(I) = DATA(J)
WORK(I+1)=DATA(J+1)
GO TO 230
220 WORK(I) = DATA(J)
WORK(I+1) = J+C
230 IFP2=NP2
240 IFP1 = IFP2/IFACT(IF)
J = J+IFP1
250 IF(J-I2=IFP2) 250,250,250
260 IFP2 = IFP1
IFP1 = IFP2
260 CONTINUE
I3MAX = I3+NP2-NP1
I = 1
DO 27C I3=1,I3MAX,NP1
DATA(I3) = WORK(I)
DATA(I3+1) = WORK(I+1)
I = I+2
300 IF(NTHO-NP1) 305,305,305
305 NTW = NP1+NP1
IPAF=NTW/IP1
310 IF(IPA=-2) 315,330,320
320 IPAF=IPAF/4
GO TO 310
330 DO 340 I1=1,IPAF,2
DO 340 I2=1,NTOT,NP1TW
K2 = K1+NP1
TEMPR=DATA(K2)
TEMPI=DATA(K2+1)
DATA(K2)=DATA(K1)-TEMPR
DATA(K2+1) = DATA(K1+1) - TEMPI
DATA(K1) = DATA(K1) + TEMPR
MAX = 1, PI
IF (MAX - NTX0/2) > 370, 350, 330
IF (P1TW - MAX - (MAX/2)) > 32, 375, 375
MAX = MAX / 2
30 TO 377
MAX = NPI1W
L = L
M = M
420 DO 53L I = 1, I1 - TV5, 2
MP1 = I1 * P1PW + M
IF (MAX - NPI1) > 36, +3C, 440
530 KMIN = K1
540 KDIFF = KMAX
550 KSTEP = KDIFF
60 TO 530
K1 = KMIN, NTO1, KSTEP
K2 = K1 + KDIFF
K3 = K2 + KDIFF
K4 = K3 + KDIFF
70 IF (MAX - NPI1) > 70, 72, 480
J1 = DATA(K1) + DATA(K2)
J2 = DATA(K1) + DATA(K2+1)
J3 = DATA(K1) + DATA(K4)
J4 = DATA(K1+1) + DATA(K4+1)
J5 = DATA(K1) + DATA(K2+1)
J6 = DATA(K1) + DATA(K4+1)
J7 = DATA(K1) + DATA(K3)
71 U1 = DATA(K3) - DATA(K1)
U2 = DATA(K3+1) - DATA(K1+1)
72 IF (ISIGN) = 471, 72, 472
J8 = DATA(K4) - DATA(K3)
50 TO 416
J9 = DATA(K4+1) - DATA(K3+1)
J10 = DATA(K3) - DATA(K4)
J11 = DATA(K4) - DATA(K3+1)
J12 = DATA(K3+1) - DATA(K4)
80 TO 416
T2 = W2*DATA(K2) - W2*DATA(K2+1)
T3 = W3*DATA(K3) - W3*DATA(K3+1)
T4 = W3*DATA(K3+1) - W3*DATA(K4+1)
81 J13 = DATA(K1) + T2
J14 = DATA(K1) + T3
J15 = DATA(K1) + T4
J16 = DATA(K1) + T2
J17 = DATA(K1) + T3
J18 = DATA(K1) + T4
90 IF (ISIGN) = 493, 500, 500
J19 = T1 - T2
J20 = T1 - T3
50 TO 519
J21 = T1 - T2
J22 = T1 - T3
U1 = DATA(K1) + U1
U2 = DATA(K1) + U2
U3 = DATA(K1) + U3
U4 = DATA(K1) + U4
U5 = DATA(K1) + U5
U6 = DATA(K1) + U6
516
JATA(K3) = U1R-U2R
      JATA(K3+1) = U1I-U2I
      JATA(K3+1) = U1R-U2R
      KMIN = L*(KMIN-I1)+I1
      IF(KDI = NP2HF) 450, 530, 530
      CONTINUE
      M = M+MAX
      IF(M=MMAX) 540, 540, 570
      IF(ISIGN) 550, 560, 560
      TEMP = AR
      AR = (WR+WI)*RTHLF
      MI = (MI-TEMP)*RTHLF
      GO TO 410
      TEMP = AR
      AR = (WR-WI)*RTHLF
      MI = (MI+TEMP)*RTHLF
      GO TO 410
      JPAR = 3-IPAR
      MMAX = MMAX+MMAX
      GO TO 350
      IF(ITWO-NP2) 6D5, 7D5, 700
      IP1 = NTWO
      IF = INQN2
      NP1HF = 4/2
      IP2 = IFACT(IF)*IPF1
      J1MIN = NP1+1
      IF(J1MIN=IPF1) 615, 615, 640
      J1 = J1MIN, IPF1, NP1
      THETA = -TA*FLOAT(J1-1)/FLOAT(IPF1)
      IF(ISIGN) 625, 525, 520
      THETA = THETA
      STPE = COS(THETA)
      STPI = SIN(THETA)
      4 = WSTP3
      4 = WSTPI
      J2MIN = J1+IPF1
      J2MAX = J1+IPF2-IPF1
      GO E35 J2 = J2MIN, J2MAX, IPF1
      I1MIN = J2+I1NG-2
      GO E35 I1 = J2, I1MAX, 2
      GO E35 J3 = I1+NTOT, IFP2
      TEMP = DATA(J3)
      JDATA(J3) = DATA(J3)*WR-DATA(J3+1)*WI
      JDATA(J3+1) = TEMP*WI+DATA(J3+1)*WR
      MI = (J3-13)/NP1HF
      IF(13= IFP1*(1+IFACT(IF)/2)
      GO E9L I1 = I1, I1NG, 2
      GO E9L I3 = I3, I3TNG, NP2
      J2MAX = J3+J2TNG-IPF1
      GO E9C J2 = J3, J2MAX, IPF1
      J1MAX = J2+IPF1-NP1
      GO E9C J1 = J2, J1MAX, NP1
      J3MAX = J1+NP2-IPF2
      GO E9L J3 = J1, J3MAX, IPF2
      JMIN = J3-J2+13
      JMAX = JMIN+IPF2-IPF1
      I = 1+(J3-13)/NP1HF
      IF(J2-13) 655, 655, 565
SUMF=0.
SUMI=0.
660 SUMF=SUMF+DATA(J)
SUMI=SUMI+DATA(J+1)
665 ICONJ = 1+(IFP2-2*J+I3+J3)/NP1+F
J=JMAX
670 SUMF=DATA(J)
SUMI=DATA(J+1)
675 TEMP=F*SUMF-OLDSR+DATA(J)
680 CONTINUE
IF(J-I2) 685,686,686
IF(IFP1-1) 685,685,686
685 MR=WSTP
WI=WSTPI
686 TEMP=WR
MR=WR+WSTP-WI+WSTPI
690 IWORK=WR+WR
I=1
IFMAX = I3+NP2-NP1
695 IF = IF+1
660 IF(IFP1-1) 513,763,760
700 GO TO (300,830,930,701), ICASE
701 NHALF=N
N=N+N
THETA=-TWOPI/FLOAT(N)
702 IF(ISI3) 703,702,702
THETA=THETA
703 WSTP = COS(THETA)
WSTPI = SIN(THETA)
WR=WSTP
WI=WSTPI
IMIN=3
JMIN=2*NHALF-1
705 TO 725
J=JMIN
710 SUMF=(DATA(I)+DATA(J))/2.
SUMI=(DATA(I+1)+DATA(J+1))/2.
715 JMIN=J+1
JMAX=JMIN
TEMPR = WR * SUMI + WI * DIFR
TEMP1 = WI * SJMI - WR * DIFR
DATA(I) = SUMR * TEMPR
DATA(I+1) = DIFI * TEMPI
DATA(J) = SUMR * TEMPR
DATA(J+1) = -DIFI * TEMPI

720  J = J + NP2
IMIN = IMIN + 2
JMIN = JMIN - 2
TEMPR = AR
AR = WR * WSTPR - WI * WSTPI
WI = TEMPR * WSTPI + WI * WSTPR

725  IF (IMIN < JMIN) 710, 730, 740
730  IF (I3 > G3) 731, 740
731  IF (I3 + 1 < IMIN) 705, NP2
740  NP2 = NP2 + NP2
NTOT = NTOT - NTOT
J = NTOT + 1
IFAX = I.TOT / 2 + 1
IMAX = IMAX - 2 * \HALF

745  GO TO 755
750  DATA(J) = DATA(I)
DATA(J+1) = -DATA(I+1)
755  I = I + 2
IF(I = IMAX) 750, 760, 760
DATA(J) = DATA(IMIN) - DATA(IMIN+1)
DATA(J+1) = 0.
IF(I = J) 710, 760, 780
760  DATA(J) = DATA(I)
DATA(J+1) = DATA(I+1)
770  I = I - 2
J = J - 2
IF(I = IMIN) 770, 775, 785
DATA(J) = DATA(IMIN) + DATA(IMIN+1)
DATA(J+1) = 0.
IMAX = IMIN
GO TO 745
780  DATA(I) = DATA(I) + DATA(2)
DATA(2) = C.
GO TO 200
800  IF(I = ENG) 800, 840, 860
805  DO 860  I = 1, NTOT, NP2
IMAX = I + NP2 - NP1
DO 860  I = 2, I2MAX, NP1
IMIN = I2 + 11 + N2
IMAX = I2 + NP2 - 2
JMAX = 2 * I2 + NP1 - IMIN
IF(I2 = 13) 820, 820, 820, 810
JMAX = JMAX + NP2
810  IF(I1DIM = 2) 851, 850, 830
820  J = JMAX + NP2
DO 840  I = IMIN, IMAX, 2
DATA(I) = DATA(J)
DATA(I+1) = -DATA(J+1)
840  JE = J - 2
850  J = JMAX
DO 860  I = IMIN, IMAX, NP0
DATA(I) = DATA(J)
DATA(I+1) = -DATA(J+1)
860  J = J - NP0
900  NP0 = NP1
NP1 = NP2
910  NPSEVEN = N
920  IF(ISISEN) 945, 930, 930
930  END = 2.0 / FLDAT(ISAVE)
940  DATA(I) = DATA(I) * FACT
950  RETURN.
SUBROUTINE P,OTT(D,Y,I,ICO)
DIMENSION J(2,485),Y(I,485),X(485)
DIMENSION IY(20),XLAGS(30)
DIMENSION LUM(I)
DIMENSION XP100(50)
DIMENSION CHECK(75),YSP(10)
COMMON/YAM/AM(200),IHO(200),ZMAM(200),ZD
COMMON/POL/YHASE(30),YCOHER(50)
COMMON/PLT/XN13(485),FACTM,INTER
INIT=0,Z,ZZ,ZNAME
DATA ICOUNT=1/0
ICOUNT=ICOUNT+1
LUM(1)=1CHMICRO-3ML
LUM(2)=1CHX 1C(-3) G
LUM(3)=1CHMILLI-3ML
LUM(4)=1CHGRAM/L
LUM(5)=1CHX 1C(-3)
LUM(6)=1CHX 1C(-3)
LUM(7)=1CH
LUM(8)=1CH(EXP).MEQ
LUM(9)=1CHUMO/CM-25
LUM(11)=1CH
LOAD=0
DO 91 I=1,ND
IF(ICO .NE. NAM(I)) GO TO 91
Z=ZTAM(I)
J=IHO(I)-(IHO(I)/10)*10+LOAD
ZL=LUM(J)
GO TO 92
91 CONTINUE
92 CONTINUE
XMAX=-99.0
XMIN=1.0E+20
DO 1 1=1,M
Y(I)=0(1,1)
XMAX=A MAX(XMAX,Y(I))
XMIN=A MIN(XMIN,Y(I))
CONTINUE
1 IF((ICOUNT.EQ.5).OR.(ICOUNT.EQ.6)) GO TO 27
CHECK(I)=0.0
DO 25 I=1,19
CHECK(I)=CHECK(I)+2.0
IF(XMAX.LE. CHECK(I)) GO TO 26
25 CONTINUE
Y(M+2)=CHECK(I)+5.0
LADD=(Y(M+2)/15.0)*3.0
Y(M+2)=FLOAT(LADD)*5.0
X(M+1)=5.0
X(M+2)=4.1
Y(M+1)=0.0
DO 20 L=1,M
X(L)=L-1
CONTINUE
20 CONTINUE
GO TO 21
21 Y(M+2)=XMAX
Y(M+1)=XMIN
YADD=(XMAX-XMIN)/7.0
X(M+1)=3.0
X(M+2)=0.5
XCM=24.0
XHAFG=-1.0
IF((ICOUNT.EQ.6)) GO TO 28
YMAX=12.0
YCM=19.0
GO TO 9
28 CONTINUE
YCM=1.0
YMAX=4.0
GO TO 9
X(1) = 0.1
X(1) = 0.3

DO 8 L = 2, M
X(L) = X(L-1) + XDEL

CONTINUE
8 IF (ICOUNT .EQ. 7) GO TO 10
IF (ICOUNT .EQ. 5) 0, 10, (ICOUNT .EQ. 5)) M = M + 2

DO 46 I = 1, M

Y(M+1) = 0.0
Y(M+2) = 1.5
DO 47 I = 1, M
Y(I) = YC09HER(I)

47 CONTINUE
DO 46 I = 1, M

Y(M+1) = 0.0
Y(M+2) = 1.5
DO 47 I = 1, M
Y(I) = YC09HER(I)

47 CONTINUE
DO 46 I = 1, M

DO 20 I = 1, M
Y(I) = YCALIB(IPTS, X2, Y2, YINCR)

20 CONTINUE

DO 45 I = 1, M
M = M + 2
CALL PLTMSP(X, Y, 12, 16, X2, Y2, YINCR)
CALL PLTMSPL(X, Y, M)
X2 = Y2 = 0.0
IPTS = 16
YINCR = 1.0
CALL YCALIB(IPTS, X2, Y2, YINCR)
IPTS = M
XM = 1.0
XINCR = 21.0 / XM
X2 = Y2 = 1.0
CALL XCALIB(IPTS, X2, Y2, XINCR)
X2 = X2 = 23.0
IPTS = 16
YINCR = 1.0
CALL YCALIB(IPTS, X2, Y2, YINCR)
IF (ICOUNT .EQ. 1) 30 TO 40
IF (ICOUNT .EQ. 2) 30 TO 41
IF (ICOUNT .EQ. 3) 30 TO 43
IF (ICOUNT .EQ. 4) 30 TO 41
IF (ICOUNT .EQ. 5) 30 TO 42
IF (ICOUNT .EQ. 6) 30 TO 41

41 CALL LETTER(17, 3, 9, 12, 18, 5, 17, DATA-TRAND, REMOVE)
CALL LETTER(12, 3, 9, 12, 4, 9, 12, TIME(MONTHS))
CALL LETTER(13, 3, 9, 13, 8, 13, CONCENTRATION)
P.11, 13, 2, 22

15 IY(I) = 6
IPTS = 5
DO 3 I = 2, IPTS

3 CONTINUE

IY(I) = IY(I-1) + IADD
CONTINUE
XX = 3.1
YY = 6.0
THETA = 3.0
HEIGHT = 0.20
DO 1 = 1, IPTS
INUM = IY(I)
CALL NUMBER(XX, YY, HEIGHT, INUM, THETA, 4H(I4), 4)
YY = YY + 3.0
CONTINUE
HEIGHT = 0.20
XX = 4.0
YY = 3.2
THETA = 3.0
XNS = XNS(1) - 1.0
INUM = XNS(IPTS)
CALL NUMBER(XX, YY, HEIGHT, INUM, THETA, 4H(I4), 4)
XX = XX + 5.0 * XINC
IPTS = M - 1
DO 5 = 1, IPTS + 6
INUM = XNS(IPTS)
CALL NUMBER(XX, YY, HEIGHT, INUM, THETA, 4H(I4), 4)
IF (IPTS * XINC + 4.0 - XX) LT. 6.0 * XINC) GO TO 22
XX = XX + 5.0 * XINC
CONTINUE
5 XX = IPTS * XINC + 4.0
INUM = XNS(IPTS)
YY = 16.2
GO TO 7
42 CALL LETTER(*2, 3, 30, 12, 9, 7, 0)
XX = IPTS + XINC + 4.0
INUM = XNS(IPTS)
CALL NUMBER(XX, YY, HEIGHT, INUM, THETA, 4H(I4), 4)
YY = 16.2
GO TO 7
CONTINUE
IPTS = 4
YSP(I) = XMIN
DO 11 = 1, IPTS
YSP(I) = YSP(I - 1) + 2 * YADD
CONTINUE
11 XX = 3.0
YY = 12.3
IF (ICOUNT .EQ. 5) YY = 4.0
THETA = 3.0
HEIGHT = 0.20
DO 12 = 1, IPTS
INUM = YSP(I)
CALL NUMBER(XX, YY, HEIGHT, XNUM, THETA, 6H(F5.3), 6)
YY = YY + 2
CONTINUE
XNUM = XX
YY = 19.2
IF (ICOUNT .EQ. 5) YY = 11.3
CALL LETTER(23, 2, 3, 12, 2, 3, 3, 23, FREQUENCY (CYCLES/MONTH))
CALL LETTER(14, 2, 3, 12, 2, 7, 14, PERIOD (MONTHS))
XLAGS(I) = 0.0
IPTS = Y / 2 + 1
XCEL = L - 1 / FLOAT (M - 1)
DO 13 = 1, IPTS
XLAGS(I) = XLAGS(I - 1) + 2 * XDDEL
XPIOD(I) = 1.0 / XLAGS(I - 1) + XDDEL
CONTINUE
XX = 3.0
YY = 3.7
THETA = 3.0
HEIGHT = 0.20
DO 14 = 1, IPTS
INUM = XLAGS(I)
CALL NUMBER(XX,YY,HEIGHT,XNUM,THETA,6H(F4.3),4)
XX=FLOAT(IPTS-1)*2;
IF((F*XINC+4.-XX).*EQ.((3.*XINC))goto 71
XX=XX+2*XINC
CONTINUE
GO TO 72
71 XNUM=5.
XX=F*XINC+4.6
CALL NUMBER(XX,YY,HEIGHT,XNUM,THETA,6H(F4.3),5)
XX=X+2
YY=3.*4.
IPTS=IPTS-1
GO TO 2, 1=2, IPTS
XNUM=XX+000(I)
CALL NUMBER(XX,YY,HEIGHT,XNUM,THETA,6H(F5.2),6)
XX=XX+2*XINC
CONTINUE
IF(COUNT .EQ. 7)GO TO 32
IF(COUNT .EQ. 8)GO TO 48
IF(COUNT .EQ. 21.5)YY=11.5
GO TO 72
CALL LETTER(16,.3,6.,12..0,18.5,15HRAW-DATA AND TREND)
CALL LETTER(12.3,6.,12.0,2.3,12HTIME(MONTHS))
CALL LETTER(13.3,36.0;3.5,6.1,13HCONCENTRATION)
PRINT 101,103,2,2Z
X1=1.0
Y1=AINTER
X2=1-1
Y2=FACTY*X2+4*INTER
CALL UNIITO(X1,Y1,XT1,YT1)
CALL UNIITO(X2,Y2,XT2,YT2)
CALL PLOT(XT1,YT1,3)
CALL PLOT(XT2,YT2,2)
GO TO 102
FC=INTER(I1X,15,2(2X,A10))

INUM=IC3
XX=5.6
HEIGHT=.2
THETA=6.8
CALL NUMBER(XX,YY,HEIGHT,INUM,THETA,4H(A13),3)
IF(COUNT .EQ. 5)GO TO 17
CALL LETTER(2.12.4.3,YY,2HX)
XX=5.8
INUM=Z4
CALL NUMBER(XX,YY,HEIGHT,INUM,THETA,4H(A7),7)
XX=7.4
INUM=ZZ
CALL NUMBER(XX,YY,HEIGHT,INUM,THETA,5H(A10),10)
IF(COUNT .EQ. 5)RETURN
CALL PLOT(28.5,6.-3)
IF(COUNT .EQ. 6)RETURN
IF(COUNT .EQ. 7)GO TO 9
RETURN
999 M=M-2
CALL P.IMSP(X,Y,.12.1H+,0.,M)
CALL P.IMPL(X,Y,M)
GO TO 30
CALL LETTER(2.26.4.5,11.0,2H+)
30 TO 52
CALL LETTER(3.3,9.7.0,19.3,5HPHASE)
CALL LETTER(14.3,6.12.18.11HPHASE SPECTRUM)
IPTS=13
YY(I)=180
GO 33, I=1, IPTS
IY(I)=IY(I)+30
CONTINUE
XX=5.1
YY=1.6
HEIGHT=.2
THETA=0,0
DO 34 I=1, IPTS
CALL NUMBER(XX, YY, HEIGHT, INUM, THETA, 4H(I4), 4)
YY=YY+1.0
34 CONTINUE
CALL PLOT(4, 0, 1, 0, 3)
CALL PLOT(2, 1, 10, 2, 3)
IF(ICONJO=7) ICONJ=3
IF(ICONJO=3) ICONJO=9
CALL LETTER(3, 3, 30, 3, 0, 10.0, YHCOHERENCE)
IPTS=1
CALL LETTER(26, 3, 3, 11, 4, 18, 0)
CALL SQUARE_COHERENCY_SPECTRUM
YSP(1)=3.0
DO 61 I=2, IPTS
YSP(I)=YSP(I-1)+0.1
61 CONTINUE
YY=4.0
DO 62 I=1, IPTS
YY=YY+YSP(I)
CALL NUMBER(3.1, YY, 2, XNUM, 0.0, 6H(F4.2), 4)
YY=YY+1.0
62 CONTINUE
CALL PLOT(28, 0, -3)
99 RETURN
END

SUBROUTINE XCALIB(IPTS, X2, Y2, XINC)
DO 1 I=1, IPTS
IFLAG=3
CALL PLOT(X2, Y2, IFLAG)
Y2=Y2+X2*XINC
1 CONTINUE
RETURN
END

SUBROUTINE YCALIB(IPTS, X2, Y2, YINC)
DO 1 I=1, IPTS
IFLAG=3
CALL PLOT(X2, Y2, IFLAG)
X2=X2+Y2*YINC
1 CONTINUE
RETURN
END
APPENDIX B

B.1 Data, Station 12

The raw data and trends are displayed graphically in the Figures to follow. The data after the trends are removed are not given, but can be visualized if one considers the trend line as the time-axis. (Compare Figures B.1.1 and B.1.2).

Table B.1.1 gives the parameters considered at this station and the length of the time series.

**TABLE B.1.1: Parameters studied at station 12**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Code No.</th>
<th>Time Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd T</td>
<td>101</td>
<td>7210-7511</td>
</tr>
<tr>
<td>Cd T</td>
<td>101</td>
<td>7210-7511</td>
</tr>
<tr>
<td>Cu T</td>
<td>107</td>
<td>7206-7511</td>
</tr>
<tr>
<td>Fe T</td>
<td>110</td>
<td>7206-7511</td>
</tr>
<tr>
<td>Ni T</td>
<td>116</td>
<td>7210-7511</td>
</tr>
<tr>
<td>Zn T</td>
<td>119</td>
<td>7206-7511</td>
</tr>
<tr>
<td>pH</td>
<td>123</td>
<td>7206-7511</td>
</tr>
<tr>
<td>SO₄</td>
<td>127</td>
<td>7206-7511</td>
</tr>
<tr>
<td>T PART</td>
<td>128</td>
<td>7206-7511</td>
</tr>
<tr>
<td>P T</td>
<td>240</td>
<td>7210-7511</td>
</tr>
</tbody>
</table>
Figure B.1.1: Cd T data and trend, station 12 (7210-7511)
Figure B.1.2: Cd T data-trend removed, station 12 (7210-7511)
Figure B.1.3: Cu T data and trend, station 12 (7210-7511)
Figure B.1.4: Fe T data and trend, station 12 (7206-7511)
Figure B.1.6: Zn T data and trend, station 12 (7206-7511)
Figure B.1.7: pH data and trend, station 12 (7206-7511)
Figure B.1.8: SO$_4$ data and trend, station 12 (7206-7511)
Figure B.1.10: P T data and trend, station 12 (7210-7511)
B.2 Data, Station 2

Table B.2.1 gives the parameters considered and the length of the time series. The data are displayed graphically in the figures to follow.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Code No.</th>
<th>Time Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd T</td>
<td>101</td>
<td>7206-7510</td>
</tr>
<tr>
<td>Cu T</td>
<td>107</td>
<td>7206-7510</td>
</tr>
<tr>
<td>Fe T</td>
<td>110</td>
<td>7206-7510</td>
</tr>
<tr>
<td>Ni T</td>
<td>116</td>
<td>7206-7510</td>
</tr>
<tr>
<td>Zn T</td>
<td>119</td>
<td>7206-7510</td>
</tr>
<tr>
<td>pH</td>
<td>123</td>
<td>7206-7510</td>
</tr>
<tr>
<td>$\text{SO}_4$</td>
<td>127</td>
<td>7206-7510</td>
</tr>
<tr>
<td>T PART</td>
<td>128</td>
<td>7206-7510</td>
</tr>
<tr>
<td>P T</td>
<td>240</td>
<td>7211-7510</td>
</tr>
</tbody>
</table>
Figure B.2.1: Cd T data and trend, station 2 (7206-7510)
Figure B.2.2: Cu T data and trend, station 2 (7206-7510)
Figure B.2.3: Fe T data and trend, station 2 (7206-7510)
Figure B.2.4: Ni T data and trend, station 2 (7206-7510)
Figure B.2.5: Zn T data and trend, station 2 (7206-7510)
Figure B.2.6: pH data and trend, station 2 (7206-7510)
Figure B.2.7: SO₄ data and trend, station 2 (7206-7510)
Figure B.2.8: T PART data and trend, station 2 (7206-7310)
Figure B.2.9: PT data and trend, station 2 (7211-7510)
**B.3 Data, Station 3**

Table B.3.1 gives the parameters considered and the length of the time series. The data are displayed graphically in the figures to follow.

**TABLE B.3.1: Parameters studied at station 3**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Code No.</th>
<th>Time Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd T</td>
<td>101</td>
<td>7211-7511</td>
</tr>
<tr>
<td>Cu T</td>
<td>107</td>
<td>7211-7511</td>
</tr>
<tr>
<td>Fe T</td>
<td>110</td>
<td>7206-7511</td>
</tr>
<tr>
<td>Ni T</td>
<td>116</td>
<td>7211-7511</td>
</tr>
<tr>
<td>Zn T</td>
<td>119</td>
<td>7206-7511</td>
</tr>
<tr>
<td>pH</td>
<td>128</td>
<td>7206-7511</td>
</tr>
<tr>
<td>SO₄</td>
<td>127</td>
<td>7206-7511</td>
</tr>
</tbody>
</table>
Figure B.3.1: Cd T data and trend, station 3 (7211-7511)
Figure B.3.2: Cu T data and trend, station 3 (7211-7511)
Figure B.3.3: Fe T data and trend, station 3 (7206-7511)
Figure B.3.4: Ni T data and trend, station 3 (7211-7511)
Figure B.3.5: Zn T data and trend, station 3 (7206-7511)
Figure B.3.6: pH data and trend, station 3 (7206-7511)
Figure B.3.7: SO$_4$ data and trend, station 3 (7206-7511)
B.4 Data, Station 4

Table B.4.1 gives the parameters considered and the length of the time series. The data are displayed graphically in the figures to follow.

TABLE B.4.1: Parameters studied at station 4

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Code No.</th>
<th>Time Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd T</td>
<td>101</td>
<td>7204-7507</td>
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<tr>
<td>Cu T</td>
<td>107</td>
<td>7204-7509</td>
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<tr>
<td>Fe T</td>
<td>110</td>
<td>7204-7509</td>
</tr>
<tr>
<td>Ni T</td>
<td>116</td>
<td>7204-7509</td>
</tr>
<tr>
<td>Zn T</td>
<td>119</td>
<td>7204-7509</td>
</tr>
<tr>
<td>pH</td>
<td>123</td>
<td>7203-7509</td>
</tr>
<tr>
<td>$SO_4$</td>
<td>127</td>
<td>7203-7509</td>
</tr>
</tbody>
</table>
Figure B.4.1: Cd T data and trend, station 4 (7204-7507)
Figure B.4.2: Cu T data and trend, station 4 (7204-7509)

CONCENTRATION

TIME (MONTHS)
Figure B.4.3: Fe T data and trend, station 4 (7204-7509)
Figure B.4.4: Ni T data and trend, station 4 (7204-7509)
Figure B.4.5: Zn T data and trend, station 47204-7509

RAW-DATA AND TREND

CONCENTRATION

TIME (MONTHS)
Figure B.4.6: pH data and trend, station 4 (7203-7509)
Figure B.4.7: SO$_4$ data and trend, station 4 (7203-7509)
**B.5 Data, Sudbury Area**

Table B.5.1 gives the parameters considered and the length of the time series. The data are displayed graphically in the figures to follow.

**TABLE B.5.1: Parameters studied for the Sudbury area**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Code No.</th>
<th>Time Interval</th>
</tr>
</thead>
<tbody>
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Figure B.5.2: Cu F data and trend, Sudbury area (7204-7511)
Figure B.5.3: Cu T data and trend, Sudbury area (7208-7511)
Figure B.5.4: Fe F data and trend, Sudbury area (7204-7511)
Figure B.5.5: Pb T data and trend, Sudbury area (7201-7511)
Figure B.5.6: Ni T data and trend, Sudbury area (7208-7511)
Figure B.5.7: Zn F data and trend, Sudbury area (7204-7511)
Figure B.5.8: Zn T data and trend, Sudbury area (7204-7511)
Figure B.5.9: SP CON data and trend, Sudbury area (7108-7511)
Figure B.5.10: pH data and trend, Sudbury area (7108-7511)
Figure B.5.11: SO$_4$ data and trend, Sudbury area (7108-7511)
### B.6 Data, U.G.L. Area

Table B.6.1 gives the parameters considered and the length of the time series. The data are displayed graphically in the figures to follow.

**TABLE B.6.1: Parameters studied for the U.G.L. area**

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Figure B.6.1: Cd T data and trend, U.G.L. area (7201-7511)
Figure B.6.2: Cu F data and trend, U.G.L. area (7204-7511)
Figure B.6.3: Cu T data and trend, U.G.L. area (7201-7511)
Figure B.6.4: Fe T data and trend, U.G.L. area (7201-7511)
Figure B.6.5: Pb T data and trend, U.G.L. area (7201-7511)
Figure B.6.6: Ni T data and trend, U,G,L, area (7201-7511)
Figure B.6.7: Zn F data and trend, U.G.L. area (7204-7511)
Figure B.6.8: Zn T data and trend, U.G.L. area (7204-7511)
Figure B.6.9: SP CON data and trend, U.G.L. area (7108-7511)
Figure B.6.10: pH data and trend, U.G.L. area (7108-7511)
Figure B.6.11: SO₄ data and trend, U.G.L. area (7108-7511)
Figure B.6.12: T PART data and trend, U.G.L. area (7204-7511)
Figure B.6.13: P T data and trend, U.G.L area (7201-7511)
### B.7 Spectra

The following Figures give the spectra of pairs of parameters which are given in Table B.7.1.

**TABLE B.7.1: Pairs of spectral parameters considered**

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Figure B.7.4: Power spectrum for PH & SO4 station 2 (7206-7510)

Relative Spectral Intensities

X 123 PH
+ 127 SO4 MILLI-GM/L

FREQUENCY (CYCLES/MONTH)

PERIOD (MONTHS)
SQUARED COHERENCY SPECTRUM

Figure B.7.5: Coherency spectrum for pH & SO₄²⁻, station 2 (12/06-7/710)

FREQUENCY (CYCLES/MONTH)
PERIOD (MONTHS)
SQUARED COHERENCY SPECTRUM

Figure 3.7.6: Coherence spectrum for pH & SO₄, station 3 (1976-75).
Figure B.7.10: Power spectrum for PH & SO4, station 4 (7203-7209)
SQUARED COHERENCY SPECTRUM

Figure B.7.14: Coherence spectrum for pH & SQ, Sudbury area (7/89-7/91)

COHERENCE

FREQUENCY (CYCLES/MONTH)
PERIOD (MONTHS)
PHASE SPECTRUM

Figure B.7.15: Phase spectrum for pH & SO4, Sudbury area (71.08-75.11)
RELATIVE SPECTRAL INTENSITIES

Ph
SO4
MILLI-GM/L

Frequency (cycles/month)
Period (months)

Figure B.7.16: Power spectrum for pH & SO4, u.c.l. area (7206-7511)
Figure B.7.19: Power spectrum for pH & SP CON, Sudbury area (7/68-7/71)
SQUARED COHERENCY SPECTRUM

Figure B.7.20: Coherency spectrum for pH & SP COM, Sudbury area (7108-7211)
SQUARED COHERENCY SPECTRUM

Figure B.23: Coherence spectrum for pH & SP COM, U.G.I. area (7/08-7/11)
PHASE SPECTRUM

Figure B.7.24: Phase spectrum for pH & SP CON, U.G.I. area (708-751L)
SQUARED COHERENCY SPECTRUM

Figure B.7.26: Coherency spectrum for Fe T & Zn T, station 12 (7206-7511)
Figure B.7.27: Phase spectrum for Fe T & Zn T, station 12 (7206-7511)
SQUARED COHERENCY SPECTRUM

Figure B. 7.29. Coherence spectrum for Fe T & Zn T, station 2 (7206-7510)

COHERENCE

FREQUENCY (CYCLES/MONTH)
PERIOD (MONTHS)
Figure B.7.30: Phase spectrum for Fe T & Zn T, station 2 (7206-7510)
Figure B.7.21: Power spectrum for Fe T & zn T, station 3 (7206-7511)

X 110 FE T MICRO-GM/L
+ 119 ZN T MICRO-GM/L

RELATIVE SPECTRAL INTENSITIES

FREQUENCY (CYCLES/MONTH)
PERIOD (MONTHS)
Figure 5.32: Coherence spectrum for Pe 1 & Zn 1, station 3 (7206-7511)
SQUARED COHERENCY SPECTRUM
PHASE SPECTRUM

Figure E.7.36: Phase spectrum for Fe, T & Zn, station 4, (7201-7509)

PHASE

180
150
120
90
60
30
0
-30
-60
-90
-120
-150
-180

FREQUENCY (CYCLES/MONTH)
PERIOD (MONTHS)

0.00 0.048 0.095 0.143 0.190 0.238 0.286 0.333 0.381 0.429 0.476 0.5
Figure E.7.27: Power spectrum for Fe T & Pb T, Sudbury area (7204-7311)

RELATIVE SPECTRAL INTENSITIES

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X 113  PB T MICRO-GM/L
+
110  FE T MICRO-GM/L
Figure E.7.39: Phase spectrum for Fe T & Pb T, Sudbury area (7204-7211)
SQUARED COHERENCY SPECTRUM

Figure B.7.41: Coherence spectrum for Pb T & Pb T, U.G.I. area (7201-7511)
Figure B.7.47: Power spectrum for PH & P.T. station 2 (721-7510)
Figure B.7.48: Power spectrum for PH & PT, U.G.L. area (7201-7511)