Analysis of Some Particle Size Distributions
Collected as Part of a Pilot Plant Study
Utah Valley Water Treatment Plant
Orem, Utah

By
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COLLEGE OF
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Collected as Part of a Pilot Plant Study
Utah Valley Water Treatment Plant
Orem, Utah

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EXECUTIVE SUMMARY

The Utah Valley Water Treatment plant treats water from the Deer Creek Reservoir located in Utah County, Utah. Due to increased demand the plant capacity needed to be increased. A pilot study was performed in 1995 to determine the best treatment options for expansion. During the pilot study, a large volume of particle count data was collected. Analysis of the particle count data was restricted to determining total particulate removal efficiencies. Similar pilot studies not only examined total particulate removal efficiencies but also the effect the different treatment options had on the particle size distribution of the suspension.

The specific objective of this study was to examine the particle size distributions contained in the particle count data and try to reproduce the method of analysis used by other researchers. This consisted of applying a model known as the power law to the particle size distribution data to see if the model fit the data and what trends, if any, could be detected.

The particle count data were screened in order to select pilot filter runs during which similar raw water characteristics were present and from which different treatment processes could be compared. This was accomplished by searching the database for pilot study filter runs in which as few process parameters were varied as possible. This selection process yielded 7 pilot filter runs that became the subject of this study. For each run, three particle size distributions were analyzed. These were taken from the raw water and two different pilot filter configurations.
The results of the study revealed that the power law model of particle size distribution fit the particle size distributions examined in most of the data studied. When the particle size distribution did not fit the power law model it appeared that some external factor must have been affecting the filtration process. The results also showed a statistically significant difference in particle size distributions resulting from preoxidation with ozone versus chlorine.

Additional studies aimed specifically at better understanding what particle size distributions can reveal about the efficacy of the filtration process, when different filter configurations and pretreatment options are evaluated, are warranted. The power law model should be one of the main tools for analysis.
1.0 INTRODUCTION

The Utah Valley Water Treatment Plant (UVWTP) located in Orem, Utah, treats water from the Deer Creek Reservoir. The plant was originally designed to produce 50 MGD and licensed by the state of Utah to process up to 42 MGD. The plant went on line in the late 70's. The original design had provisions to increase capacity to an ultimate 100 MGD. A pilot study was performed by Montgomery Watson Incorporated between April 25, 1995 and February 9, 1996 to develop design criteria for plant expansion. The pilot plant (Figure 1) had three pretreatment options configured in parallel. The effectiveness of direct filtration, conventional settling, and solids contact clarification were evaluated based on the following parameters:

Turbidity
Particle removal and particle concentration
Disinfection by-products
Total organic carbon
Threshold odor number
Residual aluminum (alum was found to be the preferred coagulant)

Raw water to each of the three pretreatment trains was preoxidized for most filter runs. The oxidizers tested were potassium permanganate, chlorine, and ozone.

Particle concentrations were measured for particles in the 2 to 150 micrometer range. Overall particle removal efficiency was evaluated
by comparing total particle count data of the raw and finished waters. The particle counter employed in the pilot study was capable of breaking the particle counts into many size ranges. It was programmed to group the particle sizes in the following ranges: 2 to 5 μm, 5 to 7 μm, 7 to 15 μm, and 15 to 150 μm. The main reason for this size range configuration was to test the effectiveness of using particle size as a surrogate indicator for Giardia cysts and Cryptosporidium oocysts which occur in the 5 to 15 μm and 2 to 7 μm size ranges, respectively.

Prior research of this type not only examined overall particle removal efficiency but also the effect that the different treatment options had on particle size distributions. Kavanaugh et al. (1980) noted that particulate size data reported for numerous particulate systems in natural waters can be modeled accurately with a two-parameter power law. This study suggested that the particle size distribution characterized using the power law model could be useful in treatment process selection. Wilczak et al. (1992) used the power law model to describe particle size distributions and as a basis for statistical data analysis in a study on how preoxidation affects particle removal during clarification and filtration. Size distribution analysis of the particle count data collected as part of the UVWTP pilot study was not performed. The purpose of this project is to analyze the size distributions contained in the UVWTP pilot study data using the methods of Wilczak et al. to see (1) how well the particle size
distributions fit the power law model, and (2) if significant trends in the data can be detected.

2.0 METHODS

During the pilot study, particle count data was collected by real time analysis with a laser particle size analyzer. Analyzers of this type are capable of providing particle counts in size ranges from 0.02μm to 1000μm. Within this size range spectrum the data can be divided into particle counts per sub size range. The number of sub-ranges varies from analyzer to analyzer but generally the particle size spectrum can be divided into as many as 100 subdivisions (Wilczak et al, 1992). The author feels that the decision to limit the number of size ranges to four limited the value of the data unnecessarily. Be that as it may, the data collected does lend itself to the method of analysis used by Wilczak et al.

It is well known that preoxidation destabilizes particles which, in turn, enhances filter operation and final effluent quality in treatment of municipal drinking water. Although primary drinking water standards for filtered water are still based on, among other parameters, turbidity (EPA, 1998), particle counting is a more direct measure of suspended solids. By examining particle size distributions (PSDs) before and after treatment a more detailed analysis of the effectiveness of the process is possible. One method of analyzing PSDs is the application of the Power Law. In
this study, 21 of the PSDs measured during the pilot study are analyzed using this method.

2.1 Analysis of Particle Size Distribution using the Power Law

When an observable phenomena behaves as the function of some constant raised to a power, the function is referred to in general as a power law (Serway, 1996). The power law of particle size distribution is a function that can be used to describe PSDs. The power law states that the number of particles in a size range is a two-parameter power function of the mean particle size within that range. It can be written as

\[
\left( \frac{N}{\Delta d} \right) = A (d_p)^\beta
\]

where

- \( (N/\Delta d) \) = The number of particles within a size range
- \( A \) = Coefficient related to the concentration of particles in suspension
- \( \beta \) = An indicator of the relative distribution of number concentration as a function of particle size.
- \( d_p \) = The mean particle size within a range

In other words, the number of particles within a size range increases exponentially with a decrease in the mean size (diameter) within the range. After linearizing by taking the log of both sides of the equation the relation appears as follows:

\[
\log \left( \frac{N}{\Delta p} \right) = \log A + \beta \log (d_p)
\]
If the particle size distribution of a particular suspension obeys the power law, a linear regression analysis can be used to estimate values of the parameters A (y intercept = log A) and β.

According to Montgomery (1985), the heterogeneous particulate suspensions commonly found in surface source water and wastewater treatment plant effluent can be characterized by the power law. Prior studies (Wilczak et al, 1992, Kavanaugh et al, 1980) focused on the value of β as the key parameter in this type of analysis. This is because it describes the number distribution (number per subrange) of particles over the entire measurement range. However, it is important that both the slope and intercept of the power law model be taken into account when interpreting the results (Wilczak et al, 1992). By using linear regression, both parameters can be determined simultaneously.

Linear regression analysis was performed using built in spreadsheet utilities. The log of the particle count in each size range was plotted versus the log of the mean particle size of each size range. This process yielded four data points for each PSD. The linear regression utility was then applied to these four data points. The $R^2$ values as well as the equation of the best fit line are displayed on each of the graphs (see Appendix I, Figures A1-1 through A1-7). Interpretation of the regression analysis was made with the fact in mind that with four data points, an $R^2$ value of 0.810 means there is a one in ten chance that the power law model fit is a coincidence. $R^2$ values of 0.903 and 0.980
correspond to a one in twenty and a one in a hundred chance, respectively, that the power law model fit is a coincidence (Berthouex and Brown, 1994). Therefore, an $R^2$ value of 0.810 or greater was used to infer that the estimates of $\beta$ and logA were significant for the PSD analyzed.

2.2 Selection of Filter Runs

During the course of the pilot study a large amount of particle count data was collected during three different test periods. Test period 1 was from April 25, 1995 through July 12, 1995. During this period raw water quality was most affected by the spring runoff conditions. Test period 2 was from September 20, 1995 through October 26, 1995 and corresponded to the period of lake turnover for Deer Creek Reservoir. Test period 3 was from January 17, 1996 through February 9, 1996 during which raw water is at its lowest temperature and turbidity. Numerous pilot filter runs were performed during each test period.

Because of the volume of data collected, only data from selected runs was analyzed. This made it necessary to develop criteria with which a portion of the data could be selected for analysis.

As mentioned earlier, the pilot study evaluated the effectiveness of different treatment alternatives. After reviewing the database and using several different search criteria it became apparent that no two filter runs were performed with only one parameter varied. The search was finally
narrowed to a group of filter runs from Test Period 1 in which most of the parameters were similar and what varied was the preoxidant used. Runs 1, 3, 4, and 6 used chlorine as the preoxidant. Runs 6, 10, and 12 used ozone. Table 1 shows the variance in parameters for the selected filter runs. All filter runs selected for this study were direct filtration runs. According to treatment plant personnel, Runs 1 and 8, 4 and 10, and 6 and 12 were paired to compare the performance of chlorine and ozone when used as preoxidants.

Table 1. Parameter values for the selected filter runs.

<table>
<thead>
<tr>
<th>Filter Run</th>
<th>Pre-Oxidant</th>
<th>Dose (mg/l)</th>
<th>Coagulant</th>
<th>Dose (mg/l)</th>
<th>Polymer</th>
<th>Dose (mg/l)</th>
<th>Filtration Rate (gpm/ft²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chlorine</td>
<td>1.6</td>
<td>Al</td>
<td>8.7</td>
<td>CT</td>
<td>1.8</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>Chlorine</td>
<td>1.6</td>
<td>Al</td>
<td>6</td>
<td>CT</td>
<td>1.8</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>Chlorine</td>
<td>1.8</td>
<td>Al</td>
<td>6</td>
<td>CT</td>
<td>1.8</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>Chlorine</td>
<td>1.6</td>
<td>Al</td>
<td>6</td>
<td>CT</td>
<td>1.9</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>Ozone</td>
<td>1.25</td>
<td>Al</td>
<td>6</td>
<td>CT</td>
<td>1.8</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>Ozone</td>
<td>1.4</td>
<td>Al</td>
<td>6</td>
<td>CT</td>
<td>1.8</td>
<td>8</td>
</tr>
<tr>
<td>12</td>
<td>Ozone</td>
<td>1.4</td>
<td>Al</td>
<td>6</td>
<td>CT</td>
<td>1.8</td>
<td>10</td>
</tr>
</tbody>
</table>

2.3 Data Reduction within a Filter Run

Figure 2 shows a graph of continuous particle count data collected during a typical filter run. Three distinct phases can be seen. The start of the filter run is marked by rapid decrease in the particle counts. The middle or "stable" part is marked by relatively constant and low particle counts. The third phase is marked by a rapid increase in particle counts and represents breakthrough. The particle counts used in this study represent the average of the particle counts taken from within the stable portion of the filter run.
Figure 2. Typical plot of real time particle counts in size ranges monitored. Stable portion of this run is approximately between 180 and 420 minutes.
The power law model was applied to the particle count data for each run, and a linear regression was performed to see how well the data fit the model. For each filter run, particle count data from the raw water and two filtered water effluent streams are analyzed. The two filtered water streams differ in that one filter was configured as a deep bed (60 inches of anthracite over 10 inches of sand) as opposed to a normal (20 inches of anthracite over 10 inches of sand) bed design. In each case, Filter 1 is the normal bed and Filter 2 is the deep bed.

3.0 RESULTS

The results of the study are shown in the graphs presented in Appendix I (Figures A1-1 through A1-7). A summary of the results for each run is given below. $R^2$ values are reported for each of the three PSDs. $\beta$ values are not reported for PSDs which yielded poor (less than 0.810) $R^2$ values.

In Run 1, each of the measured PSDs conformed to the power law model. The $R^2$ values calculated were 0.8963, 0.952, and 0.8139 for Raw, Filter 1, and Filter 2 waters, respectively. The $\beta$ values were 1.4097, 1.6355, and 1.3602, respectively.

In Run 3, only the Raw and Filter 1 PSDs conformed to the power law model. The $R^2$ values calculated were 0.8831, 0.851, and 0.4786 for
Raw, Filter 1, and Filter 2 waters, respectively. The \( \beta \) values were 1.4023 and 0.9814 for the Raw and Filter 1 waters, respectively.

In Run 4, only the Raw and Filter 1 PSDs conformed to the power law model. The \( R^2 \) values calculated were 0.8721, 0.9519, and 0.5651 for Raw, Filter 1, and Filter 2 waters, respectively. The \( \beta \) values were 1.4633 and 1.9856 for the Raw and Filter 1 waters, respectively.

In Run 6, only the Raw and Filter 1 PSDs conformed to the power law model. The \( R^2 \) values calculated were 0.8952, 0.9335, and 0.021 for Raw, Filter 1, and Filter 2 waters, respectively. The \( \beta \) values were 1.5234 and 1.0109 for the Raw and Filter 1 waters, respectively.

In Run 8, only the Raw and Filter 1 PSDs conformed to the power law model. The \( R^2 \) values calculated were 0.8916, 0.9594, and 0.4206 for Raw, Filter 1, and Filter 2 waters, respectively. The \( \beta \) values were 1.4752 and 2.3310 for the Raw and Filter 1 waters, respectively.

In Run 10, only the Raw and Filter 1 PSDs conformed to the power law model. The \( R^2 \) values calculated were 0.8462, 0.9163, and 0.0243 for Raw, Filter 1, and Filter 2 waters, respectively. The \( \beta \) values were 1.3277 and 0.8709 for the Raw and Filter 1 waters, respectively.

In Run 12, only the Raw and Filter 1 PSDs conformed to the power law model. The \( R^2 \) values calculated were 0.8149, 0.9310, and 0.1022 for Raw, Filter 1, and Filter 2 waters, respectively. The \( \beta \) values were 1.2076 and 0.9432 for the Raw and Filter 1 waters, respectively.
4.0 DISCUSSION

In this section a defense of the Power Law Model of PSDs is proposed. Also, the success and failure of the model to fit the subject PSDs is discussed. The trends revealed by analysis of different PSDs resulting from comparable filter runs in which the only parameter change was ozone versus chlorine as the preoxidant are also presented.

![Figure 3. Normal distribution of precipitation. Source: Wanielistia, 1990.](image)

4.1 Why the Power Law Model fits Particle Size Distributions

It is not unusual for natural phenomena to fit mathematical models. For example, the graph shown in Figure 3 shows that the total yearly rainfall for Scranton, Pennsylvania for the years 1950 to 1985 is normally distributed, albeit possibly slightly skewed to the left. Other examples include the log-normal distribution of hydraulic conductivity and exponential growth of bacteria cultures.
As mentioned earlier, the power law model of PSDs in aqueous particulate suspensions predicts that the number of particles within a size range increases exponentially with a decrease in the mean size within each size range. There are two reasons why one could expect this to be so, at least for naturally occurring particulate suspensions. First, consider a hypothetical particle source. Whatever the mechanism of its division into particles, each division results in two or more particles now members of a smaller size range. In other words, take some fragment of matter, divide it in two and then each successive piece in two, and the number of smaller fragments increases exponentially. The second has to do with energy. It takes energy to resist the pull of gravity and keep a particle in suspension. Larger particles tend to settle out sooner or at higher energies than smaller particles.

4.2 Power Law Correlation of the Subject PSDs

Fifteen of the twenty-one (71.4%) PSDs had $R^2$ values greater than 0.810, which indicates that most seemed to be described well by the power law model. All of the raw or natural water PSDs fit the power law model. The PSDs from the normal bed filter effluents also had good correlation with the power law model. Only the deep bed filter effluents had PSDs that failed to adhere to the power law model, this in 6 out of 7 cases. It is interesting to note that filter effluents gave good correlation with the power law even though a man-made process had altered the
PSDs\(^1\). Table 2 lists the \(R^2\) values for each of the runs. It shows that in six out of seven runs, the normal bed filter (filter 1) had a slightly greater \(R^2\) value than the raw water PSD.

**Table 2. Calculated Values for the Coefficient of Determination, \(R^2\).**

<table>
<thead>
<tr>
<th>Run/Filter Number</th>
<th>(R^2) value</th>
<th>Run/Filter Number</th>
<th>(R^2) value</th>
<th>Run/Filter Number</th>
<th>(R^2) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/r</td>
<td>0.90</td>
<td>4/1</td>
<td>0.95</td>
<td>8/2</td>
<td>0.42</td>
</tr>
<tr>
<td>1/1</td>
<td>0.95</td>
<td>4/2</td>
<td>0.57</td>
<td>10/r</td>
<td>0.85</td>
</tr>
<tr>
<td>1/2</td>
<td>0.81</td>
<td>6/r</td>
<td>0.90</td>
<td>10/1</td>
<td>0.92</td>
</tr>
<tr>
<td>3/r</td>
<td>0.88</td>
<td>6/1</td>
<td>0.93</td>
<td>10/2</td>
<td>0.02</td>
</tr>
<tr>
<td>3/1</td>
<td>0.85</td>
<td>6/2</td>
<td>0.02</td>
<td>12/r</td>
<td>0.81</td>
</tr>
<tr>
<td>3/2</td>
<td>0.48</td>
<td>8/r</td>
<td>0.89</td>
<td>12/1</td>
<td>0.93</td>
</tr>
<tr>
<td>4/r</td>
<td>0.87</td>
<td>8/1</td>
<td>0.96</td>
<td>12/2</td>
<td>0.10</td>
</tr>
</tbody>
</table>

The departure of the PSDs from the power law model for the deep bed filters occurred in two distinct ways. In Runs 4 and 6 (Figures A1-3c and A1-4c), the departure can be seen in the jump in the number concentration\(^2\) of the 7-15\(\mu\)m range. In Runs 3, 8, 10, and 12 (Figures A1-2c, 5c, 6c, and 7c), the relatively high number concentration in the 2-5 \(\mu\)m range breaks the power law model. In Runs 3 and 8, the number concentrations decrease with the larger size range while runs 10 and 12 showed a gradual increase in number concentration. UVWTP personnel speculated that microbial growth on the deep bed filters might have begun to slough off during the higher filtration rate runs.

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\(^1\) Wilczak *et al* did not report any cases where a PSD did not fit the power law model.

\(^2\) Number concentration simply refers to the number of particles per unit volume. Kavanaugh *et al* used this term to differentiate this quantity from surface area concentration and volume concentration. See that reference for a more detailed explanation of the latter two quantities.
4.3 Comparison of Preoxidants

The author initially set out to examine the PSD data to look for trends in response to different doses of the preoxidants evaluated. This was not possible due to the fact that within any test period in which raw water conditions would be relatively constant, preoxidant doses were kept relatively constant. What did lend itself to comparison was the PSD response to chlorine versus ozone at three different filtration rates.

As mentioned earlier, UVWTP personnel stated that runs 1 and 8, 4 and 10, and 6 and 12 were set up to compare the performance of chlorine versus ozone as the preoxidant. Table 3 and Figures 4 and 5 and show the results of this comparison. Recall that the value of $\beta$ indicates the number distribution of particles. Larger (more negative)

Table 3. Comparison of Parameter Response.

<table>
<thead>
<tr>
<th>Filtration Rate (gpm/ft²)</th>
<th>$\beta$ chlorine</th>
<th>$\beta$ ozone</th>
<th>logA chlorine</th>
<th>logA ozone</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>-1.64</td>
<td>-2.33</td>
<td>1.82</td>
<td>3.94</td>
</tr>
<tr>
<td>8</td>
<td>-1.97</td>
<td>-0.87</td>
<td>2.96</td>
<td>2.00</td>
</tr>
<tr>
<td>10</td>
<td>-1.01</td>
<td>-0.94</td>
<td>2.93</td>
<td>2.27</td>
</tr>
</tbody>
</table>

values indicate relatively higher concentrations of smaller particles. The value of logA is related to the concentration. Higher logA values indicate higher concentrations of particles as can be seen in the linear regression graphs. The logA value is always greater for the raw water PSDs than for the filter effluent PSDs. We see from the values in Table 3 that as the
filtration rate increases, the response of the power law parameters to the different preoxidants is very different. For chlorine, there is an increase in both $\beta$ (more negative) and $\log A$ from 6 to 8 gpm/ft$^2$, and then a decrease in each value with the increase in the filtration rate from 8 to 10 gpm/ft$^2$. For ozone, the trend is just the opposite.

![Graph showing the response of $\beta$ to chlorine and ozone preoxidation at different filtration rates.](image)

**Figure 4. Response of $\beta$ to chlorine and ozone preoxidation at different filtration**

The graphs of the trends in the parameter values (see Figures 4 and 5) show an almost 180 degree phase shift between chlorine and ozone. This suggests that the two substances act in different ways as
preoxidants. Tobisason et al (1992) noted that Ozone is a strong oxidant and can react with constituents in water via two mechanisms: the direct mechanism, which involves the reaction of dissolved molecular ozone, and the indirect mechanism, which involves the reaction of the hydroxide radical and other radicals. Ozone is more soluble than chlorine but chlorine is more stable in solution (Tchobanoglous and Burton, 1991). Both ozone and chlorine react with natural humic substances but the byproducts of ozone's reaction with humic material are more susceptible to biological degradation than the natural humic materials (Sawyer et al, 1994). This is interesting because it appears from the data that ozone
was more effective than chlorine at the higher filtration rate. It may be that the lower hydraulic retention time was beneficial for ozone preoxidation.

A statistical method known as the extra sum of squares was used to determine whether this is a significant trend (see Appendix II for calculations). It showed that, at each filtration rate, the PSDs resulting from chlorine preoxidation were significantly different from the PSDs resulting from preoxidation with ozone. The traces on the graphs shown in Figure 4 and Figure 5 do seem to converge which may show that as filtration rates are increased, the preoxidant used made less difference.

One final observation should be noted in the comparison of the PSDs resulting from chlorine versus ozone preoxidation. Even though the $R^2$ values for filter 2 on runs 4, 6, 10, and 12 (see Appendix 1, Figures A1-3(c), A1-4(c), A1-6(c), and A1-7(c) ) indicate the PSDs did not fit the power law model, the PSDs for the two different preoxidants were similar.

5.0 CONCLUSION

Linear regression analysis performed on PSDs by applying the linearized power law model revealed trends in PSDs that may have been over looked otherwise. In the majority of cases, the PSDs appear to fit the power law model. The usefulness of the information that can be gained by regression analysis of the two-parameter power law deserves
further research. This type of analysis was beyond the objectives of the pilot study as planned by the Central Utah Water Conservancy District and Montgomery Watson. A research project aimed at examining PSDs under more controlled conditions would be beneficial. In such a study, the number of size range divisions should be increased to fully utilize the capabilities of modern particle counters and gain as much detail for analysis as possible. Kavanaugh et al (1978) suggested that whatever the number of divisions, the ratio of the size range span to its mean size should remain nearly constant. For example, \(d_{p_{n+1}} = \sqrt{d_{p_n}}\) satisfies this constraint. The purpose of this would be to help ensure statistical reliability.

Application of the power law model to particle size distributions revealed interesting trends even in showing that the subject PSD did not fit the power law model. Statistical analysis can reveal trends in data not readily apparent by examining the patterns in the way the data diverges from the model. After fitting a model, the residuals can be examined for randomness. This can tell the researcher whether the model is accurate or some other model parameter is needed to accurately describe the process. Also, the fact that the PSDs did not conform to the power law model for deep bed filters at higher filtration rates indicates some external factor must be influencing the process. Therefore, divergence from the power law could be used as a process upset indicator.
REFERENCES


APPENDIX I

LINEAR REGRESSION GRAPHS
Run 1 Raw

\[ y = -1.4097x + 4.1684 \]
\[ R^2 = 0.8963 \]

Run 1 Filter 1

\[ y = -1.6355x + 1.8237 \]
\[ R^2 = 0.952 \]

Run 1 Filter 2

\[ y = -1.3602x + 1.0376 \]
\[ R^2 = 0.8139 \]

Figure A1-1
Run 3 Raw

\[ y = -1.4023x + 4.0935 \]
\[ R^2 = 0.8831 \]

Run 3 Filter 1

\[ y = -0.9814x + 1.5477 \]
\[ R^2 = 0.851 \]

Run 3 Filter 2

\[ y = -0.8836x + 1.0663 \]
\[ R^2 = 0.4786 \]

Figure A1-2
Figure A1-3
Figure A1-4

(a) Run 6 Raw

(b) Run 6 Filter 1

(c) Run 6 Filter 2

Equations:

(a) \( y = -1.5234x + 4.0943 \)

(b) \( y = -1.0109x + 2.93 \)

(c) \( y = 0.1071x - 0.326 \)

\( R^2 \) values:

(a) 0.8952

(b) 0.9335

(c) 0.021
Figure A1-5
Figure A1-6
Figure A1-7
APPENDIX II

STATISTICAL CALCULATIONS
The following formula for the extra sum of squares was used to evaluate whether the difference in the PSD response between Runs 1 and 8, 4 and 10, and 6 and 12 was statistically significant. A quantity designated as \( f \) was calculated according to

\[
f = \frac{\sum (y_i - \eta_i)^2 - \left[ \sum e_i^2 + \sum \tilde{e}_i^2 \right]}{\left( \frac{\sum e_i^2 + \sum \tilde{e}_i^2}{\text{degrees of freedom}} \right)}
\]

where \( \Sigma_1 e + \Sigma_2 e \) = The sum of the individual sums of squares of the residuals for the two runs to be compared

\( \Sigma (y_i - \eta_i)^2 \) = The sum of the squares of the residuals for both runs combined to form one model and one regression equation

The calculated \( f \) is compared to a value for \( F \) obtained from standard statistics tables. If the calculated \( f \) is less than the critical \( F \), the difference in the \( \beta \) or \( A \) values is rejected as a coincidence. The basis for testing the coincidence hypothesis this way is known as the extra sum of squares principle, also known as the principle of conditional error.

In order to determine the critical \( F \) value from the tables, it is necessary to determine the degrees of freedom for the numerator and the denominator in the expression for \( f \). The degrees of freedom for the numerator are calculated by first determining the degrees of freedom for the combined data, which is number of observations - number of parameters estimated or 8 - 2 = 6. Then the degrees of freedom for the separate data (the term in brackets in the numerator) are subtracted.
Each set contributes $4 - 2 = 2$ degrees of freedom for a total of 4. Therefore the total degrees of freedom for the numerator is $6 - 4 = 2$. The degrees of freedom for the denominator were determined in the second step above.

The coincidence hypothesis test for chlorine versus ozone in runs 1 and 8 is calculated below. Table A2-1 shows the separate sums of squares calculations for Runs 1 and 8.

**Table A2-1. Separate sum of squares calculations for Runs 1 and 8.**

<table>
<thead>
<tr>
<th>Run 1</th>
<th>Run 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log 10 of measured count</td>
<td>Regression equation prediction</td>
</tr>
<tr>
<td>1.055205</td>
<td>0.9338767</td>
</tr>
<tr>
<td>0.250851</td>
<td>0.5510336</td>
</tr>
<tr>
<td>0.320867</td>
<td>0.1205023</td>
</tr>
<tr>
<td>-1.33199</td>
<td>-1.31066</td>
</tr>
<tr>
<td>Sum of Squares</td>
<td>0.145431</td>
</tr>
</tbody>
</table>

**Figure A2-1. Linear regression equation for combined data from Runs 1 and 8,**

$$y = -1.9832x + 2.881$$

$$R^2 = 0.658$$
Combining the data from Runs 1 and 8 and then performing a linear regression analysis gives a new model differs significantly from the first two models, then the difference between the PSDs for Runs 1 and 8 significant. The graph shown in Figure A2-1 shows the new regression equation. Table A2-2 shows the calculation of the $\Sigma(y_i-\eta_i)^2$ term.

**Table A2-2. Calculation of the $\Sigma(y_i-\eta_i)^2$ term.**

<table>
<thead>
<tr>
<th>Runs 1 and 8 combined</th>
<th>Log 10 of measured count</th>
<th>Regression equation prediction</th>
<th>Residuals Squared</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.055205</td>
<td>1.8021043</td>
<td>0.557859</td>
</tr>
<tr>
<td></td>
<td>0.250851</td>
<td>1.3378704</td>
<td>1.181612</td>
</tr>
<tr>
<td></td>
<td>0.320867</td>
<td>0.81581</td>
<td>0.244969</td>
</tr>
<tr>
<td></td>
<td>-1.33199</td>
<td>-0.919611</td>
<td>0.170057</td>
</tr>
<tr>
<td></td>
<td>2.553788</td>
<td>1.8021043</td>
<td>0.565028</td>
</tr>
<tr>
<td></td>
<td>1.935399</td>
<td>1.3378704</td>
<td>0.357041</td>
</tr>
<tr>
<td></td>
<td>1.939847</td>
<td>0.81581</td>
<td>1.263459</td>
</tr>
<tr>
<td></td>
<td>-0.65185</td>
<td>-0.919611</td>
<td>0.071699</td>
</tr>
<tr>
<td>Sum of squares</td>
<td></td>
<td></td>
<td>4.411723</td>
</tr>
</tbody>
</table>

Plugging the sums of squares into the expression for $f$ gives

$$f = \frac{4.41 - (0.145 + 0.248)}{0.098} = 40.8$$

Therefore $f = 40.8 > F_{2,4,\alpha=0.05} = 6.94$ which shows that the two PSDs are significantly different. The $f$ values calculated for Runs 4 and 10 and Runs 6 and 12 were 24.9 and 18.6, respectively.