ASSESSMENT OF FIELD MONITORS FOR CONSENT MONITORING - PHASE 2

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Statement of use
This report outlines the relationship between turbidity and BOD and the possible application to predicting BOD on-site by the measurement of turbidity. The findings of this report are to be reviewed by the Discharge Consents Steering Group and the Field Instrument Implementation Group, who will decide the appropriate follow-up route.

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Potential benefits arise from obtaining a useful surrogate for BOD and suspended solids which can be used for continuous monitoring. This raises the possibility of a low-cost mass screening system for sewage effluents.

II OBJECTIVES

The objectives were to develop the optimal algorithm for transforming hand-held meter data into predictions for BOD and suspended solids for sewage effluents, and to provide an estimate of the reliability of such predictions.

III REASONS

The Environment Agency has a requirement to identify instrumentation for the continuous monitoring of determinands involved in discharge consents, particularly BOD, suspended solids and ammonia. BOD and suspended solids are not compatible with continuous monitoring so the emphasis is on identifying surrogate parameters.

IV CONCLUSIONS

Non-constant variance and the presence of outliers in the data make ordinary least squares regression methodology unreliable because the assumptions necessary for its application are no longer satisfied. It is not clear at present which of several alternatives is the most useful. In any case, a log-transformed model relating BOD to turbidity for sewage treatment works appears more appropriate than a simple model. For the relationship between suspended solids and turbidity, the simple model appears more appropriate.

The confidence limits for predictions from the fitted model are rather wide, but they can be narrowed by restricting the model to low values of turbidity and by introducing other explanatory variables. The fitted coefficients varied from region to region and also between different types of STW.

V RECOMMENDATIONS

A universal relationship between BOD and turbidity does not exist, but it may be possible to find relationships that can be applied locally for a given type of STW. However, this report has not examined whether the relationship is different at different single STWs nor whether the relationship is stable over time either within a single type of works or across a region. These possibilities should now be investigated.

VI RESUMÉ OF CONTENTS

Data sets giving turbidity observations from hand-held meters used in the field and BOD observations based on laboratory analysis were provided by five regions. Two other regions provided laboratory observations for turbidity and a number of other determinands.

The relationships between BOD and *field* turbidity were first investigated using the traditional method, ordinary least squares regression. Because the variance of BOD increases with increased turbidity, a log transformation was found to be more appropriate. Because of the log transformation, confidence limits on predicted values of BOD are multiplicative. The upper 95% confidence limits on predicted BOD were on average about 4.3 times more than the predicted value and the lower 95% limits were about 4.3 times less than the predicted value - i.e. the precision factor was about 4.3. The lines of best fit were significantly different for the different regions.

Different types of STW were also found to have different slopes. Fitting different models to each type of STW within each region improved the precision factor to an average of 3.3.

BOD was also regressed on *laboratory* turbidity for the two regions. It was observed that the goodness of fit of the regression line improved when turbidity was restricted to values less than thirty NTU. Further improvements could be made to the model by introducing various other determinands, specifically ammonia, suspended solids chloride, pH, phosphate and TON. The coefficient for TON in North West Region was not significantly different from zero.

Various other methods of line fitting were examined to overcome problems arising from departures from the assumptions of the ordinary least squares - in particular, the presence of outliers and the absence of constant variance. These more robust methods were considered to be more reliable and less likely to be influenced by one or two extreme points.

Comparisons were made between a number of different turbidity instruments for a number of sewage effluents.

KEY WORDS

BOD, turbidity, field monitoring

1. INTRODUCTION

1.1 Background

The Environment Agency has a requirement to identify instrumentation for the continuous monitoring of determinands, in particular BOD, suspended solids and ammonia, involved in discharge consents. This project has concentrated on instrumentation for monitoring BOD and, to a lesser extent, suspended solids. In practice, neither determinand is compatible with continuous monitoring and so the emphasis has been on identifying *surrogate* parameters which track BOD and suspended solids and which are also compatible for continuous monitoring.

Phase 1 of this project established that turbidity correlated well with BOD for sewage effluents although not for trade effluents or river water, and with suspended solids for all three types of samples. Turbidity measurement can be provided by hand-held meters, which are used widely in the Environment Agency, giving rise to the possibility that a low-cost mass screening system for sewage effluent could be developed. There was also some indication that other water quality determinands measured together with turbidity on hand-held meters (principally ammonia) improved the correlation with effluent BOD. A considerable amount of relevant data exists in a variety of files within the Environment Agency.

1.2 Objectives

The objective of Phase 2 was to develop the optimal algorithm for transforming hand-held meter information into predictions for BOD and suspended solids for sewage effluents and to provide an estimate of the reliability of such predictions in terms of confidence limits.

This was to be achieved using an in-depth knowledge of correlation and other relevant statistical techniques and an appreciation of current advances in chemometrics. The relationships were to be examined to determine whether they could be improved by splitting the data into subsets, based on the type and size of sewage works.

2. EXPLORATORY DATA ANALYSIS

2.1 Source of data

Five regions - Northumbria & Yorkshire, Southern, South Western, Thames, and Welsh - provided data sets giving turbidity observations from hand-held monitors used on-site and BOD results based on laboratory analysis. Two further data sets, from North West and Midland regions respectively, contained laboratory-based measurements of STW effluent samples for turbidity, ammonia, BOD, SS, phosphate and TON. In addition, the Midland region data set contained measurements for chloride and pH.

2.2 BOD and field turbidity

Initially, graphical methods were used to investigate the plausibility of a linear relationship between BOD and field turbidity, and to examine whether the variance was constant throughout the range of the data. Constant variance (otherwise known as homoscedasticity) is required to satisfy the assumptions of ordinary least squares (OLS) linear regression analysis. Where this condition is not justified, transformation of the data is sometimes used to stabilise the variance before applying OLS regression. Alternatively, some other, more robust, method can be used to fit the best straight line to the data.

Figures 2.1 to 2.5 show scatter plots of BOD against field turbidity for the five sets of data using hand-held meters, i.e. for Northumbria & Yorkshire, Southern, South Western, Thames and Welsh regions. In these graphs, any values of turbidity recorded as zero have been converted to 0.1 so that they can be plotted on a logarithmic scale. Also, any BOD which was recorded as a less-than value has been replaced by half the recorded face value, e.g. <3 has been plotted at 1.5.

In each figure, there are four graphs, one in each quadrant of the page. In each upper left quadrant is a simple scatter graph of all the available data. In all five figures, the graph reveals that the mass of points is concentrated close to the origin with just a few very high values. This means that most values of BOD and turbidity are small compared with the range, and many points are plotted on top of others.

In each upper right quadrant, the scatter of data points is plotted on a log scale. The logarithmic transformation has the effect of spreading out the lower values and bringing down the higher ones. Therefore, this graph enables more of the pattern among the low values to be discerned. In each region, the graph reveals a positive correlation between log BOD and log turbidity. Note that in all five figures, there is a reasonably constant vertical spread of log BOD throughout the range of log turbidity.

The mass of points near zero is revealed in more detail in the graph in the lower left quadrant where both the BOD and the turbidity axes are once more plotted on linear scales but both axes have been truncated at 30 NTU. The graphs reveal a strong positive correlation between BOD and turbidity, but there is evidence that the variability in BOD increases with increasing turbidity.

Finally, the graph in the lower right quadrant displays all the points not plotted in the lower left quadrant, again on linear scales. These graphs illustrate that, occasionally, very high turbidity was recorded at relatively low BOD and very high BOD was recorded at relatively low turbidity. There were no occasions on which very high turbidity and very high BOD occurred together. It is conceivable that these high values were caused by lapses in recording or analysis. However, without confirmation of this, it was considered unsafe to discard these potential outliers from the statistical analysis. Instead, they were taken to be rare but valid members of the joint distribution of BOD and turbidity.

2.3 SS and field turbidity

Suspended solids data was available only for Thames Region. Figure 2.6 shows the same four scatter graphs as used for turbidity. The great mass of SS values lie between 0 and 10 but the range extended as far as 176 with quite a large number of values over 30. There is a strong positive correlation between SS and turbidity but the vertical scatter does not seem to widen with increasing turbidity when the graphs are plotted on linear scales. In fact, the graph on the logarithmic scales appears to have greater scatter at lower turbidity.

2.4 Conclusions from data exploration

The BOD graphs indicate that transforming BOD and turbidity by taking logs stabilises the variance in BOD throughout the range of turbidity. It is therefore worthwhile performing regression analysis of log BOD on log turbidity rather than BOD on turbidity. A possible alternative is to trim the data by removing the very high values of BOD and turbidity. However, the graphs of the trimmed data in the lower left quadrants of Figures 2.1 to 2.5 show that the variance is not stable even after trimming.

The SS graphs in Figure 2.6 suggest that a linear relationship exists between SS and turbidity and that log transformation is unnecessary.

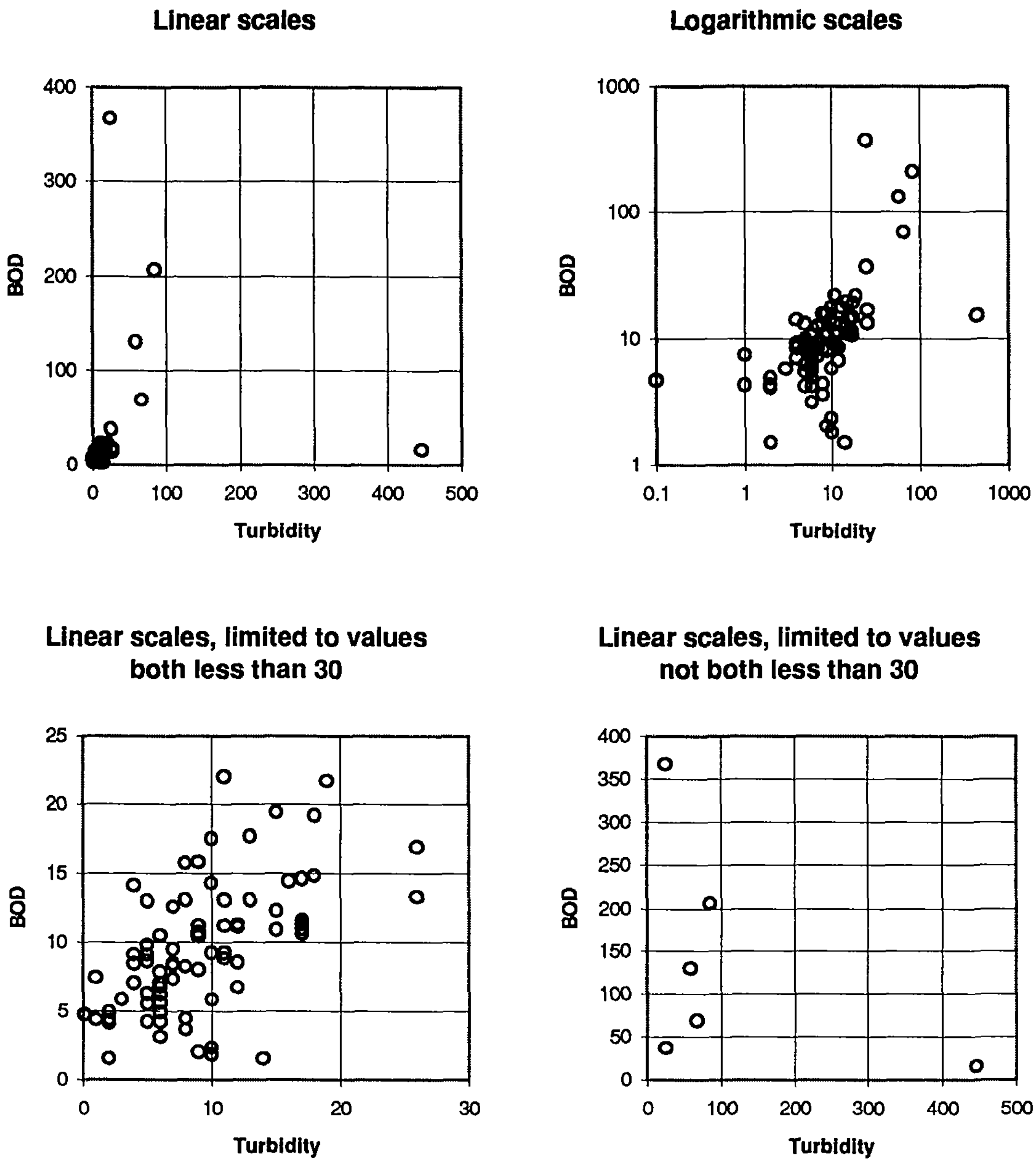


Figure 2.1 **Scatter plots of BOD against field turbidity - Northumbria & Yorkshire Region**

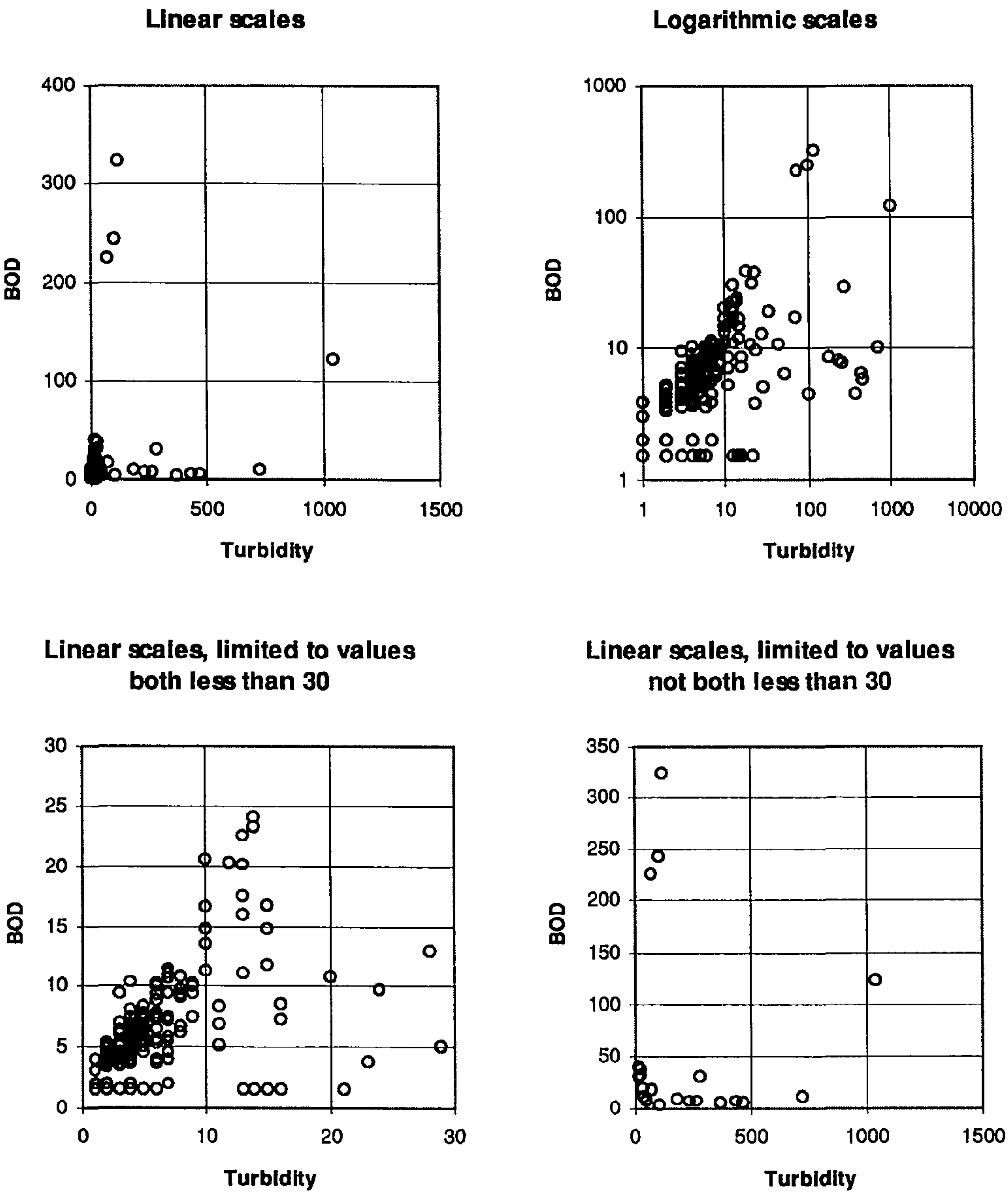


Figure 2.2 Scatter plots of BOD against field turbidity - Southern Region

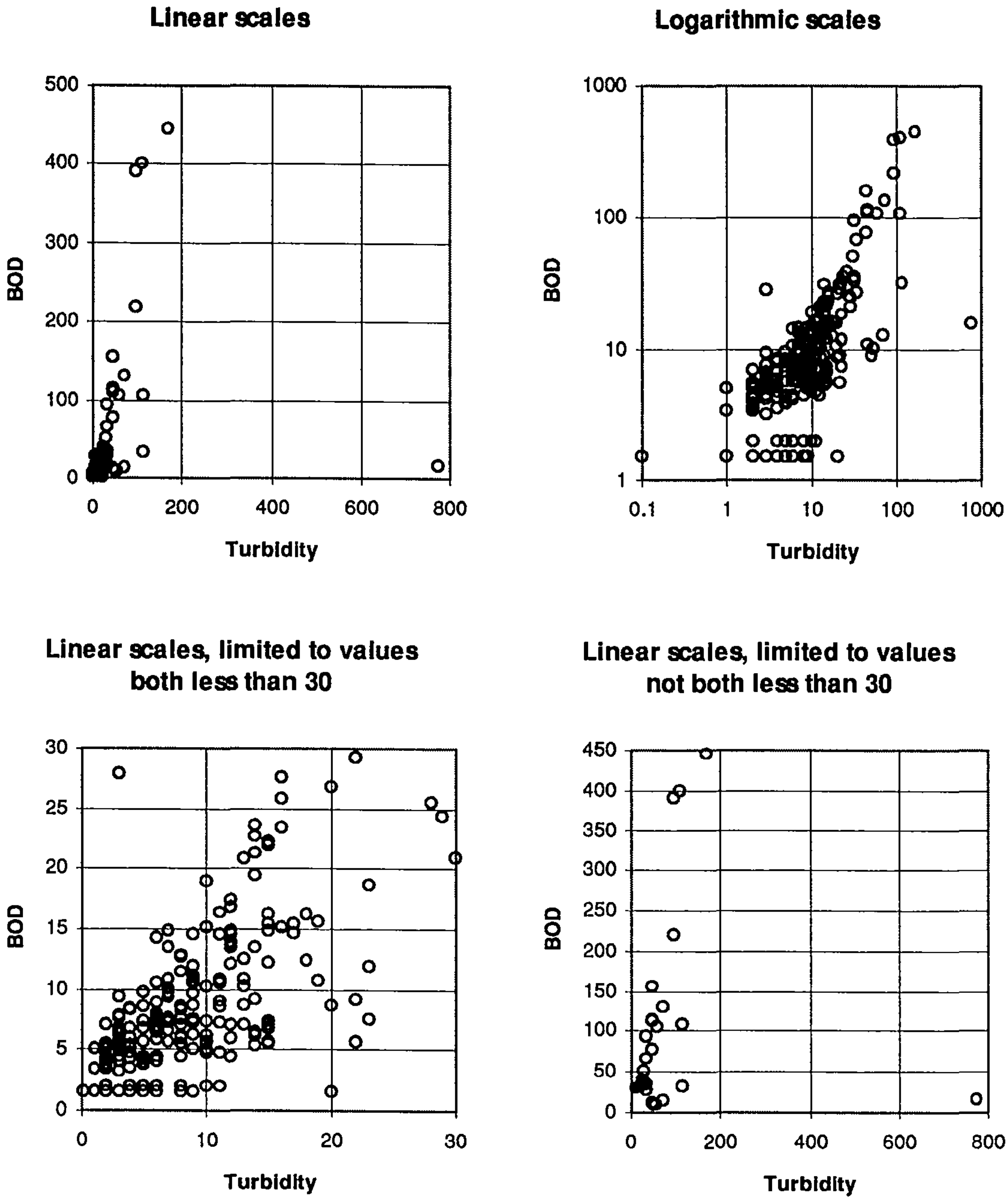


Figure 2.3 Scatter plots of BOD against field turbidity - South Western Region

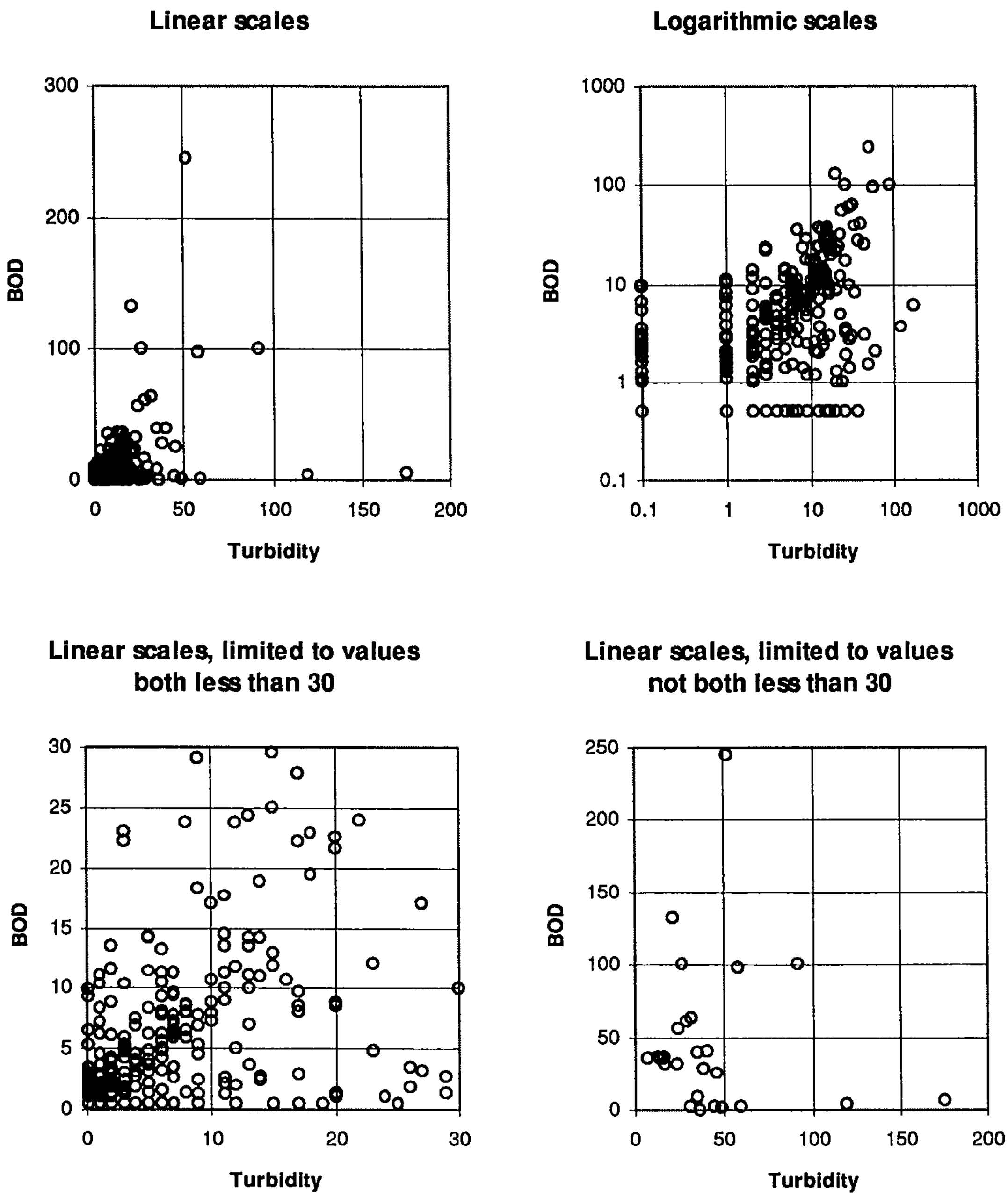


Figure 2.4 Scatter plots of BOD against field turbidity - Thames Region

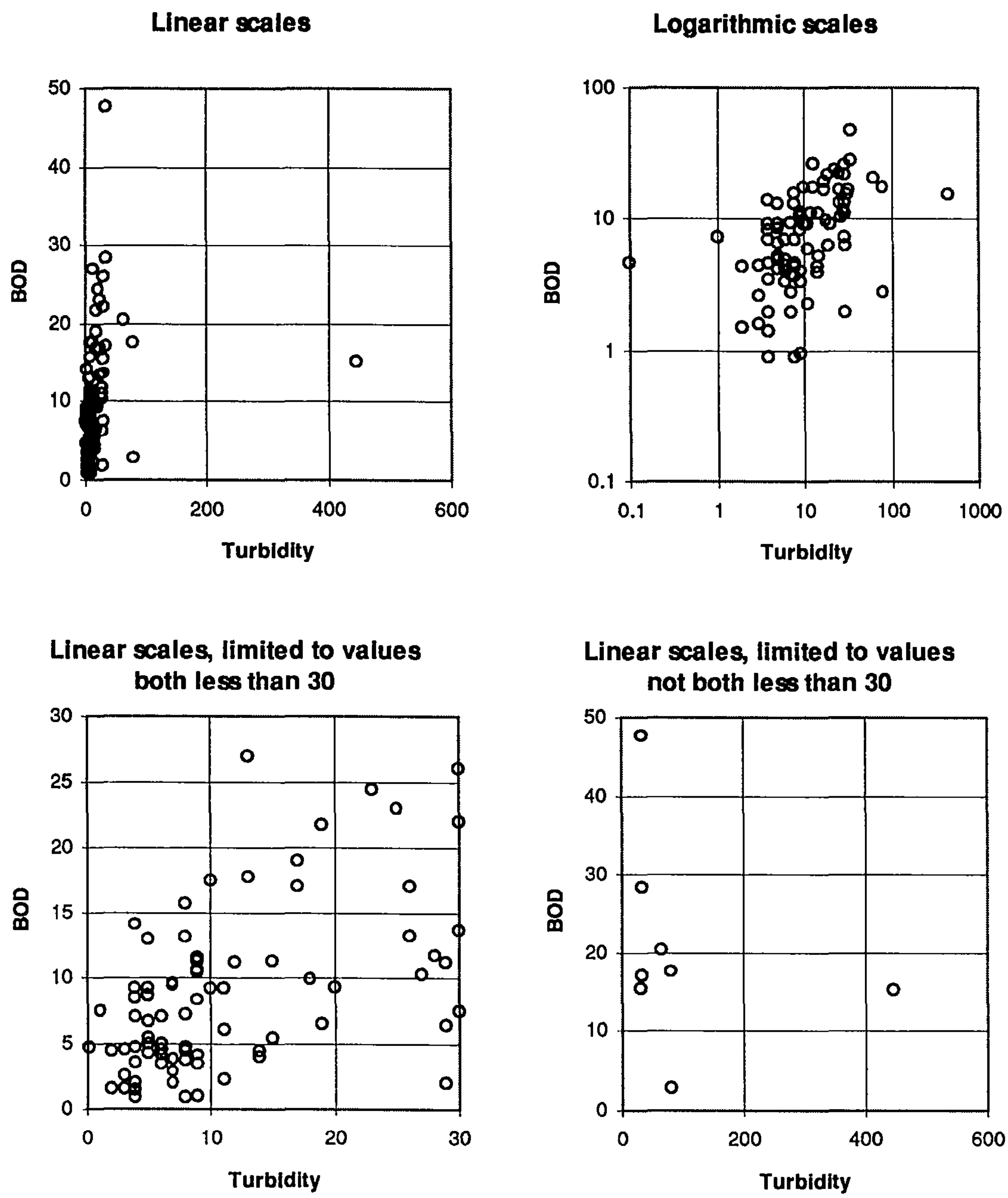


Figure 2.5 Scatter plots of BOD against field turbidity - Welsh Region

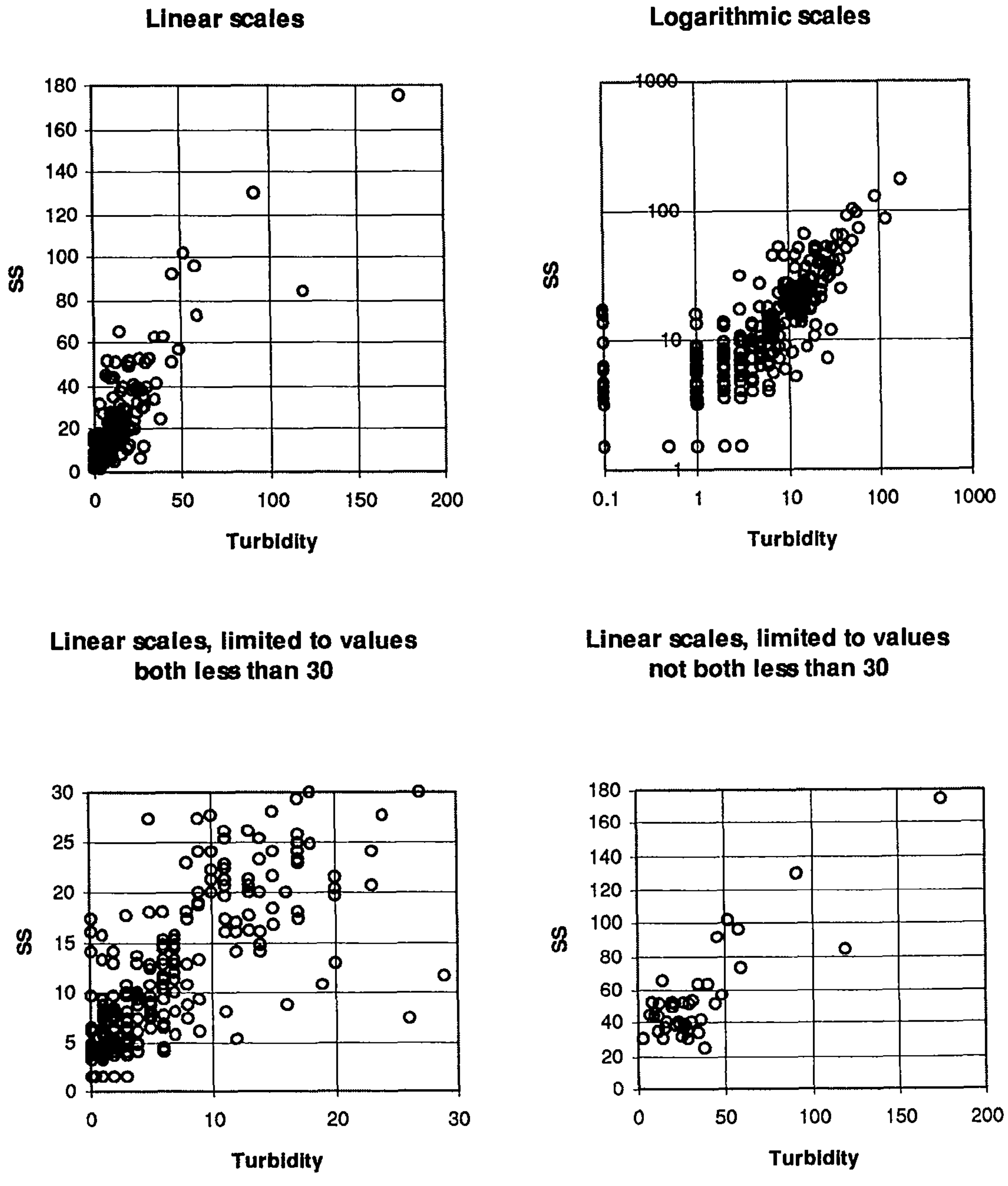


Figure 2.6 Scatter plots of suspended solids against field turbidity - Thames Region

3. USING FIELD TURBIDITY TO PREDICT BOD AND SS BY MEANS OF OLS REGRESSION

3.1 Introduction

Using the insight gained from the exploratory data analysis described in Section 2, it was decided to transform the data by taking logs (to base 10) when modelling the relationship between BOD and turbidity but not to transform for SS and turbidity. Ordinary least squares (OLS) regression was used to estimate the parameters of linear models relating:

- log BOD to log turbidity;
- SS to turbidity.

The results are shown in Table 3.1 and described in the following three subsections. When performing the regression analysis, any observations with zero turbidity were excluded and any BOD values recorded as less than the limit of detection were set to half the limit of detection.

Table 3.1- Summary statistics for seven regression models (with *standard errors*)

Region	**Slope estimate** b *with standard error*	**Intercept estimate** a *with standard error*	**Sam-ples** n	**Residual s.d.** s	**Precision** $z.s$	**Precision. factor** $10^{z.s}$
$\log_{10}$ BOD	**$\log_{10}$ turbidity**					
Northumbria & Yorkshire	0.486 *0.078*	0.531 *0.081*	88	0.315	0.617	4.14
N&Y trimmed	0.450 *0.090*	0.523 *0.085*	82	0.233	0.456	2.86
Southern	0.447 *0.042*	0.377 *0.041*	209	0.330	0.646	4.43
South Western	0.830 *0.043*	0.128 *0.043*	265	0.311	0.610	4.08
Thames	0.481 *0.069*	0.296 *0.066*	237	0.509	0.998	9.96
Thames excl. non-STWs	0.684 *0.059*	0.306 *0.054*	167	0.370	0.724	5.23
Welsh	0.664 *0.110*	0.090 *0.126*	61	0.320	0.627	4.23
SS	**turbidity**					
Thames	1.069 *0.035*	6.338 *0.697*	274	9.767	19.14	NA

3.2 BOD in Northumbria & Yorkshire region

In this subsection, we present the regression results for Northumbria & Yorkshire Region in some detail. The results for the other regions are summarised in the next subsection.

The coefficients relating *log BOD* to *log turbidity* for Northumbria & Yorkshire Region are shown in Table 3.1. The fitted relationship is:

$$log\ BOD = 0.486\ (log\ turbidity) + 0.531$$

This line is shown as the central line drawn through the scatter plot of *log BOD* versus *log turbidity* in the upper graph in Figure 3.1.

The lines on either side of the central line show the 95% confidence interval for predicting future values of *log BOD*. These are obtained (to a close approximation) by adding and subtracting the precision (based on 95% confidence) $z.s$, where s is the residual standard deviation about the regression line and $z = 1.96$, which is the value of the deviate that cuts 2.5% from each tail of the standard Normal distribution.

Let us take an example to illustrate how we might use these results. Suppose we have a field turbidity value of 5 NTU, then our best estimate of *log BOD* is obtained by calculating

$$log\ BOD = 0.486\ (log\ 5) + 0.531 = 0.871$$

So our estimate of *BOD* is $10^{0.871}$ which is 7.43.

Then, 95% confidence limits on the estimate of *log BOD* are given by adding and subtracting the precision, $z.s$, which is 0.617. Thus, 95% confidence limits for *log BOD* are

$$0.871 \pm 0.617 = (0.254,\ 1.488).$$

Taking antilogs of these values, we get the 95% confidence limits on *BOD* which are (1.79, 30.76). Alternatively, we can obtain confidence limits directly from our estimate of *BOD* (i.e. 7.43) if we divide and multiply it by the antilog of the precision ($10^{0.617} = 4.14$) to get 1.79 and 30.76, respectively. We shall call this factor (4.14 in this example) the 'precision factor'. Note that in Table 3.1, the precision factors are typically around 4.3.

The lower graph in Figure 3.1 provides the same information as the upper graph except that it uses linear axes and it is drawn only for values of turbidity less than 50 NTU. Note how the straight lines in the upper graph become curves in the lower one and how additive confidence bands on the log scales translate into multiplicative confidence bands on the linear scales. Although the central fitted line looks reasonable in both graphs, the confidence intervals appear rather wider than indicated by the data at lower values of turbidity. The exaggerated width is caused by the higher variation in the BOD values about the regression line at the higher values of turbidity.

To try to overcome this problem, we decided to trim the data by limiting turbidity to values less than 30 NTU and to values above zero (remember, the zero value were plotted at 0.1 on the log scale). We also removed the high BOD reading at a turbidity of 25. The deleted points are shown as solid circles in the upper graph in Figure 3.2, which also shows the regression line fitted to the trimmed data. Note that the fitted line is virtually unchanged but the confidence intervals are considerably narrower, particularly in the central part of the graph. The precision factor was reduced from 4.14 to 2.86.

Although trimming the data improved the width of the confidence interval, data manipulation such as this must be justified. It is quite acceptable to restrict the use of the model for prediction to values of turbidity less than 30 NTU. However, it is difficult to justify the removal of any high BOD values within this limited turbidity range without corroborative evidence explaining why the alleged outliers were atypical. For example, they may have arisen by some mistake in the chemical analysis or in data transcription or by some unusual occurrence in the effluent. Such corroboration would have to be based on local knowledge.

3.3 BOD in the other four regions

For the data from the other four regions, Table 3.1 shows that the precision factors are in the range 4.08 to 4.43 except for Thames Region which has a factor of approximately 10. The wide Thames interval is largely due to the presence of 63 data points not from sewage treatment works. When these are removed from the regression, the precision factor is reduced to a value of 5.23 and the residual standard deviation is also brought into line with the other regions.

Figures 3.3 to 3.6 show the fitted lines (and 95% confidence limits for predicted observations) for BOD in these four regions. The regression lines appear satisfactory, but the confidence intervals appear to be rather too wide in the region of turbidity less than 10. Again, it would appear that it might be worthwhile trimming the data to values of turbidity less than 30.

3.4 Suspended solids

For SS, the data was not log-transformed before performing the regression for reasons given in Subsection 2.3. Therefore, in Figure 3.7, the upper graph is plotted on linear scales rather than logarithmic ones. The lower graph shows the fitted model drawn for values of turbidity less than 50 NTU. Again the confidence interval around the fitted model, calculated using the full range of turbidity, appears a little too wide for turbidity values less than 10.

3.5 Assessment of the effect of subsets of the data

The next stage of the analysis was to determine whether subsets of the data provided better predictive models. The data sets from Northumbria & Yorkshire, South Western and Thames Regions were split into subsets according to type of STW. The data sets from Southern and Welsh Regions contained no information on types of STW and so could not be investigated in this way. Table 3.2 gives the breakdown of the available data into STW types.

Table 3.2 Types of STW

Code	Type of STW	Size of STW	No. of samples N&Y	SW	Thames
PS	Percolating filter	Small	68	154	237
PM	Percolating filter	Medium	-	6	12
PL	Percolating filter	Large	6	-	49
AS	Activated sludge	Small	1	66	-
AL	Activated sludge	Large	10	7	28
APL	Activated sludge Percolating filter	Large	-	-	6
APM	Activated sludge Percolating filter	Medium	3	-	-
BS	Biodisk	Small	-	28	-
SS	Settlement only	Small	-	7	-
TS	Septic Tank	Small	-	3	-
V	Private	Not specified	-	-	93
N	Not sewage effluent	Not applicable	-	-	63

Fitting separate lines for the different types of works invariably improves the goodness of fit compared with a single line fitted to all types. However, the statistical significance of the improvement can be assessed using the reduction in the sum of squares of the residuals about the fitted model (see, for example, Davies and Goldsmith, 1972). For all three regions, the improvement in the goodness of fit was statistically highly significant.

Table 3.3 summarises the regression models. The rows for 'All types' are taken from Table 3.1. Regressions based on a greater number of samples give more reliable predictions than those based on fewer samples. In the table, STW types with less reliable results are shown by means of shading, using an arbitrary cut-off of 15 samples.

Among the unshaded rows of the table, it can be seen that confidence intervals are narrower when each type of STW is treated separately than when they are all amalgamated. The average precision factor among the unshaded rows (excluding the private STWs - code V) was 3.3.

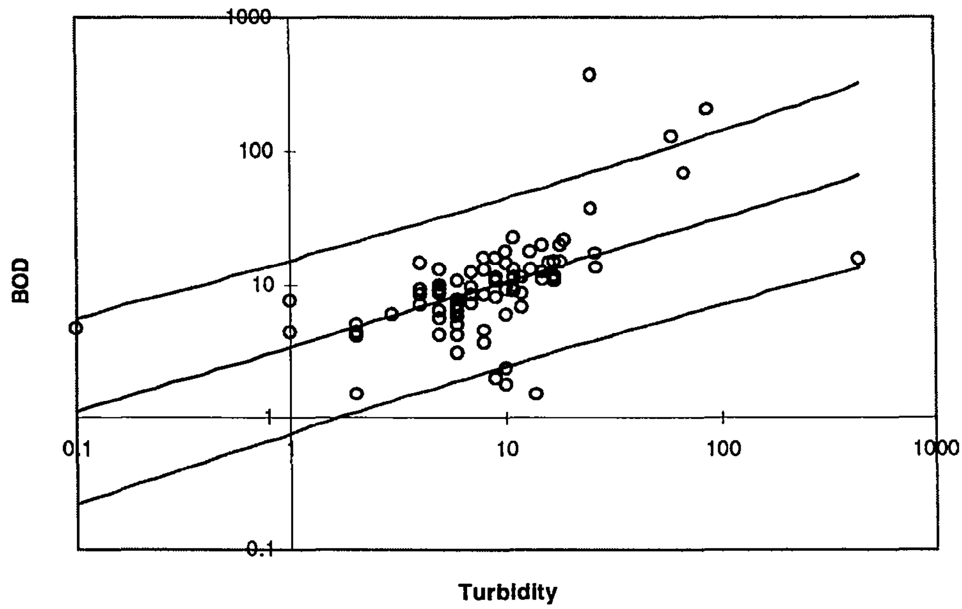
Note that the slopes for percolating filter STWs (indicated by codes PS, PM, PL) are steeper than for activated sludge STWs (AS, AL).

For Thames Region, the private STWs (V) have a relatively large residual standard deviation, and consequently a large precision factor. It may therefore be worthwhile investigating the effect of splitting these private works further, for example by size or type, to try to obtain better regressions. The non-sewage effluents (N) in Thames Region had a statistically insignificant slope implying that turbidity and BOD were not related. For the STW data in Thames Region, the intercepts for the different types of works were significantly different but the slopes were not.

Table 3.3 Separate regression lines for each type of STW

Type of STW	Slope *b*	Intercept *a*	Samples *n*	Residual s.d.	Precision	Precision factor
log_{10} BOD	**log_{10} turbidity**					
Northumbria & Yorkshire						
All types	0.486	0.531	88	0.315	0.617	4.14
PS	0.871	0.147	68	0.300	0.588	3.87
PL	0.187	0.821	6	0.018	0.035	1.08
AL	0.163	0.717	10	0.293	0.574	3.75
South Western						
All types	0.830	0.128	265	0.330	0.647	4.08
PS	0.724	0.277	154	0.256	0.502	3.18
PM	0.948	0.165	6	0.076	0.149	1.41
AS	0.370	0.522	66	0.238	0.466	2.93
AL	0.135	0.681	7	0.201	0.394	2.48
SS	0.787	0.520	7	0.456	0.894	7.83
TS	1.710	-1.290	3	0.809	1.586	38.52
BS	0.284	0.547	28	0.218	0.427	2.67
Thames						
All types	0.481	0.296	237	0.509	0.998	9.95
STWs only	0.684	0.306	167	0.370	0.724	5.23
PS	0.336	0.566	15	0.402	0.788	6.14
PM	0.529	0.561	12	0.234	0.459	2.88
PL	0.568	0.229	49	0.278	0.545	3.51
AL	0.224	0.609	28	0.305	0.598	3.96
APL	0.772	0.163	6	0.089	0.174	1.49
V	0.489	0.600	93	0.404	0.792	6.19
Not STWs	0.062	0.160	63	0.212	0.416	2.60

Logarithmic scales



Linear scales, limited to values less than 50

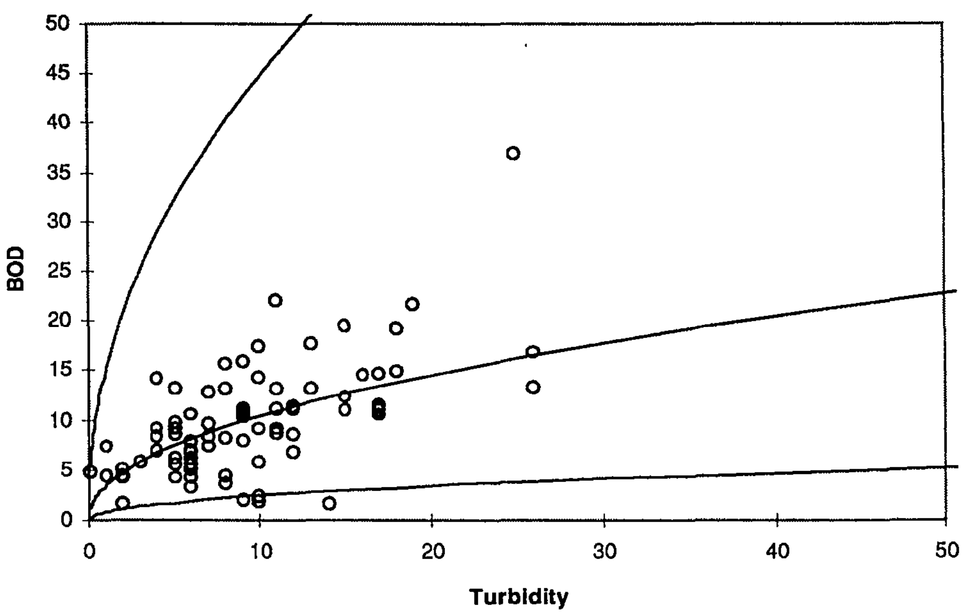


Figure 3.1 Fitted model with 95% confidence limits for predicted observation - Northumbria & Yorkshire region

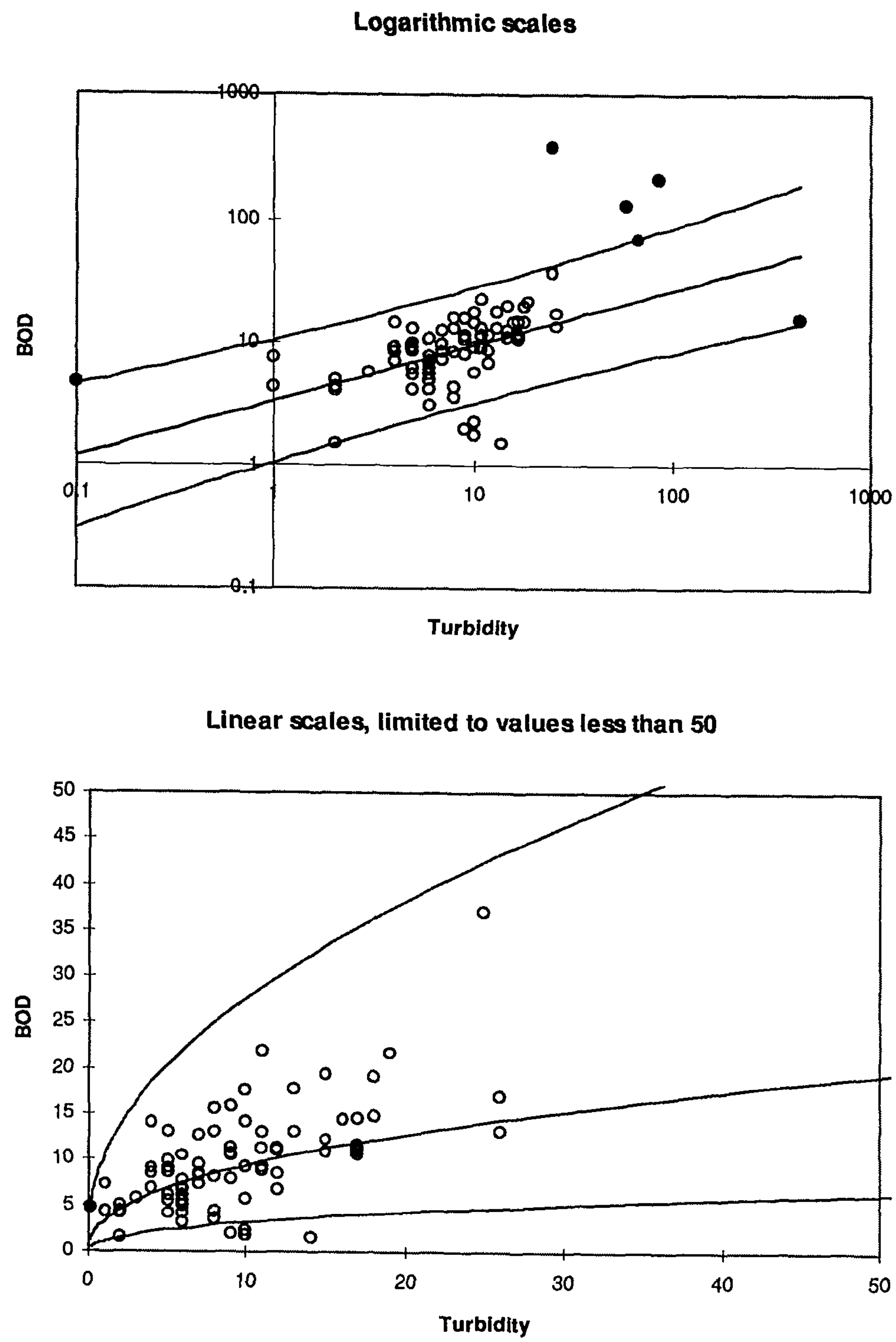
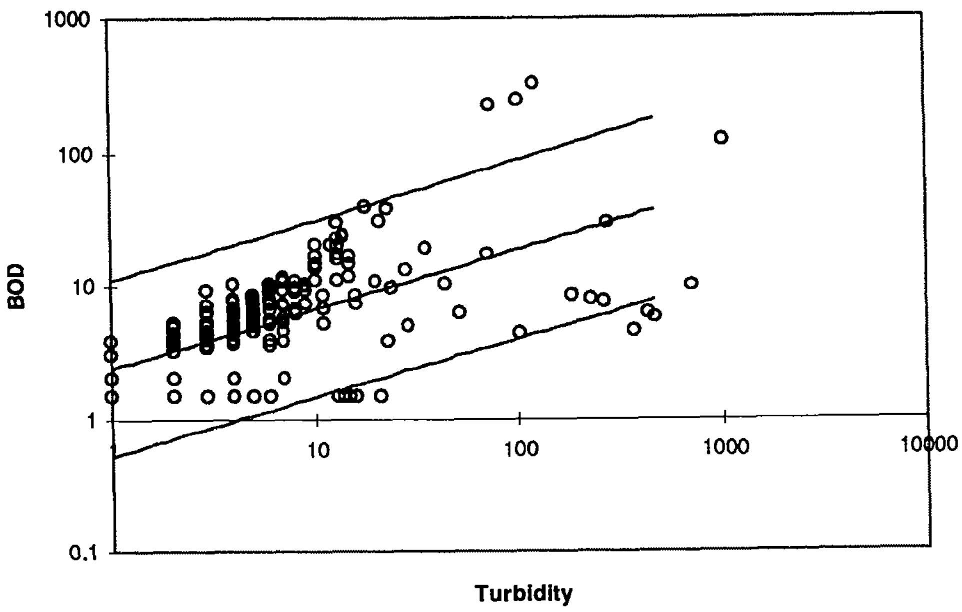


Figure 3.2 Fitted model to trimmed data with 95% confidence limits for predicted observation - Northumbria & Yorkshire region

Logarithmic scales



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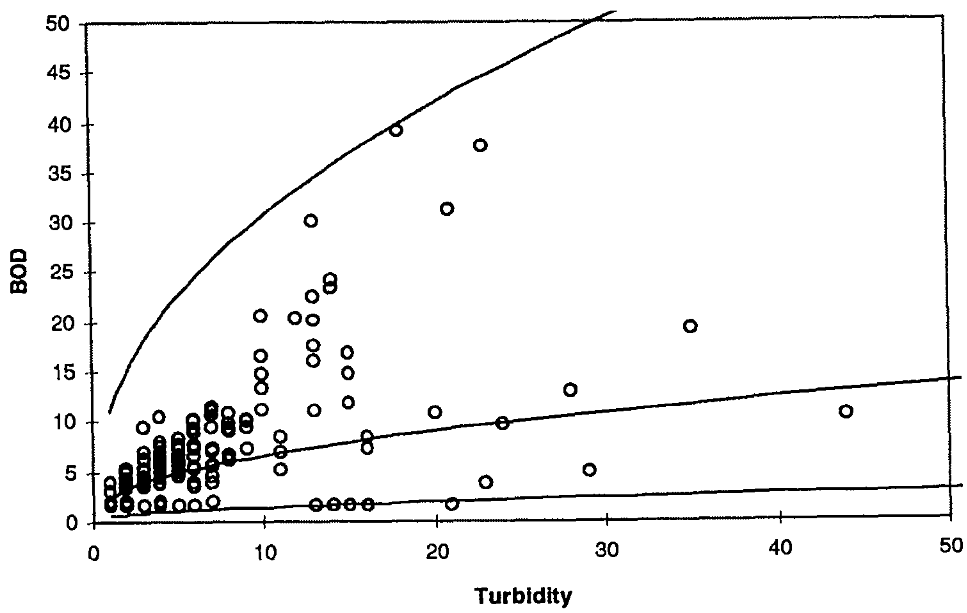
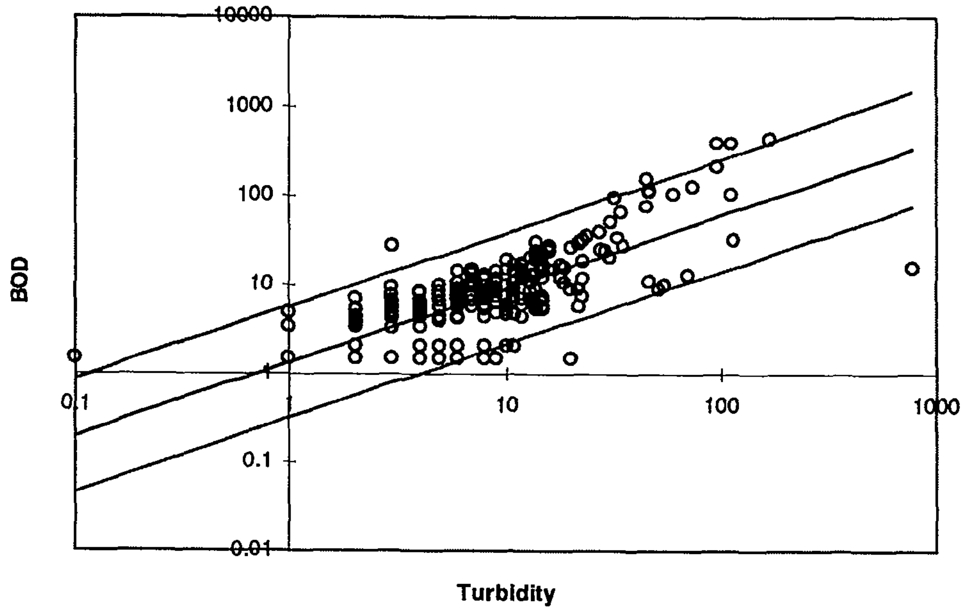


Figure 3.3 Fitted model with 95% confidence limits for predicted observation - Southern region

Logarithmic scales



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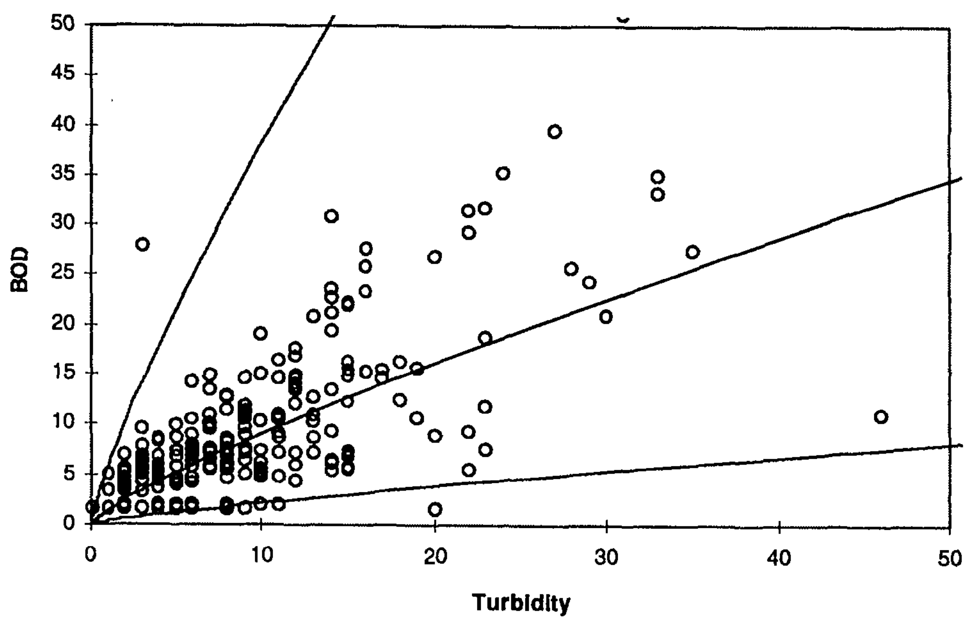
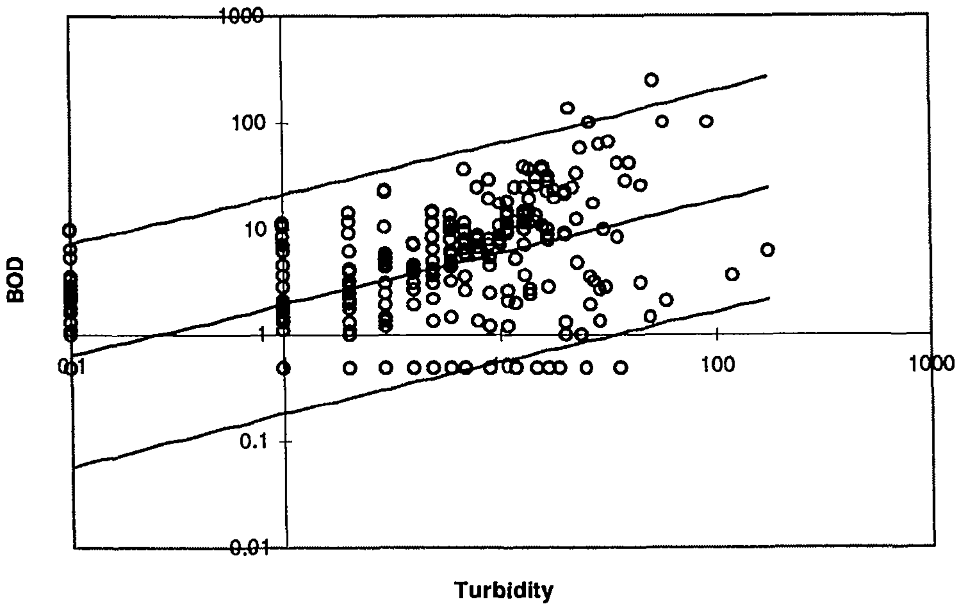


Figure 3.4 Fitted model with 95% confidence limits for predicted observation - South Western region

Logarithmic scales



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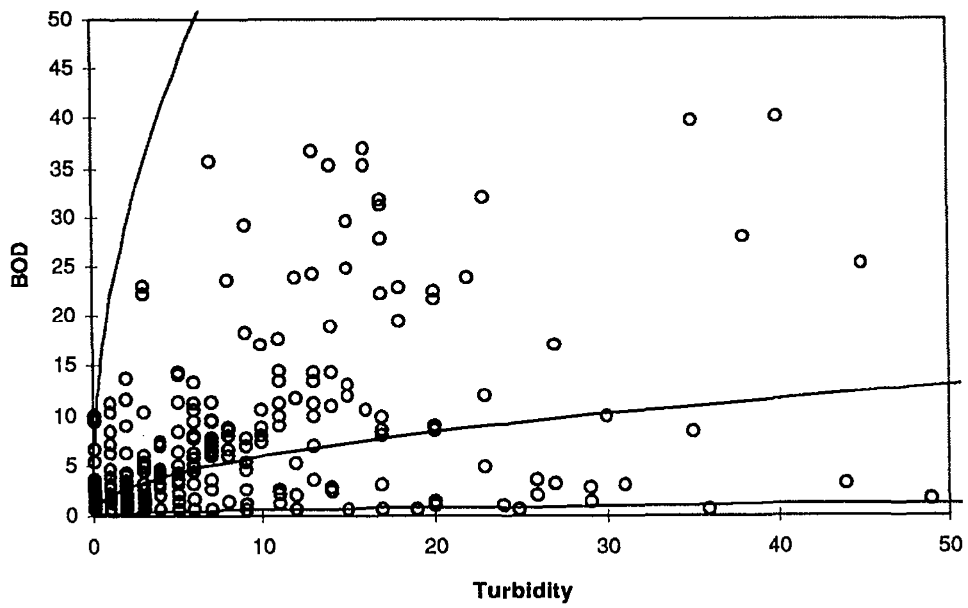
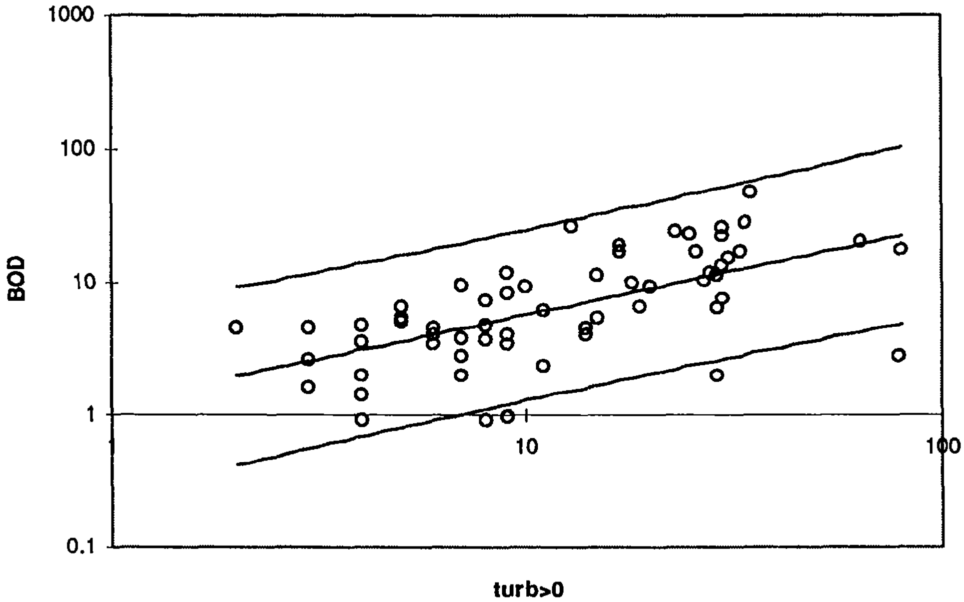


Figure 3.5 Fitted model with 95% confidence limits for predicted observation - Thames region

Logarithmic scales



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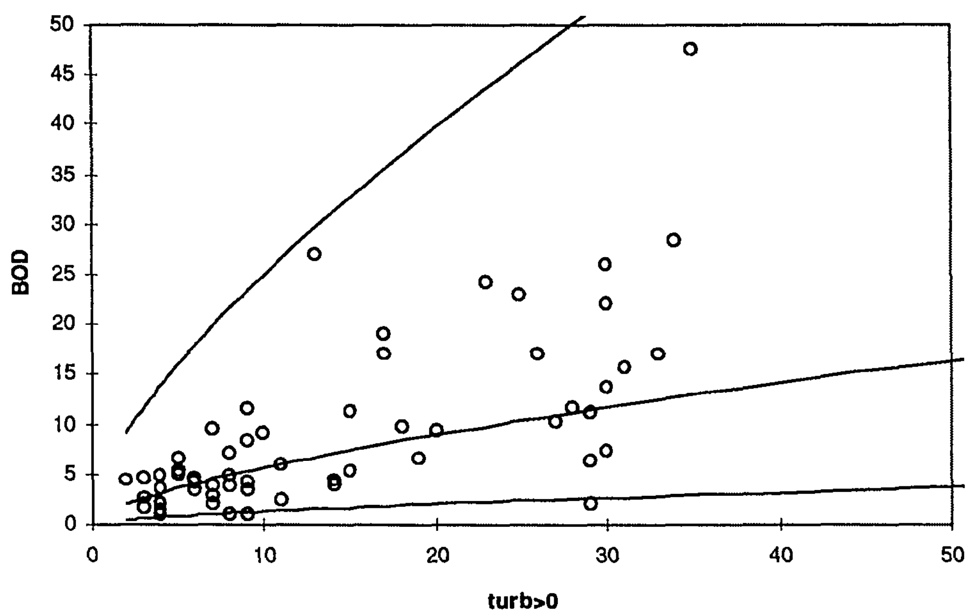
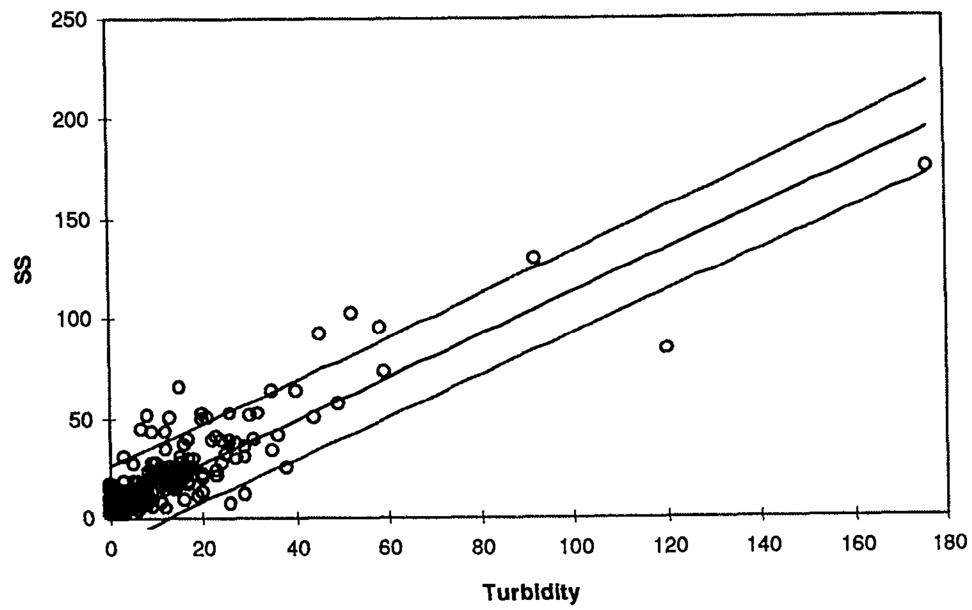


Figure 3.6 Fitted model with 95% confidence limits for predicted observations- Welsh region

Linear scales



Linear scales, limited to values less than 50

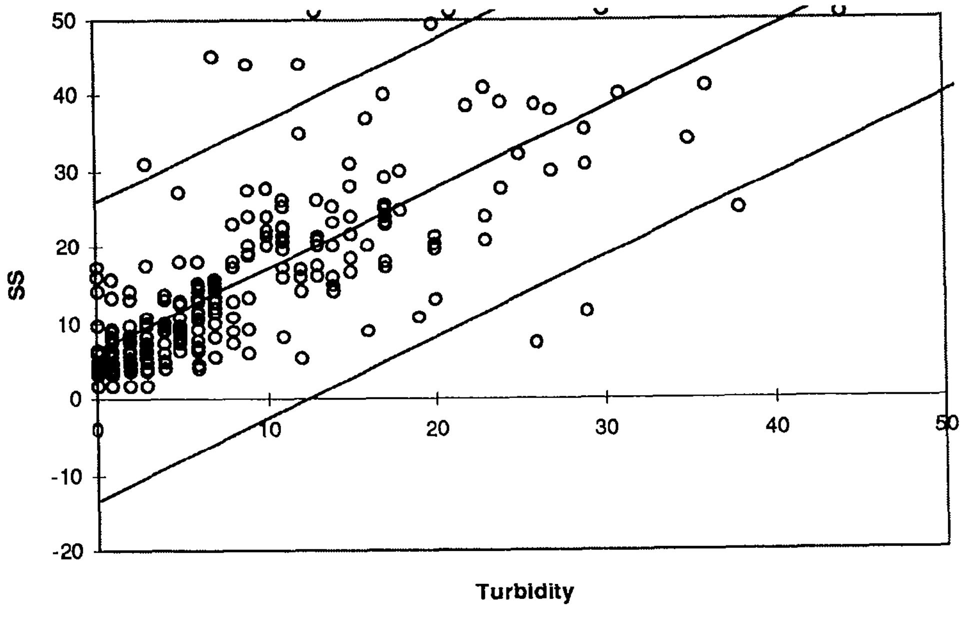


Figure 3.7 Fitted model for SS with 95% confidence limits for predicted observation - Thames region

4. USING LABORATORY-BASED TURBIDITY TO PREDICT BOD BY MEANS OF OLS REGRESSION

4.1 Introduction

Sections 2 and 3 above involved *field-based* turbidity data. This section deals with *laboratory-based* turbidity data. Two data sets were available, supplied by Midland and North West Regions. As well as laboratory-based turbidity, these data sets contained BOD, ammonia, SS, phosphate and TON. The data set from Midland Region also contained chloride and pH. As well as fitting BOD to turbidity, regressions were performed to fit BOD to all the available determinands, including turbidity, to see whether these additional determinands helped to explain significantly more of the variability in BOD.

4.2 Turbidity alone

The regression results for turbidity alone are given in Table 4.1. Because of the general widening of the variability with higher turbidity, three ways of restricting the data were tried, namely:

1. no restriction;

2. restricting turbidity to be less than 30 NTU;

3. restricting turbidity to be less than 10 NTU.

The first six rows of Table 4.1 show the fitted models when no transformations were used, i.e. *BOD* is regressed directly on *turbidity*. We shall call this the simple model. The precision term is then additive as illustrated in the following example. Using the row, at a turbidity of five, the estimate of *BOD* is given by

$2.295 + 0.872 \times 5$
i.e. 6.655

The precision is 7.29, so the 95% confidence limits on this estimate are given by:

$6.655 - 7.29$ and $6.655 + 7.29$
i.e. -0.635 and 13.945

The last six rows in the table are for log-transformed data, where *log BOD* is regressed on *log turbidity* (using logs to base 10). We shall call this the transformed model. The precision term is a multiplicative precision factor as described in Section 3. Thus, for example using the last sixth row, at a turbidity of 5, the estimate of *log BOD* is given by

$0.364 + 0.618 \times \log(5)$
i.e. 0.796

which, by taking antilogs, transforms back to a *BOD* value of 6.25.

Using the precision factor, 2.34, the 95% confidence limits on this estimate are given by:

$6.25 \div 2.34$ and 6.25×2.34
i.e. 0.427 and 14.625

From the table it is clear that confidence limits are narrower for the North West data than for the Midlands data. Furthermore, restricting the data to turbidity values less than 30 leads to a considerable improvement in the precision in the simple model, and to at least a 12% reduction in the precision factor in the transformed model.

Table 4.1 Regression results using laboratory-based turbidity

Variable	Region	Restriction on turbidity	Samples	Intercept *with standard error*	Slope *with standard error*	Residual S.D.	Precision term (95% confidence)
Simple model							
BOD					Turbidity		
	Midland	none	1938	3.942	1.217	51.89	101.70
				1.232	*0.025*		
		≤30	1781	1.297	1.417	31.92	62.57
				1.285	*0.139*		
		≤10	1374	0.559	1.583	30.32	59.42
				1.876	*0.332*		
	North West	none	701	-10.749	2.181	22.56	44.22
				1.067	*0.047*		
		≤30	653	2.264	0.892	5.87	11.50
				0.491	*0.045*		
		≤10	394	2.295	0.872	3.72	7.29
				0.572	*0.085*		
Transformed model							
$\log_{10}$ BOD					$\log_{10}$ Turbidit		
	Midland	none	1938	0.268	0.809	0.288	3.67
				0.014	*0.015*		
		≤30	1781	0.297	0.765	0.255	3.16
				0.016	*0.019*		
		≤10	1374	0.334	0.697	0.233	2.86
				0.017	*0.025*		
	North West	none	701	0.167	0.861	0.241	2.97
				0.029	*0.028*		
		≤30	653	0.319	0.688	0.211	2.60
				0.031	*0.033*		
		≤10	394	0.364	0.618	0.189	2.34
				0.039	*0.049*		

4.3 All determinands

Following the regression analysis of BOD on turbidity alone, regressions were performed using the full set of explanatory determinands:

- turbidity, ammonia, SS, phosphate, chloride, pH and TON from Midland region;
- turbidity, ammonia, SS, phosphate and TON from North West region.

The estimated coefficients (with their standard errors) are shown in Table 4.2, which gives the results for (a) the simple model with BOD regressed directly on the available determinands and then (b) the transformed model with log BOD regressed on the logged determinands - pH was not logged because it is already logged by definition. Logs were taken to base 10. As before, additional runs were performed with turbidity restricted to values below 30 or below 10 NTU Where the standard error is high relative to the coefficient, this indicates that the determinand does not make a useful contribution to the overall goodness of fit when the other variables are present. Thus, for example, TON generally makes an insignificant contribution, except in the Midland additive model.

The regressions were generally not very satisfactory because there were large numbers of influential points and also many points had unacceptably high residuals.

Table 4.3 shows the residual standard deviations and the precision term (based on 95% confidence) for these regressions in the same way as in Table 4.1.

It is clear from comparing the precision in Tables 4.1 and 4.3 that the use of additional determinands led to smaller residual standard deviations and so helped to explain more of the variability in BOD. As a consequence the confidence limits on predictions were considerably reduced by using additional explanatory variables. For example, in the transformed models, the 95% precision factor was around 2.0.

Table 4.2 Regression coefficients for BOD and log BOD with standard errors

Variable	Region	Restrict Turbidity	Constant	Estimated coefficients for explanatory variables *with standard errors*						
Simple model										
BOD				Turb	AmmN	SS	Chloride	pH	Phos	TON
	Midland	none	184.149	1.311	0.188	-0.241	-0.009	-23.711	0.340	-0.406
			15.494	*0.050*	*0.043*	*0.030*	*0.003*	*2.041*	*0.130*	*0.065*
		≤30	54.731	0.556	0.088	0.338	-0.002	-6.859	0.082	-0.159
			5.550	*0.057*	*0.015*	*0.025*	*0.001*	*0.728*	*0.046*	*0.023*
		≤10	63.656	0.419	0.261	0.314	-0.003	-8.175	0.037	-0.079
			6.119	*0.109*	*0.035*	*0.031*	*0.003*	*0.798*	*0.050*	*0.027*
	North West	none	-3.016	0.311	0.278	0.501			0.242	0.016
			0.691	*0.045*	*0.041*	*0.031*			*0.087*	*0.035*
		≤30	-1.287	0.270	0.209	0.465			0.238	0.004
			0.538	*0.050*	*0.028*	*0.030*			*0.062*	*0.024*
		≤10	-0.112	0.272	0.078	0.436			0.264	-0.021
			0.562	*0.082*	*0.023*	*0.037*			*0.061*	*0.019*
Transformed model										
log BOD				log Turb	log AmmN	log SS	log Chloride	pH	log Phos	Log TON
	Midland	none	0.801	0.249	0.136	0.487	-0.043	-0.071	0.060	-0.066
			0.123	*0.023*	*0.008*	*0.024*	*0.020*	*0.016*	*0.014*	*0.016*
		≤30	0.682	0.289	0.126	0.472	-0.044	-0.057	0.060	-0.058
			0.121	*0.024*	*0.008*	*0.023*	*0.019*	*0.015*	*0.013*	*0.015*
		≤10	0.820	0.294	0.122	0.445	-0.064	-0.073	0.051	-0.017
			0.133	*0.028*	*0.009*	*0.025*	*0.022*	*0.017*	*0.015*	*0.019*
	North West	none	0.028	0.236	0.111	0.523			0.159	-0.023
			0.036	*0.037*	*0.013*	*0.039*			*0.022*	*0.021*
		≤30	0.020	0.255	0.108	0.509			0.147	-0.008
			0.036	*0.039*	*0.012*	*0.038*			*0.022*	*0.021*
		≤10	0.067	0.242	0.065	0.492			0.145	-0.014
			0.046	*0.050*	*0.014*	*0.043*			*0.026*	*0.023*

Table 4.3 Regression results from laboratory-based turbidity and other determinands

Region	Transformation	Restrict Turbidity	Number of Points	Residual S.D.	Precision term (95% confidence)
Simple model					
Midland	none	none	1939	24.06	47.17
	none	≤30	1781	8.13	15.94
	none	≤10	1374	7.66	15.01
North West	none	none	701	6.22	12.19
	none	≤30	653	4.29	8.41
	none	≤10	394	2.81	5.50
Transformed model					
Midland	log	none	1939	0.183	2.28
	log	≤30	1781	0.169	2.15
	log	≤10	1374	0.158	2.04
North West	log	none	701	0.155	2.01
	log	≤30	653	0.151	1.98
	log	≤10	394	0.140	1.88

5. ALTERNATIVES TO ORDINARY LEAST SQUARES REGRESSION

5.1 Introduction

The work described above was performed using classical methods based on ordinary least squares regression. However, it is well known that the least squares procedure is particularly sensitive to outlying points. The technique also assumes that there is constant variability of the data about the fitted line. The preliminary data analysis showed that the data sets in this project were problematical with both these aspects. Furthermore. the OLS regressions described in Sections 2 and 3 confirmed that the regressions were unreliable for these reasons. A number of alternative approaches were investigated to see how they might produce better predictive relationships.

5.2 Chemometric methods

Appendix A contains a report by Dr J M Thompson, a consultant chemometrician employed to consider the data analysis in the light of current advances in chemometrics. He looked at two data sets, one taken from Appendix 1 of NRA report "Application of the Grant/YSI 3800 Meter to Effluent Monitoring" by Neil Martin of Thames Region, and the other comprising four of the sets of regional data - Northumbria & Yorkshire, South Western, Thames and Welsh - described in Section 2 above.

He declares that OLS methods should not be used since the data are not well-behaved because of the presence of possible outliers and variable degrees of scatter. This is because OLS methods lack robustness when the OLS assumptions are violated and also lack resistance to outliers. In other words, the OLS model can easily be thrown off track by a relatively few remote points and by non-constant variance.

To overcome this problem, three robust and resistant regression methods were considered:

1. Tukey's three group resistant line;

2. Theil's median of all possible pairwise slopes;

3. Rousseeuw's Least Median of Squares (LMS).

A brief description of the methods is given in Appendix B.

All three methods were used in the analysis of the data relating laboratory BOD to turbidity measured on four Grant monitors and the results are given in Table 5.1. It is clear that there was good agreement in the slope estimates between the three robust and resistant methods. In contrast, the OLS regression yielded considerably higher regression slopes, presumably because of the influence of a few wild points. However, with the robust methods, there were differences in the slope estimates between different meters and also between different series with the same meter. Unfortunately, the data sets were not large enough to analyse possible contributory sources of variation with any great reliability. A more careful design of observational study would be needed to perform a useful analysis of the sources of variation.

Table 5.1 Comparison of OLS and robust methods for Grant meters

Data set	Method	Slope	Intercept
Grant 33 (series 1)			
	OLS	0.344	1.511
	LMS	0.051	1.285
Grant 33 (series 2)			
	OLS	1.287	-4.623
	Tukey	0.904	-1.715
	Theil	0.833	9.000
	LMS	0.867	-2.467
... 14			
	OLS	1.097	1.381
	LMS	0.738	2.331
Grant 38			
	OLS	1.655	-15.277
	LMS	0.493	1.875

Tukey's three group resistant line method was applied to the four sets of regional data - Northumbria & Yorkshire, South Western, Thames and Welsh. Comparisons with the OLS regressions (based on raw data rather than on log-transformations) are shown in Table 5.2. The OLS regression slopes were clearly influenced by just one or two extreme points and are thus unreliable.

Table 5.2 Comparison of methods for field turbidity monitors by region

	Method	Slope	Intercept
...umbria & Yorkshire			
	OLS	0.141	15.92
	Tukey	0.618	NA
South Western			
	OLS	0.301	13.06
	Tukey	0.836	1.82
Thames			
	OLS	0.451	5.67
	Tukey	0.687	1.43
Welsh			
	OLS	0.254	5.39
	Tukey	0.	2.30

The Thames data set was then analysed according to various subdivisions based on STW type (see Table 5.3). The OLS regression equations were highly influenced by just one or two extreme points and are too unreliable for any practical purpose. Following the Tukey method, examination of residuals to assess spread, the presence of outliers and evidence of nonlinearity showed that the residual scatter was smaller for the larger STWs, where there was also a smaller slope, than for the smaller STWs. There was also some evidence of nonlinearity at the smaller works but this may be misleading given the high scatter.

Table 5.3 Comparisons of methods for Thames subsets

Subset	Method	Slope	Intercept
PS			
	OLS	0.490	5.99
	Tukey	1.167	1.30
PL			
	OLS	0.592	1.52
	Tukey	0.717	1.07
AL			
	OLS	0.411	4.27
	Tukey	0.500	2.55
Private			
	OLS	0.921	7.71
	Tukey	1.156	1.00
Not sewage effluent			
	OLS	0.0227	1.88
	Tukey	0.0186	1.00

6. COMPARISONS OF TURBIDITY MEASUREMENTS MADE USING A RANGE OF DIFFERENT INSTRUMENTS

Appendix C contains a report by Steve Russell of WRc describing some measurements for comparing some field and laboratory instruments used for measuring turbidity. Three commercial bench turbidimeters and the Grant YSI 3800 multiparameter logger were set up in the laboratory and calibrated using formazine suspension. A test rig for scattered light measurement was also used.

Sewage effluent samples were collected from:

1. a biological filter works with some industrial waste but predominantly a domestic catchment;

2. an activated sludge works with a mixed domestic and industrial catchment;

3. a small rural works using an RBC with tertiary treatment using a reed bed;

4. the activated sludge pilot plants at Swindon WRc.

The turbidity of each effluent sample was measured on each of the instruments and also on the test rig. Comparisons with the Grant 3800 are shown graphically in the Appendix and summarised in Table 6.1

Table 6.1 Turbidity instrument gradients against the Grant 3800

Instrument	Gradient	R squared
Hach 2100A	0.833	0.97
Hach Ratio	1.179	0.96
Hach XR ratio	1.174	0.97
880 nm 90 degree scatter	1.169	0.91
880 nm 20 degree scatter	2.550	0.91
880 nm absorbence (40 mm path)	2.433	0.93

The results can be summarised as follows:

In a comparison between filter plant data and activated sludge plant data, the gradients comparing Hach 2100A and Grant 3800 instruments were slightly different but probably not significantly so.

The results agree with the theoretical result that 20 degree scatter is more sensitive to larger particles than 90 degrees scatter.

Readings fluctuate as particles move in and out of the cell measurement volume. Instruments with large measurement volumes (such as Hach 2100A) score over instruments with ratio optics (such as Hach 2100N) which need to take a number of readings and then calculate the average.

The Hach XR ratio and the 880 nm 90 degrees scatter gradients were very similar in this exercise. this disagrees with a previous exercise carried out at WRc where similar instruments gave a ratio of gradients of around 1.9. This discrepancy is unexplained at present. However, it does not affect the comparison between the Grant 3800 and the Hach instruments.

7. DISCUSSION

OLS regression is a well developed methodology which is easy to apply using any elementary statistical package. Methods for obtaining confidence limits about the fitted line based on OLS regression are also well-developed and understood. However, where there are outliers in the data or where the variance in BOD is not constant over the range of turbidity the OLS regression will give unreliable results.

In contrast to OLS regression, the more robust and resistant methods described in this report are less affected by outliers and non-constant variance. However, they are also generally used less frequently, partly because they are relatively unfamiliar compared with OLS regression, but also because it is not always clear which is the most appropriate method. To quote from Davies and Goldsmith (1972) in a slightly different context "they each have some degree of theoretical validity, but no single method can claim to be the only correct one and unfortunately each can lead to a different equation." It is often difficult to know which alternative approach is the most appropriate. Furthermore, they tend not to have methods in place for calculating confidence limits around the fitted line.

Outliers are a nuisance when trying to predict BOD from turbidity. High BOD may be found with low turbidity if there is soluble matter present. Low BOD at high turbidity may arise from suspended clays and silts.

Other factors can contribute to nonlinearity or to low or high values of BOD relative to the turbidity observed. There may be other important factors besides the ones made available for this project.

8. CONCLUSIONS

1. This work has confirmed that OLS regression methodology can be unreliable with the kind of data available for this project because of the presence of outliers and variable degrees of scatter. Many alternatives to OLS regression for fitting lines to data are available and several have been investigated in this project.

2. Because BOD exhibited variability which increased with increasing field turbidity, the transformed model was more appropriate than the simple model. In other words, better agreement with the requirements of OLS regression can be obtained by logarithmic transformation of both BOD and turbidity. This leads to confidence intervals which have width proportional to the BOD value, i.e. higher BOD estimates have greater absolute uncertainty than lower ones. Transformation was not required for suspended solids.

3. The confidence limits about the OLS regression line based on *all* the data were generally quite wide, the upper 95% confidence limit was typically about four times the estimated BOD and the lower limit was about one quarter of the BOD estimate. Graphical inspection showed that the confidence interval was rather too wide at the lower levels of BOD.

4. Better predictions with narrower confidence limits could be obtained by limiting the regression analysis to lower levels of turbidity, e.g. to values less than 30 NTU. This reduced the precision factor from 4.3 to 3.3.

5. The introduction of other explanatory variables into the regression made a significant improvement to the fit and reduced the precision factor to about 2.0.

6. The slope of the OLS regression lines for predicting BOD from field turbidity varied from region to region.

7. The slope of the OLS regression lines for predicting BOD from field turbidity varied between STW types within a region.

8. There was no significant correlation between BOD and turbidity for data arising from non-STW effluents in the Thames Region.

9. Alternative methods of curve fitting to OLS regression overcame the problems of outliers and non-constancy of variance and could be expected to lead to greater consistency between results from different surveys. However, they did not provide methods for calculating confidence limits about the line.

9. RECOMMENDATIONS

Because of the differences found between types of STW, the equations for predicting BOD from turbidity should be developed further by collecting appropriate data. The fitted equations for each different type of works should then be tested against additional data not used in fitting the models.

Additional variables that might usefully be measured in the field include PO2, temperature, pH and redox potential.

Since there were differences in slopes between different meters and also between different series with the same meter, possible contributory sources of variation should be investigated using a careful design of observational study.

Further work is required on alternative robust methods to enable confidence limits to be placed around the fitted lines and to decide which method would be the most appropriate for predicting BOD from turbidity.

REFERENCES

Davies, O.L. and Goldsmith, P.L. (1972) *Statistical Methods in Research and Production*, 4th edition, Longman, London

Thompson, J.M. (1992) Exploratory, Robust and Nonparametric Data Analysis, Chapter 3 in S.J. Haswel, *Practical Guide to Chemometrics*, Marcel Dekker.

APPENDIX A

REPORT ON THE CHEMOMETRIC EVALUATION OF DATA BY DR J M THOMPSON

Introduction

Two sets of data were evaluated for this report : data set 1 was from appendix 1 of the report "Application of the Grant/YSI 3800 Meter to Effluent Monitoring" by Neil Martin, NRA Thames Region, SE Area Pollution Control, Guildford, Feb. 1996 and data set 2 was supplied by Terry M. Long, EA Bristol to Peter van Dijk, WRc on September 1996 and by the latter to me on 8th October 1996. A meeting was held at WRc on 15th July 1996 to discuss the approach to the project which involved Terry Long of EA Bristol, Mike Gardner, Steven Russell and Peter van Dijk of WRc and me. A second meeting, between Peter van Dijk and me, was held on 28th Oct. 1996 to discuss progress in data analysis and a further meeting was held today 9th Dec.1996 to discuss this report.

As with many sets of environmental specimens analysed either in the laboratory or in the field, the data obtained from such measurements is not well behaved and contains what might be considered outliers, in addition to a relatively wide scatter. It is thus not amenable to analysis by conventional least squares gaussian methods because these lack both robustness (which enables us to assess the behaviour of the bulk of the data) and resistance to outlier or "wild" data. The methods used have included the robust Least Median of Squares regression method of Rousseeuw, Tukey's three group resistant line regression and Theil's nonparametric regression method of pairwise slopes. Attention has also been directed at examination of the residuals plots from such regressions, in order to assess residual spread, presence of outliers and evidence of nonlinearity. Various subsets and combinations of subsets of the data have been used to examine the behaviour of individual field instruments and of various sewage treatment plants and trade effluent sources.

Evaluation of data set 1 :

Using the program PROGRESS of Rousseeuw and Leroy (see "Robust Regression and Outlier Detection" by P.J.Rousseeuw & A.M.Leroy, 1987, Wiley) ordinary least squares (OLS), least median of squares (LMS) and a reweighted least squares (RLS) based on the LMS was performed on subsets from the various field monitors used. For one subset Theil's and Tukey's methods were also used. This illustrates the agreement between the LMS, Tukey and Theil methods which reflect the behaviour of the bulk of the data and the disagreement with the OLS. The results of the regressions, with lab BOD as the dependent variable, are outlined below :

Lab BOD vs Grant 33 (2nd series)

regression method	slope	intercept	R^2	possible outliers
OLS	1.28713	-4.62270	0.83390	
LMS	0.86667	-2.46667	0.87635	7,9,14,17,30,31
RLS	0.76068	-0.78290	0.88044	
Theil	0.33333	9.00000		7,14,27,30,31
			1/2 slope ratio	
Tukey rline	0.9037	-1.7148	2.396	7,9,14,15,17,19,30,31

Lab BOD vs Grant 33 (1st series)

	slope	intercept	R^2	
OLS	0.34442	1.51069	0.23976	
LMS	0.05102	1.28571	0.63715	5,11,14,16,18,21,24
RLS	0.04555	2.15422	0.15966	

Lab BOD vs Grant no 14

OLS	1.09739	1.38120	0.85855	
LMS	0.73846	2.33077	0.79472	23
RLS	0.68535	2.79742	0.60086	

Lab BOD vs Grant no 38

OLS	1.65452	-15.2772	0.43199	
LMS	0.49286	1.87500	0.80377	2,8,13,17,22,25,27,29,30, 37,41,43,45,54
RLS	0.49042	2.07700	0.15966	

There is clearly something suspect about the Grant 33 1st series which differs markedly from the second series and from data from Grant nos 14 and 38. Grant 33 2nd series compares reasonably well with Grant 14 but both differ considerably from Grant 38. These subsets are not really big enough to analyse possible contributory sources of variation with any great reliability. A more careful design of observational study would be needed to perform a useful analysis of the sources of variation.

Data set 2

Subsets were provided from South Western, Northumbria/Yorkshire, Welsh and Thames. Exploratory analysis using Tukey's three group resistant line regressionwas performed and the results are shown below :

	slope	intercept	1/2 slope ratio
South Western	0.8361	1.3250	1.412
Thames	0.6870	1.4310	0.520
Northumbria/Yorkshire	0.6176 0.6000	n/a 4.0000	n/a (Theil method)
Welsh	0.3658	2.3053	1.154

The two most extensive data subsets were Thames and South Western. The latter attempted to classify STWs according to size. However, it is not clear whether there was any differentiation between private and public works as in the Thames subset. There was no attempt to subdivide the South Western subset at this stage.

The Thames subset was analysed according to further subdivisions :

subset	slope	intercept	1/2 slope ratio
"not"	0.0186	1.0010	0.952
priv	1.1560	1.0000	1.648
PS	1.1667	1.3000	0.286
PL	0.7167	1.0667	0.601
AL	0.5000	2.5500	0.587
AL+APL	0.5263	2.4974	2.371
AL+APL+PL	0.6714	1.5429	1.771

Subsets from the 1st Thames set were combined with subsets from the 2nd Thames set and analysed as follows :

subset combination	slope	intercept	1/2 slope ratio
priv 1 & 2	1.0635	0.7730	1.490
AL+APL+PL & that data marked Thames in 1st set	0.5750	1.7250	1.030

Letter value analysis of the residuals from the last two regressions suggests that scatter is smaller for the Large STWs (roughly 95% lying between about -6.7 to 6.4) than for the private works (only about 50% being in a similar range). The private and small public STWs seem to have similar slopes (about 1.1-1.2) and a wide scatter. The half slope ratios of these groups are perhaps indicative of nonlinearity but in different directions. However, with such wide scatter the half slope ratio may be a misleading indicator and the scatter may be contributed by other independent variables not included in these regressions. The slope of about 0.6 for the larger STWs with a narrower scatter and a half slope ratio of approximately 1.0 suggests a reasonably linear relationship, less influenced by other variables than for the smaller works. The differences between the large STWs and small (+ private) STWs may be more apparent than real because the confidence bands probably overlap.

The influence of other factors cannot be adequately disentangled in these data sets. Such factors as geographical zone, hydrology and underlying geology, time of year or day, climatic influences such as whether there was heavy rain or a lack of rain prior to the specimen being taken, the influence of suspended particle shape and size distributions on the turbidity and various chemical/biochemical influences on b.o.d. and sample stability should perhaps be looked at in any subsequent study to determine whether there are any other significantly influential variables which it would be cost effective to include in any field monitoring estimate of b.o.d. Many of these may only be of marginal influence but it is probably desirable to establish the significance of their influence. Sufficient account of instrument and operator variability also needs to be made in estimating the uncertainty budget.

Any future observational study needs both careful design and execution to enable exploratory analysis of variance and multiple regression to yield effective algorithms fit for the intended purpose. Greater consistency in recording data than in the data sets used in this project is essential. In particular, consistency is needed in the use of "less than" which varied widely. A policy on the data structure and on data recording and auditing should be agreed, together with equipment maintenance, calibration, checking and qualification. Staff should be adequately trained in the project S.O.P.s and protocols to ensure consistency and traceability.

APPENDIX B

SUPPLEMENTARY REPORT ON THE CHEMOMETRIC EVALUATION OF DATA BY DR J M THOMPSON

1. Brief explanation of statistical methods used

a) Robust and resistant regression methods used

(i) Tukey's three group resistant line

In this method, the values of the independent variable, x, are sorted into ascending order and divided into three groups of more or less equal size : a left, a midddle and a right group. Within each group, a summary poit is formed by first determining the median x-value and then independently the median y-value. This method provides resistance to wild values of x, y or both. The slope is estimated from the left and right summary points and the intercept from all three summary points. The residuals are then used in place of the y values iteratively to determine adjustments to the slope and intercept. The breakdown bound (see below) is 0.167.

(ii) Theil's method

This method involves computing the slopes between all the possible pairs of points and obtaining the median of those pairwise slopes as the regression coefficient. The median of the intercepts resulting from drawing lines with the median slope through each point is the regression intercept. The breakdown bound is 0.29.

(iii) Rousseeuw's Least Median of Squares

This method involves minimizing the median of the squared residuals instead of the sum. The breakdown bound is ([n/2]-p+2)/n, where n is the number of points and p the number of independent variables.

b) Letter Value Analysis and Box and Whisker Plots of Regression Residuals

(i) Letter value analysis

The first step is to rank the data in ascending order, the position of the median is found (its depth). The depths of the fourths in from each end of the ordered data set are then found from ([depth of median]+1)/2 (dropping any fraction from the depth of the median). The median and fourth are termed letter values and are given one letter tags (M and F). The depth of other letter values is found from ([depth of previous letter value]+1)/2, in every case drpping any fraction from the previous depth. Thus, the letter values move progressively into the tails of the data distribution. A letter value display shows the depth of each letter value, the lower and upper letter values, the spread between upper and lower letter values and the mids (means of the upper and lower letter values). Using this to examine the residuals, enables us to assess the shape of their distribution in a useful summary form.

(ii) Box and whisker plots

The box plot consists of a rectangle which has as upper and lower bounds the upper and lower fourths and within the box is marked the position of the median. The whiskers extend beyond the fourths values to the furthest ordered data points within the inner fences. Points between the inner and outer fences are marked by "*" and those outside the outer fences with "O". Inner fences are at lower fourth - 1.5*(fourth spread) and at upper fourth + 1.5*(fourth spread). Outer fences are at lower fourth - 3*(fourth spread) and upper fourth + 3*(fourth spread). The values beyond the outer fences are probable outliers, those between the inner and outer fences are possible outliers.

c) Breakdown bounds of regression methods

This is a measure of the resistance of the regression to wild values affecting the estimation of the slope and intercept and is given by the ratio k/n, where k is the greatest number of the n data points that can be replaced while leaving the slope and intercept bounded. The ordinary least squares regression has a breakdown bound of zero.

2. Limitations of the current approach to evaluation of field monitoring

a) problems of only measuring turbidity, etc., downstream of sewage outfalls

With measurements being made only downstream of the outfall, there is no way of estimating the upstream contribution to those measurements. This is a serious deficiency in the current approach. Such upstream contributions probably account for some of the scatter in the plot of turbidity vs BOD and may vary with upstream pollution and rainfall.

b) comments on the scatter and outliers in field turbidity vs B.O.D. plots

High lab BOD at low turbidity is possible from soluble matter. Low BOD with high turbidity may arise from suspended clays and silts. Other factors may contribute to low or high values or nonlinearity.

3. Recommendation on possible improved approach to field monitor evaluation

Future studies could usefully include both upstream and downstream measurements and attempts to estimate BOD from the differences between those upstream and downstream measurements. Additional measurements in the field might usefully include pO_2, temperature, pH and redox potential.

4. The methods referred to are discussed in J.M.Thompson "Exploratory, Robust and Nonparametric Data Analysis", chapter 3 in S.J.Haswell "Practical Guide to Chemometrics", 1992, Marcel Dekker.

APPENDIX C

COMPARISON OF TURBIDITY MEASUREMENTS USING A RANGE OF DIFFERENT INSTRUMENTS

COMPARISON OF TURBIDITY MEASUREMENTS MADE USING A RANGE OF DIFFERENT INSTRUMENTS

Introduction. WRC is currently undertaking a study on behalf of the Environment Agency to examine the relationship between turbidity and BOD5. Data on turbidity and BOD is available with both field and laboratory measurements of turbidity. Measurements of turbidity in the field are normally made using the Grant 3800 multiparameter logger, whereas laboratory measurements are made on a number of instruments such as the Hach 2100A bench turbidimeter. Turbidity measurement is well known as an instrument-dependent quantity and so some comparitive measurements were needed to allow the combining of the field and laboratory data.

Procedure. Three commercial bench turbidimeters and the Grant YSI 3800 multiparameter logger were set up in the laboratory and calibrated using formazine suspension. In addition a test rig for scattered light measurement was calibrated using formazine so that it could be used to measure turbidity at 90 degrees using 880 nanometre source light, 20 degrees using 880 nanometre source light and attenuation of 880 nanometre light.

Sewage effluent samples were collected from three sewage treatment works within half an hour's drive of the Swindon laboratory. The works were:

i) A biological filter works with some industrial waste, but predominantly a domestic catchment;

ii) An activated sludge works with mixed domestic/industrial catchment;

iii) A small rural works using an RBC with tertiary treatment using a reed bed.

It was found that the reed bed effluent was so good that the Grant 3800 instrument, which reads integer NTU values, always read 0 NTU and so after the first 2 visits, no more samples from this works were used. One sample each from the activated sludge pilot plants operating at Swindon WRc were taken to supplement the main plant data. Pilot plants normally vary very little and so there was little point in collecting multiple samples from these plants. The turbidity of the effluent samples was measured on each of the instruments and the test rig and recorded.

Results. The measurements from the filter plant and the activated sludge plants are plotted separately using the Hach 2100A data against the Grant 3800 in Charts 1 and 3 respectively. It may be seen that the gradients for the data sets are slightly different. When the data is plotted together (chart 4) the difference between the data sets appears comparable to the variations in the individual data sets and for the purposes of correlation with BOD it is appropriate to treat these measurement as one data set.

The measurements on all the instruments and the test rig are shown plotted against the Grant 3800 turbidity reading in charts 5 to 10. The results are summarised in table 1. The scaling factor which needs to be applied to convert between the Grant 3800 and the laboratory instruments varies between about 0.8 and 1.2. The 880 nanometre test rig scale factors range from about 1.2 to about 2.5. The difference between the 90 degree and 20 degree gradients accords with the theoretical result that the 20 degree scatter is more sensitive to larger particles than the 90 degree scatter, the factor being about 2.2 compared with their sensitivity to formazine. The bulk of sewage effluent particles are typically in the range 5 to 100 microns, whilst formazine is typically about 0.1 microns in size.

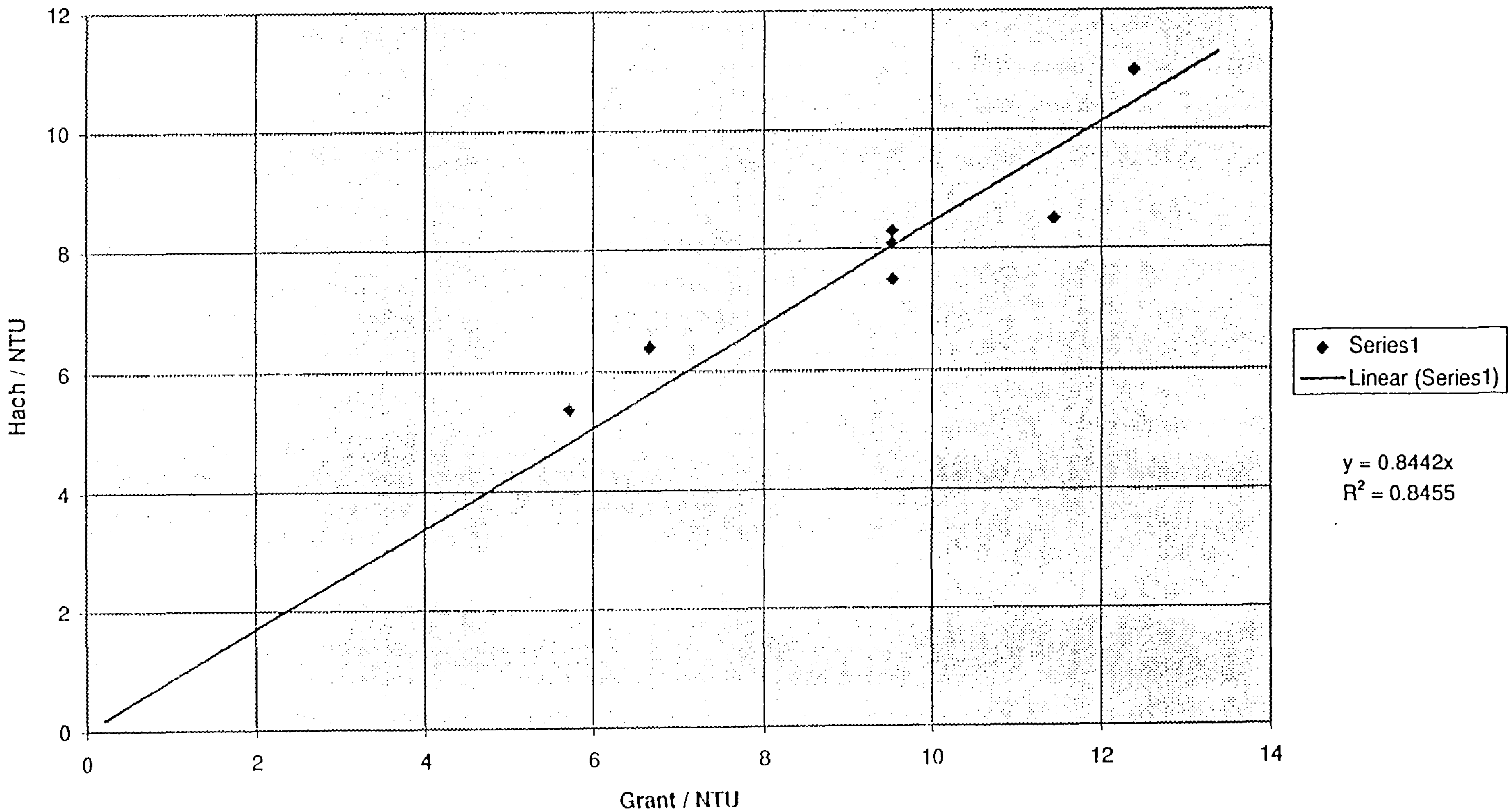
It is very noticeable when measuring sewage effluent turbidity in the laboratory that the reading fluctuates over a large range as particles move in and out of the cell measurement volume. The Hach 2100A scores over the more modern ratio instruments here as it has a large measurement volume and the turbidity averaged over a large volume can be read directly. The ratio instrument readings vary rapidly over as much as a 2:1 range and have to be dealt with by taking a number of readings and averaging. Hach's current offering, the 2100N, has ratio optics and an averaging function. The Grant 3800 has a large measurement volume and produces a steady reading within 5-10 seconds.

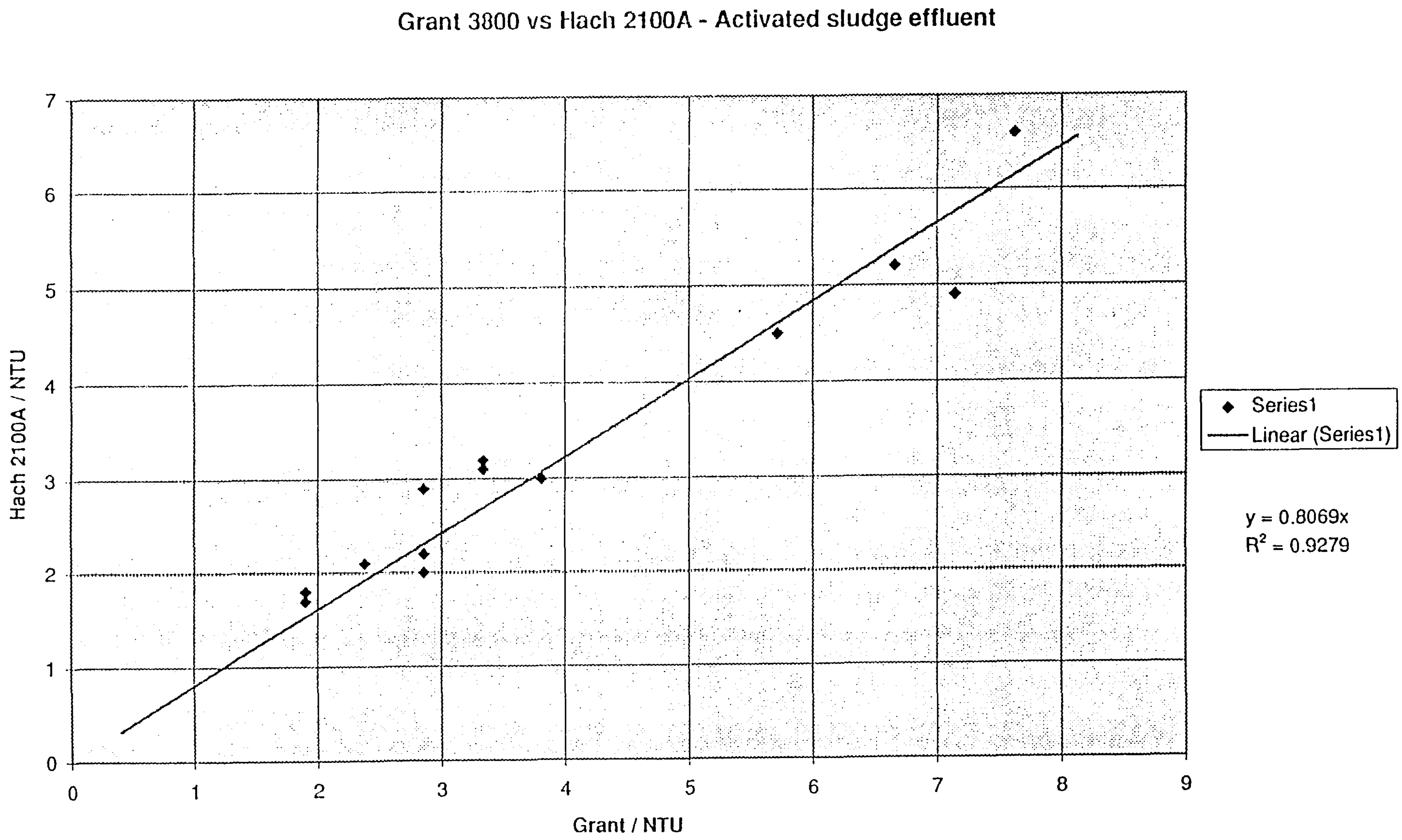
Discussion. WRc has carried out some previous work which can be compared with this exercise. In the previous work sewage effluent turbidity was measured using a Hach ratio XR and a BTG MET3000 which uses 90 degree scatter of 860 nanometre light to accord with ISO 7027. The ratio of slopes when correlated against suspended solids was about 1.9 on a range of effluent types. No particular effort was made to check the absolute value of the NTU values in this exercise as this was of secondary importance, however the difference in formazine calibration is unlikely to be more than 10%. The actual turbidity range went higher in this exercise, up to 25 NTU and this may have affected the slopes calculated. The samples will have had differences, but these are unlikely to be great compared with the difference between formazine and sewage effluent. The angle of acceptance of the BTG instrument is likely to be much larger than the test rig instrument where care was taken to restrict the detector aperture. When these factors are taken into account, the results are still not consistent with the ratio of slopes of the Hach XR and the 880 nanometre 90 degree scatter ratio in the present exercise, which is close to unity. No explanation of this difference is apparent, and the result for the 880 nanometre 90 degree scatter should be treated with some caution until the difference can be resolved. This discrepancy does not affect the comparison between the Grant 3800 and the Hach instruments.

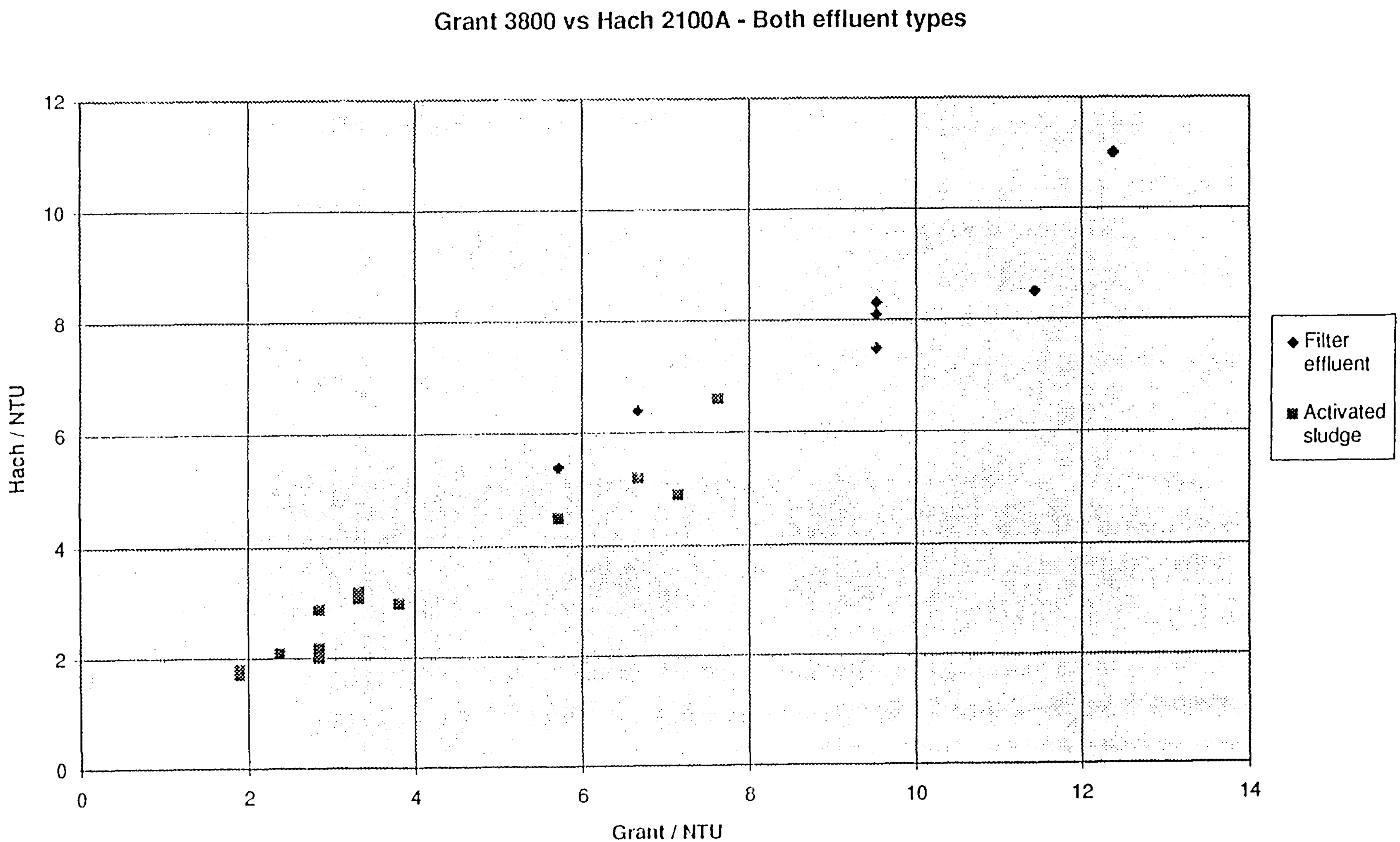
Instrumental measurement	Gradient	R squared
Hach 2100A	0.833	0.97
Hach Ratio	1.179	0.96
Hach XR ratio	1.174	0.97
880 nm 90 degree scatter	1.169	0.91
880 nm 20 degree scatter	2.55	0.91
880 nm absorbance (40mm path)	2.433	0.93

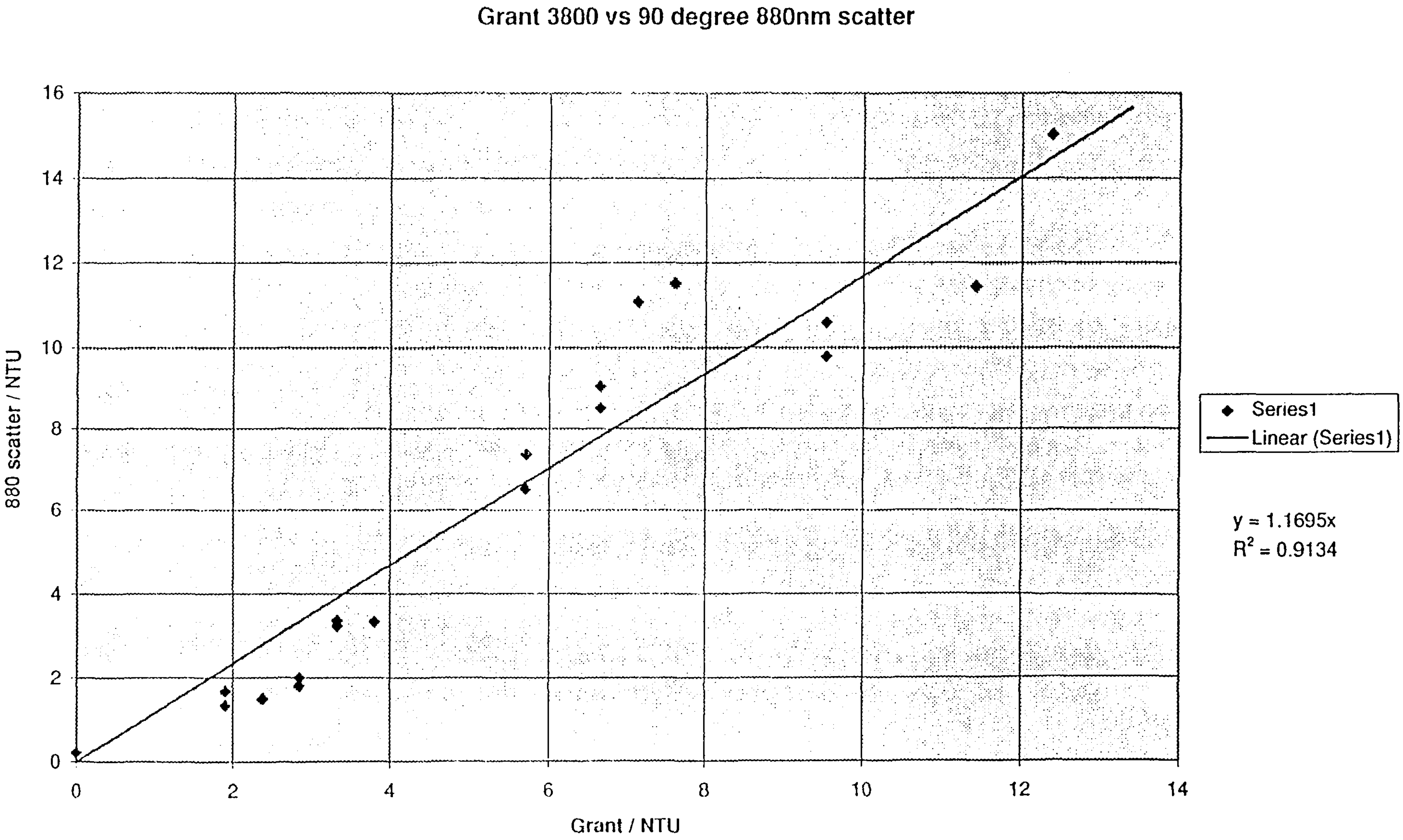
Table 1 Summary of turbidity instrument gradients against the Grant 3800.

Grant 3800 vs Hach 2100A - Filter effluent

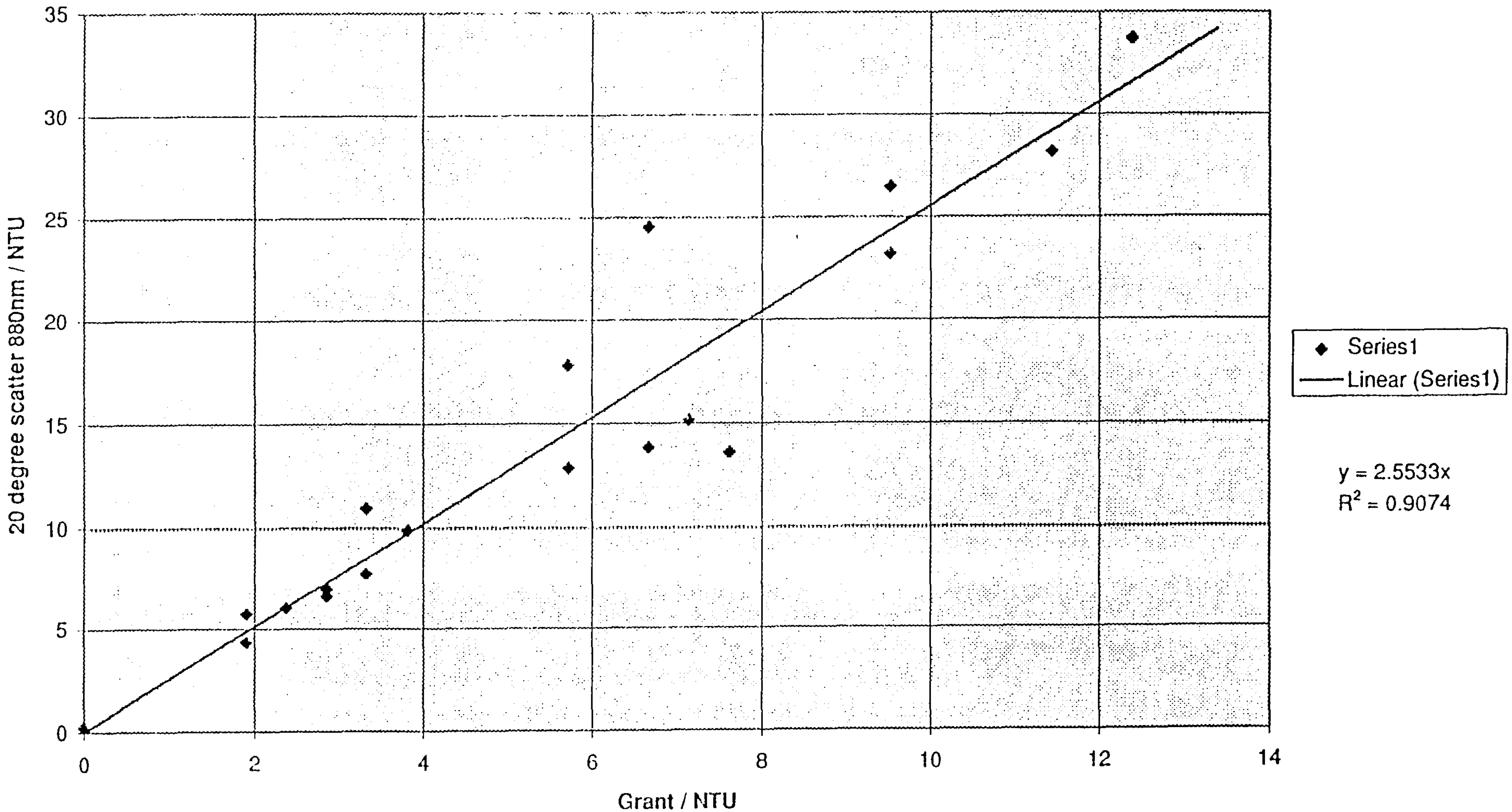



Grant 3800 vs Hach 2100A - Activated sludge effluent
Hach 2100A / NTU
Grant / NTU
0
1
2
3
4
5
6
7
8
9
Series1
Linear (Series1)
y = 0.8069x
R2 = 0.9279

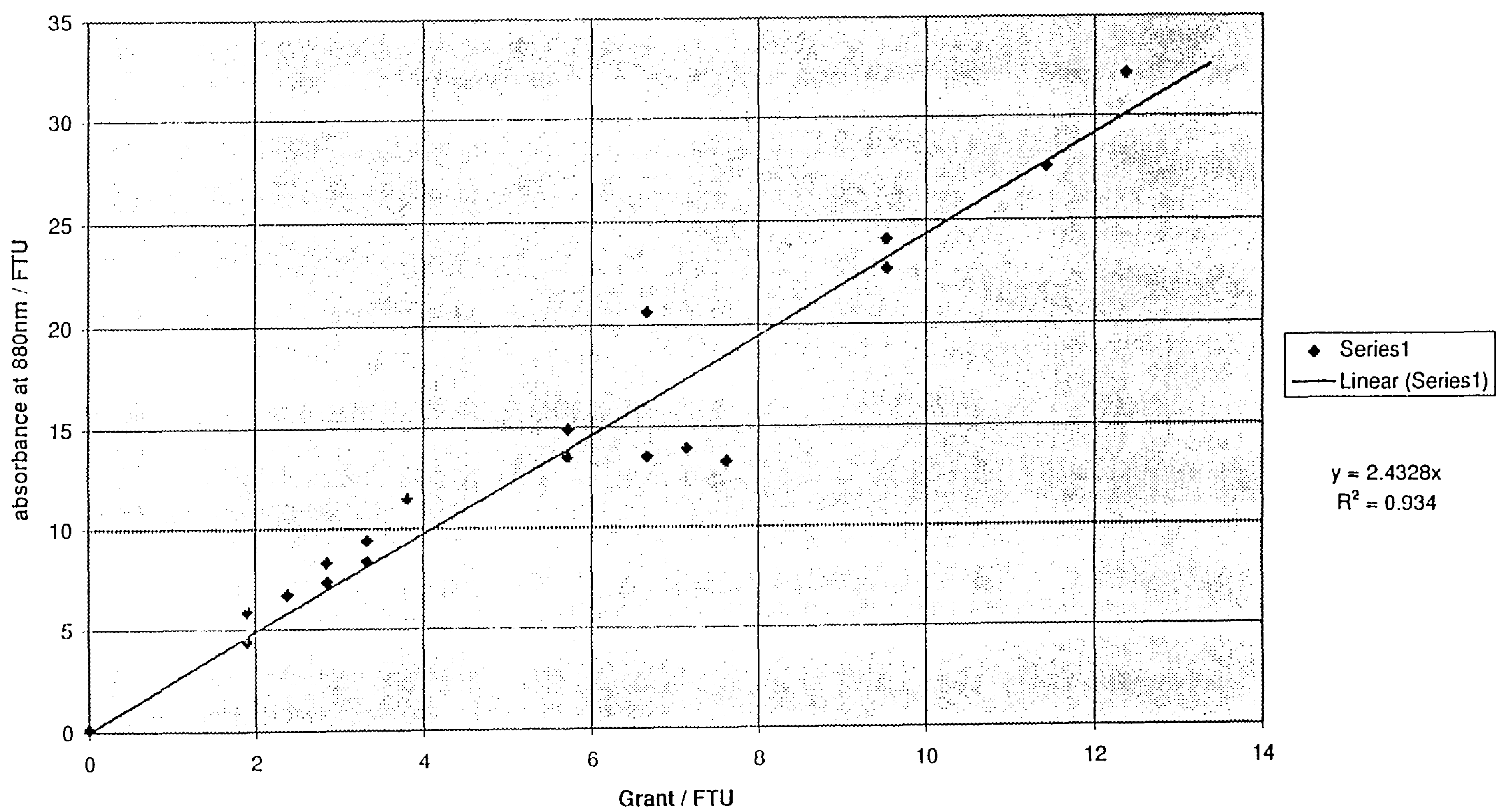

Grant 3800 vs Hach 2100A - Both effluent types
Hach / NTU
Grant / NTU
0
2
4
6
8
10
12
14
Filter effluent
Activated sludge


Grant 3800 vs 90 degree 880nm scatter
880 scatter / NTU
Grant / NTU
0
2
4
6
8
10
12
14
16
Series1
Linear (Series1)
y = 1.1695x
R^2 = 0.9134

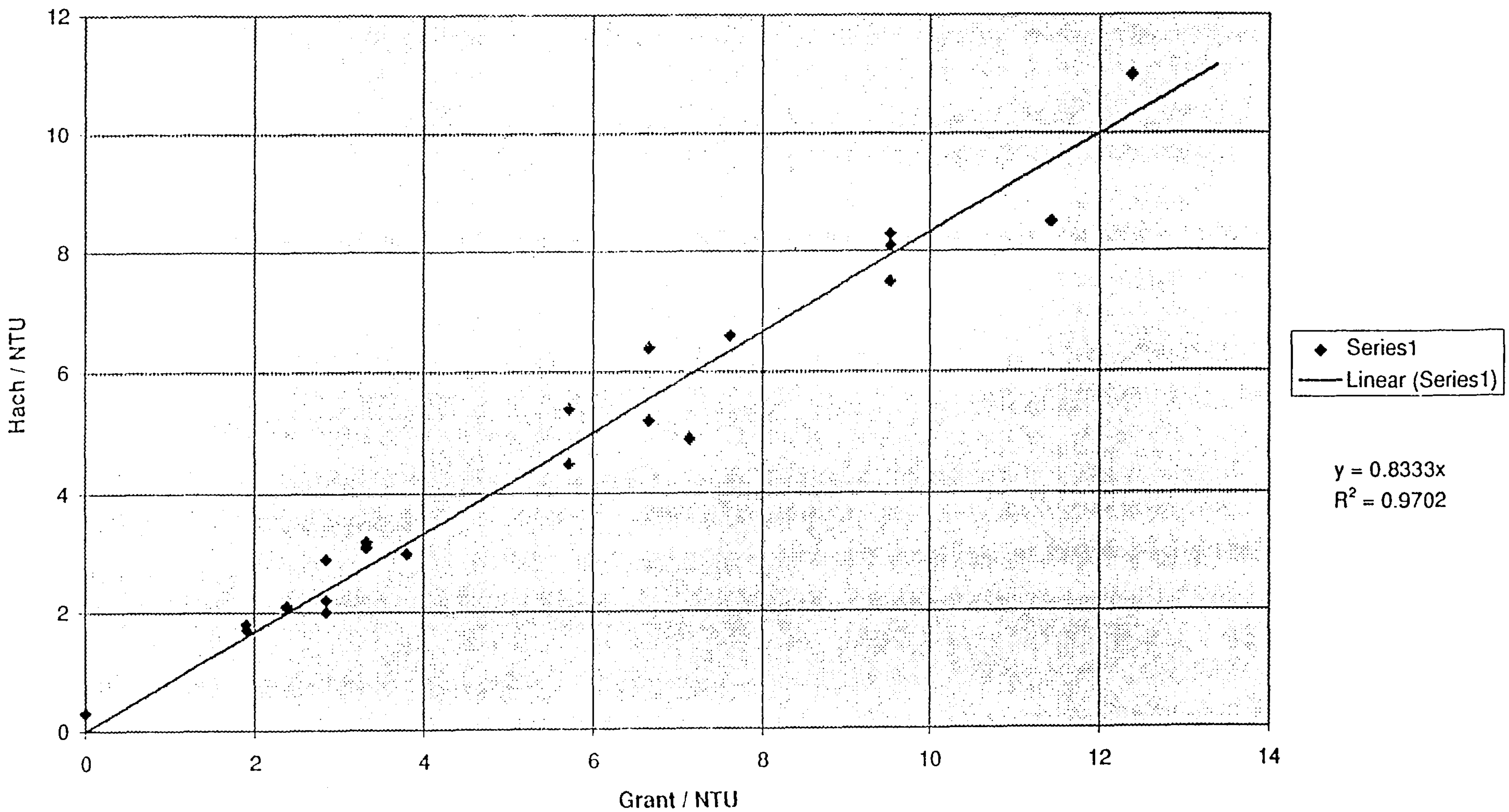
Grant 3800 vs 20 degree 880nm scatter



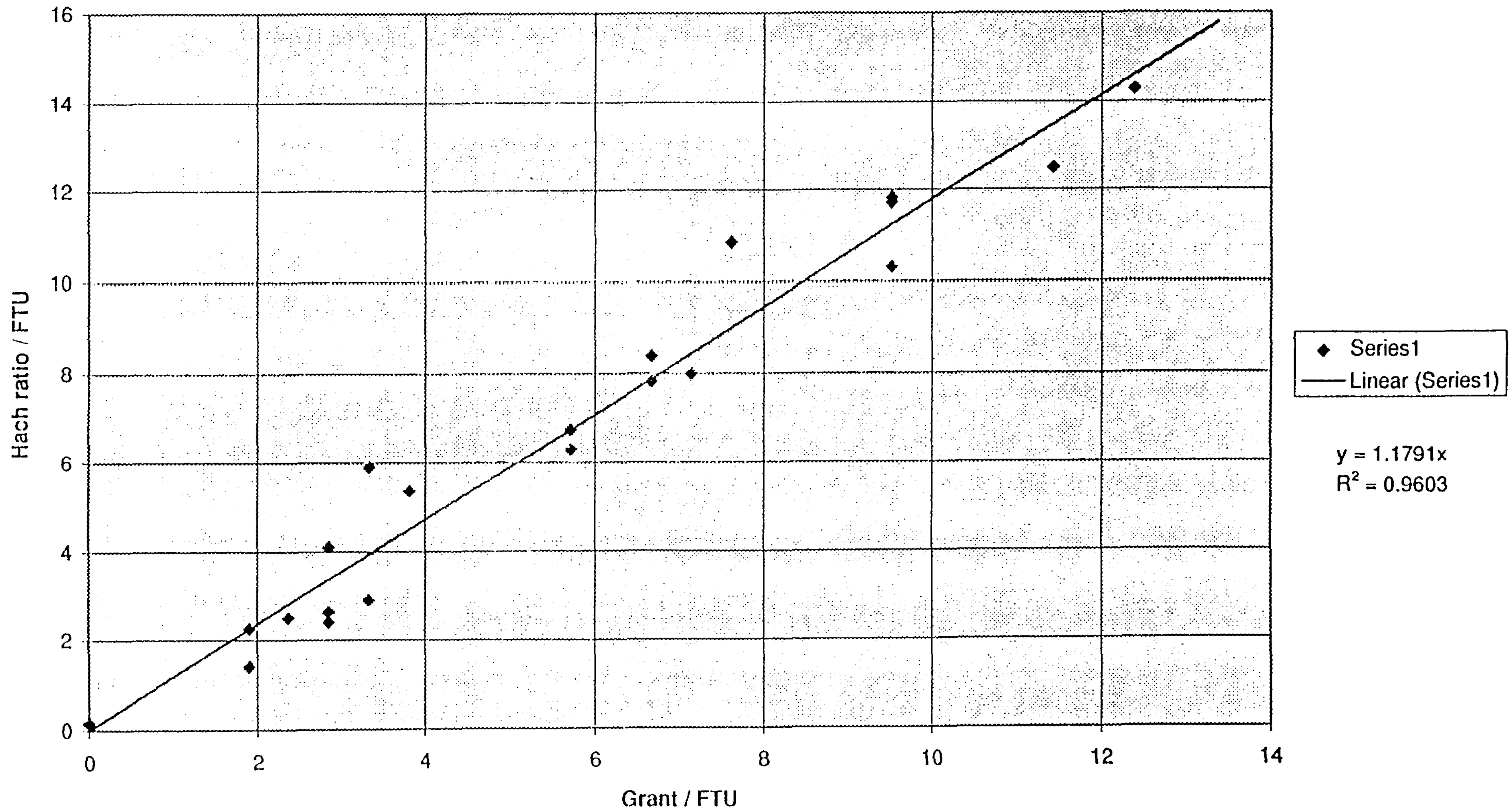
Grant 3800 vs 880nm absorbance



Grant 3800 vs Hach 2100A



Grant 3800 vs Hach Ratio



99

Grant 3800 vs Hach Ratio XR