THE EVALUATION OF GRANT/YSI 3800 WATER QUALITY MONITOR

N.R.A.
Instrument Evaluation Centre
Fobney Mead : Rose Kiln Lane
Reading : RG2 OSF

NRA
Evaluation
Centre

THE EVALUATION OF A GRANT/YSI 3800 WATER QUALITY MONITOR

A.J.Chappell BSc

Contents

Executive Summary

This report describes the evaluation of a Grant/YSI 3800 multi-parameter water quality meter. It is designed for field use and measures dissolved oxygen, temperature, pH, turbidity, conductivity, and ammonium.

The instrument responded well at different flow rates, and the ammonium probe was the only sensor to exhibit any response change with flow.

Water temperature affected the accuracy of all the sensors except turbidity and temperature.

The estuary results imply that the instrument could be used to support or replace the oxygen and chloride titration carried out during a regular monitoring run.

The ammonium probe response time changed considerably during the drift test, increasing to approximately 30 minutes to obtain a stable reading. The calibration of all the probes was stable throughout the test.

The storage cup for the sonde does not reflect the quality and price of the instrument and is difficult to remove, especially when wet.

On a number of occasion the instrument software locked up, and could only be reset by opening the logger and switching a dip switch on the main circuit board.

The instruction manual is poorly organised and difficult to use.

Grant/YSI are still developing some aspects of the instrument particularly the ammonium probe.

1. Introduction

This report describes the tests carried out to establish the reliability of data produced by a Grant\YSI 3800. Tests have been carried out on a single instrument taken new from those supplied to Thames Region for field use.

The Grant\YSI 3800 meter is a multi-parameter instrument used for field monitoring of water quality. It has six sensors to measure temperature, dissolved oxygen (%), pH, conductivity, turbidity, and ammonium. From this data values for dissolved oxygen (mg/l), ammonia, and salinity are derived.

The tests completed and reported here studied the effect of water flow rate, water temperature, water salinity, and instrument drift in one month. The tests were carried out on all instrument parameters in natural water taken from the river Kennet at the NRA National Evaluation Centre at Fobney Mead, and in the Thames Estuary. The instrument output was compared to analysis by the NAMAS accredited laboratory at Fobney Mead.

The tests were carried out over four months to the end of November 1993 to a test protocol agreed by Grant\YSI and the NRA. Further tests are being made on an instrument with a different ammonium probe after recent developments by Grant\YSI.

2. Major findings

This section provides a summary of the test results and includes subjective comments about the instrument. Comments arising from field use of 30 other instruments in Thames region are also noted here. For details of the instrument performance during the test refer to section 4.

2.1 Implications for use

The results of these tests can be used to give an estimate of the measurement uncertainty of the instrument for sampling measurements. If this is taken as three times the standard deviation of the drift test (to give 95% confidence values) we get the following values.

Dissolved Oxygen	± 6 %sat	(typically 100%)
Temperature	± 0.2°C	(typically 15°C)
pH	± 0.2	(typically pH 8)
Conductivity	± 39 µS/cm	(typically 550µS/cm)
Turbidity	± 3 NTU	(typically 2 NTU)

Since the ammonium probe requires a long time to obtain a stable reading, and because of the known interference from potassium and sodium then an uncertainty value can not be produced for the ammonium and ammonia values. Pollution officers' experience shows that the ammonium probe is useful for special surveys where it is continuously immersed, but quickly becomes useless for routine sampling tests because of the response time.

The results from the flow test show that the sonde does not need to be kept moving to obtain an accurate DO reading. Also the variations caused by temperature between +5 and +25°C are smaller than the values above.

The conductivity and pH readings are both corrected to a temperature of 25°C, optional for the conductivity. The laboratory readings are corrected to 20°C and this difference may cause some confusion and can generate differences of 11% of reading in conductivity values.

The values obtained for D/O, pH, and salinity, during a normal monitoring trip into the Thames estuary were within the measurement uncertainty of the laboratory and the uncertainty of titration carried out on the boat. Since the instrument is easy to use it could reasonably replace or support the titration measurements of oxygen and chloride.

When the problems associated with the ammonium probe are solved then regular calibration and servicing using traceable and approved techniques could lead to accurate and reliable measurements using this instrument.

2.2 Instrument performance

Water Flow rate

Only the ammonium probe showed any significant variation with flow, the other probes performed well in this test especially the dissolved oxygen which was significant better than most non - stirred DO probes. For use in high flows a sinker weight is necessary because the sonde tends to swing on its cable and lie horizontal on the water surface.

The dissolved oxygen showed a slight increase at flows greater than 0.3 m/s, but the variation was less than 1% throughout the test which is less than the reference uncertainty. This is significantly better than most non - stirred DO meters.

The temperature difference varied by 0.1°C during the test which is similar to the reference uncertainty.

The pH difference varied by less than 0.1 during the test.

The conductivity difference varied by less than the measurement uncertainty during the test.

The turbidity sensor reading increased during the test, but this was not related to the water flow. The reason is unknown, but it could be due to fouling, air bubbles forming on the probe surface, or cavitation around the sonde head.

The total ammoniacal nitrogen difference varied significantly from -1.7 mg/l at 0 m/s to -2.4 mg/l at 0.35 m/s. (The water was doped to approximately 8.6 mg/l by addition of ammonium chloride).

Water temperature

The turbidity and temperature probes showed no significant change with temperature, however the other probes all changed with temperature.

The dissolved oxygen % reading varied between 95.1 %sat at 4.6°C and 88.3 %sat at 30.2°C, in aerated water. There is an apparent reduction in output of 0.14 %sat/°C. This is larger than the manufacturer's specification of ±0.3% between 5 and 45°C.
After conversion to mg/l the reading difference compared to the theoretical value for saturated water varied from -1.13 mg/l at 9.2°C to -0.54 mg/l at 45.1°C, and it increases with temperature by approximately 0.01 mg/l per °C. This is also outside the manufacturer's specification of ±0.6% reading between 5 and 45°C.

The temperature difference decreases slightly with temperature, however since this is within the uncertainty of the reference system then it is not significant.

The pH reading difference compared to laboratory values changed from +0.47 at 9.2°C to +0.07 at 45.4°C.

The conductivity difference compared to laboratory values varied from +6 µS/cm at 9.2°C to +42 µS/cm at 45.4°C. The difference increases with temperature above 20°C

The turbidity difference varies between +1.0 NTU at 30.2°C and +3.4 NTU at 19.8°C. There does not seem to be any significant variation with temperature.

The total ammoniacal nitrogen difference compared to laboratory values varied from -2.0 mg/l at 19.8°C to -0.0 mg/l at 45.4°C. (The water was dosed to approximately 7.5 mg/l by addition of ammonium chloride).

Fouling and Drift - intermittent immersion

The only fouling observed during the test was a grey film which developed on the ammonium probe membrane. This contributed to the slow electrode response, and its removal only partially restored the probe.

There was no significant drift of any determinant, but the time needed to measure ammonium\ammonia increased from a few minutes to approximately 30 minutes, which is not suitable for field use.

The details for each sensor are given below

The **dissolved oxygen** probe did not drift significantly compared to regular Winkler tests. A drift of -4 % on the % saturation range show by the instrument is probably due to a change in the atmospheric pressure during the test, this would not cause a problem during normal operation if it is calibrated each day. The average difference (error) and standard deviation (random error) compared to winkler test is -0.46 ± 0.26 mg/l.

The **temperature** was stable within measurement uncertainty during the test. The average difference (error) and standard deviation (random error) compared to a type E thermocouple is +0.09 ± 0.05°C.

The **pH** difference compared to laboratory values fluctuated by less than 0.2 but showed no drift during the test. The average difference (error) and standard deviation (random error) compared to laboratory analysis is +0.007 ± 0.07.

During the test the **conductivity** difference compared to laboratory values fluctuated from +51 µS/cm to -10 µS/cm with no apparent drift during the test. The average difference (error) and standard deviation (random error) compared to laboratory analysis is +14.7 ± 13.1 µS/cm.

The **turbidity** difference compared to on line measurements fluctuated between 0 and +5 NTU but showed no drift during the test. The average difference (error) and standard deviation (random error) compared to on-line measurements is +1.2 ± 1.0 NTU.

The variation of **total ammoniacal nitrogen** measurements compared to laboratory values indicate the variations in the ammonium electrode combined with the calculations of ammonia within the instrument. The total ammoniacal nitrogen differences fluctuated between -1.5 mg/l and +2.7 mg/l, and show no significant drift during the test (The water was dosed to approximately 8 mg/l by addition of ammonium chloride). The average difference (error) and standard deviation (random error) compared to laboratory analysis is -0.02 ± 0.98 mg/l.

HOWEVER these readings were taken after the instrument reading had settled and so hides the significant change of response time which occurred for the ammonium measurements. At the start of the test the reading settled within 5 minutes, but near the end of the test it took approximately 30 minutes to settle which would not be practical for field use. This was discussed with Grant who suggested fouling of the electrode. A thick grey film had developed over the membrane and the settling time was reduced to approximately 15 minutes when this was removed using de-ionised water from a wash bottle. At the end of the test the response had increased again to approximately 20 minutes. Since the settling time was not measured during the test these values are estimates.

Salinity

The instrument was taken on a regular monitoring run to the lower Thames Estuary, the differences observed between the instrument readings and the laboratory results are within the laboratory uncertainty. From this comparison it is not possible to find any effects of salinity on the instrument.

2.3 Comments on use, construction and documentation

The instrument generally robust and well made, but there are a number of things which cause problems in normal use.

The probes are protected by a tight fitting plastics cup which fits over the outside of the sonde and is sealed by an O-ring. When a good water tight seal is made it is very difficult to remove the cup, more so when wet, and the water inside was spilt on a number of occasions. This is impracticable and will sometimes make it difficult or impossible to use the instrument on a river bank without help to remove the cup. The screw on cup now being developed is preferable.

On a number of occasions the instrument software "locked up" and did not respond to any keystrokes. This had to be rectified by opening the logger and resetting it using a switch on the main circuit board. The batteries are also changed by opening the logger. Both operations need to be carried out where the circuit board can be protected from damp, dust, splashes, etc.

When transported by car the instrument switched itself on, this has also been observed by pollution officers. This could be caused by vibration and may indicate a problem with the board mount or the switches, and could result in batteries failing. A rigorous vibration test may provide some useful information for the manufacturer about this problem.

The manual contains a lot of information about the instrument, software, and available probes. Unfortunately it is very badly organised with most of the useful information contained in 2 sets of addenda approximately 50 pages long (including addenda to the first addendum !). As a result the manual is very difficult to use. There is no information about cross sensitivities of the sensors, this is important since ammonium ion selective electrodes are known to be sensitive to potassium and sodium which would give a false positive reading in sea water an order of magnitude greater than an ammonium response.

The logger has been designed to IP65 (ie dust proof and splash proof), but as there is a risk that it could be accidentally immersed in a river this may be inadequate. IP67 (ie dust proof and can withstand immersion to 1m deep) would be more appropriate.

2.4 Comments from field use

This is a summary of work carried out by M Loewenthal, which is reported separately, and of comments from pollution officers.

The manual is regarded as poor, difficult to use, and tends to make use of the instrument seem more complicated than is the case. This has made one to one training necessary when issuing instruments.

The ammonium probe is not highly regarded but it is the most demanded sensor as it is an important environmental substance. It has been used successfully for in number of surveys.

For survey work there is a requirement for more versatile logging facilities, particularly for a delay of start facility or some form of timer control to start and stop logging.

There have been a number of comments about the batteries. These mainly concern the need to open the logger to change batteries. Rechargeable batteries are also requested.

2.5 Manufacturer's comments

Grant Instruments provided the following comments on the report :-

"We have separated out sensor performance and indicated our understandings based on the findings of this report and our own observations. It was, however, not possible to interpret all the results without detailed knowledge of the experimental procedure. It should be noted that tests were carried out on a single logger and sonde and the results cannot be viewed as indicative or definitive for the product line as a whole. Overall we believe that the report is thorough in its approach and will turn out to be reasonably favourable with regard to the 3800 performance.

A) Sensor Performance

i) Dissolved Oxygen Sensor
We do not fully understand how the temperature dependence of the DO probe accuracy was assessed. We would assume that the instrument was calibrated in air at 100% and that water sparged with air was measured directly with the sonde. In this case the meter should read 100% when the water is at the calibration temperature. The highest value reported was 95% saturation. Could some of the error be due to inadequate saturation and equilibration of the water as temperature was varied? We believe that the variation associated with temperature and drift with time would be eliminated by carrying out the recommended calibration immediately before making measurement.
The DO drift observed seems reasonable but it is unlikely that all 4% drift would be due to atmospheric pressure alone.

ii) pH Sensor
The offset between the instrument and laboratory measurement with changes in temperature could be due to the instrument being set for automatic buffer temperature correction during calibration, which is incorrect if non-Grant/YSI pH calibration solutions are used. This would cause an estimated error of approximately 0.2pH.
It should also be noted that the temperatures are not compensated to 25°C as indicated in our manual and the NRA report. Our manual is in error on this point and will be corrected.

iii) Turbidity Sensor
The scattered measurements with changes in water flow rate are almost certainly due to air bubbles from the air saturated water in the flow tank forming on the sensor. The bubbles would not be present in still water or water taken to the laboratory because the sample would de-aerate in transit.

iv) Ammonium Sensor
The problem of increased response time in use is being investigated and

an alternative sensor is currently on laboratory and field trials and to date no increase in response time has been noted. We also wait for results of NRA trails on the new probes.
In both cases YSI recommend storage of the ammonium probe in 'confidence solution'. The observed variations in ammonium recording with flow have been observed but not to the extent indicated in the report. It may well be that the error is due to slow response observed on this probe.

v) Conductivity Sensor
Salinity - we were glad that these tests were made and that the results indicate the instrument is useful in brackish water.

B) Other Points

i) Lock-up
We do not understand the reported lock-up and we have not received other reports with version 4 firmware which is current in all NRA 3800 loggers. We would like you to make further tests on a different logger to see if the symptoms persist.

ii) Screw on Sonde Cap
We agree entirely with your point on the plastic transit cap. A screw on rigid cap has been designed and will be available from the end of February and can be ordered for retro-fitting at £82 less NRA discount.

iii) Battery Access
Two alternative proposals to overcome the need to open logger case are being investigated with the view to designing one which can be ordered for retrofitting.

iv) Batteries
YSI are investigating use of alkaline rechargeable batteries for use in the 3800. We will keep you informed on our findings and would encourage the NRA to test these or similar batteries.

v) Instruction Manual
We acknowledge the comment made on the shortcomings of our user manual. An updated and revised manual will be produced to overcome the criticisms and we plan to have this available in March 1994.

vi) Waterproofing
The logger is water resistant to IP65 (proof against low pressure jets of water). For proofing against immersion we recommend fitting the logger in an IP66 waterproof case. We have recently quoted for 50 such cases after producing a prototype.

CONCLUSION

This report covers a wide range of tests and experiments on the 3800 Water Quality Logger and could obviously be the basis of further investigation. The following four experiments are not very time intensive and could be fairly definitive in determining if some of the problems encountered were due to the particular 3800 user.

a) With a different 3800, transfer the sonde from confidence solution to river water spiked with 10mg/L ammonium and check the time required for stabilisation on a sonde containing one of the Analytical Sensors ammonium probes supplied recently.

b) Run a separate logger over a 4/5 week basis to see if any lock-ip occurs.

c) Re-run the effect of temperature change on dissolved oxygen accuracy, but sparge the water more vigorously with air and for longer periods of time prior to recording and reading, making sure that the sparged water reads close to 100% saturation at the air calibration temperature.

We take the opportunity to thank the NRA for investing time and effort in obtaining a better understanding of water quality measurement in the field. It is from this type of basic work that we at Grant/YSI can further develop and improve our instrumentation in line with your requirements."

3. Details of instrument evaluated

The instrument tested was selected at random from a batch of instruments purchased by the NRA and supplied to Thames region for normal use

Instrument	Grant/YSI 3800 Water Quality Logger
Logger Serial Number	381 200 444
Sonde Serial Number	381 500 505
NRA reference Number	31L 444 S 505
Manufacturer	Grant Instruments (Cambridge) Ltd Barrington Cambridge CB2 5QZ Tel : 0763 260811 Fax : 0763 262410
Source	NRA Thames region

4. Test Results

Water Flow Rate

Tables 1 and 2 below and the following figures show the difference between the instrument output and the analytical results at different water velocity. The test was carried out in an isolated water sample in a flow tank at the evaluation centre. See appendix A for details of the calculations involved and an estimate of uncertainties.

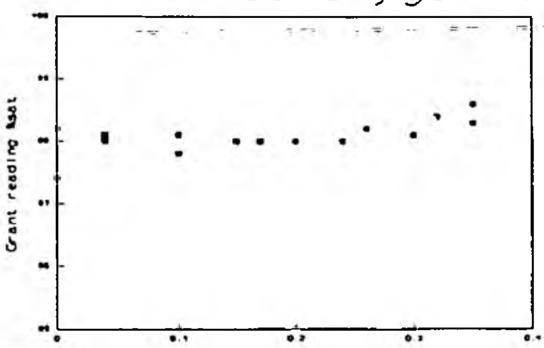
Table 1 : Instrument reading difference at different water flow rates

Water Flow rate m/s	Reading difference (Grant - Reference) D/O %	Temp. °C	Turb NTU	pH	Cond µS/cm
0	-1.8	-0.1	26	0.30	9.4
0.04	-1.9	-0.1	36	0.32	11.9
0.10	-1.9	-0.2	36	0.33	12.5
0.17	-2.0	-0.1	39	0.34	13.0
0.20	-2.0	-0.1	39	0.35	13.6
0.26	-1.8	-0.1	43	0.36	12.1
0.32	-1.6	-0.1	51	0.37	8.7
0.35	-1.4	-0.2	58	0.33	8.3
0.35	-1.7	-0.1	61	0.30	5.9
0.30	-1.9	-0.1	63	0.31	5.9
0.24	-2.0	-0.2	64	0.31	6.1
0.15	-2.0	-0.2	63	0.31	8.3
0.10	-2.2	-0.2	54	0.31	14.0
0.04	-2.0	-0.1	58	0.31	19.6
0	-2.6	-0.1	70	0.32	31.9

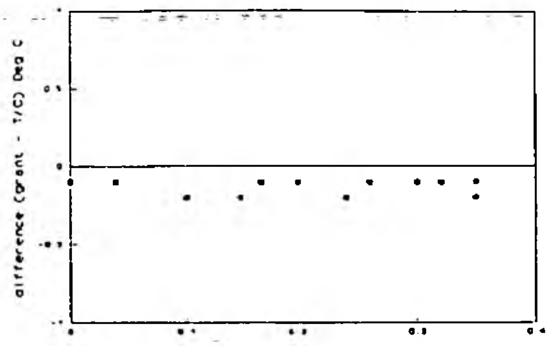
Table 2 : Instrument reading difference at different water flow rates

Water Flow rate m/s	Reading difference (Grant - Reference) Ammonium mg/l	Ammonia mg/l	Total ammoniacal Nitrogen mg/l
0	-2.5	0.27	-1.7
0.04	-3.0	0.26	-2.1
0.10	-3.2	0.25	-2.2
0.17	-3.2	0.25	-2.3
0.20	-3.3	0.27	-2.4
0.26	-3.4	0.28	-2.4
0.32	-3.4	0.30	-2.4
0.35	-3.3	0.25	-2.3
0.35	-3.2	0.23	-2.3
0.30	-3.3	0.24	-2.4
0.24	-3.2	0.24	-2.3
0.15	-3.1	0.25	-2.2
0.10	-3.0	0.29	-2.1
0.04	-2.9	0.28	-2.0
0	-2.6	0.31	-1.8

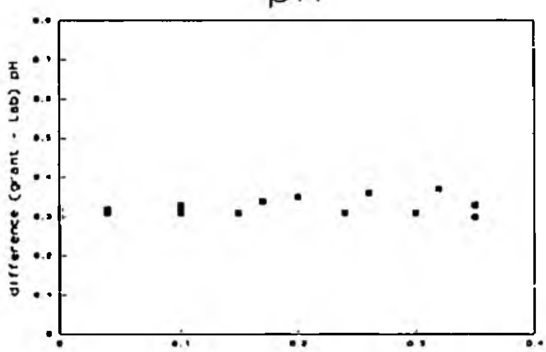
Dissolved Oxygen %



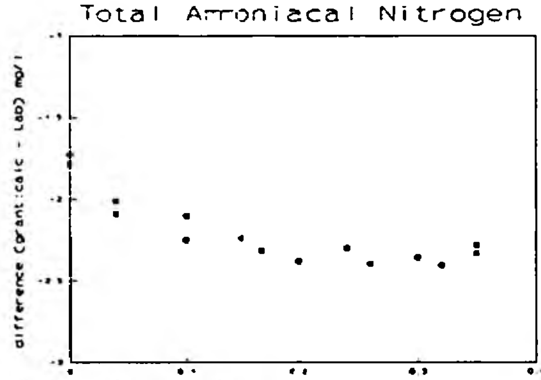
Temperature



pH

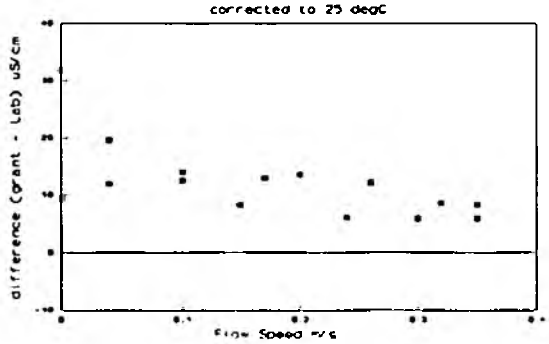


Total Ammoniacal Nitrogen

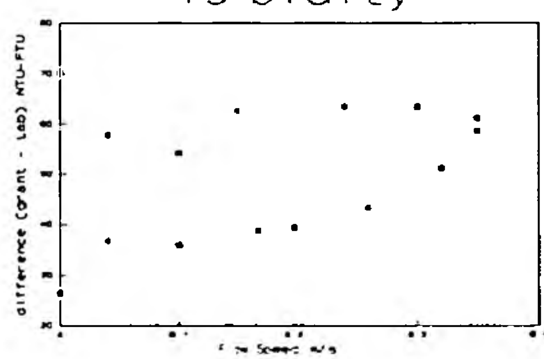


Conductivity

corrected to 25 degC



Turbidity



Water temperature

Tables 3 and 4 below, and the following figures, show the difference between the instrument output and the analytical results at different water temperatures. The test was carried out in an isolated water sample in a tank at the evaluation centre. See appendix A for details of the calculations involved and an estimate of uncertainties.

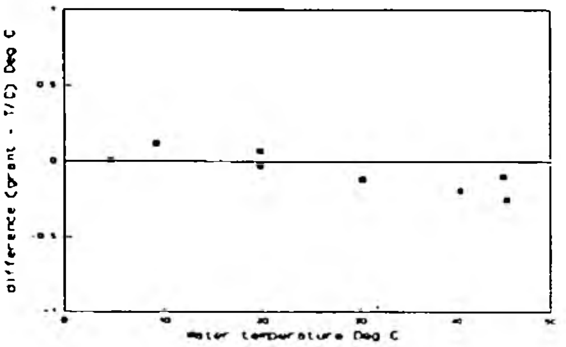
Table 3 : Instrument reading difference at different water temperatures

Water Temperature °C	Reading difference (Grant - Reference) D/O %	D/O mg/l	Temp. °C	Turb NTU	pH
4.6	-4.9	-0.8	0.0	2.3	0.46
9.2	-8.2	-1.1	0.1	2.2	0.47
19.8	-9.3	-1.0	0.1	3.4	0.41
30.2	-11.7	-0.9	-0.1	1.0	0.20
40.4	-9.8	-0.7	-0.2	1.3	0.09
45.4	-9.3	-0.6	-0.2	1.3	0.07
45.1	-8.6	-0.5	-0.1	3.0	0.14
19.8	-5.5	-0.6	-0.0	3.0	0.53

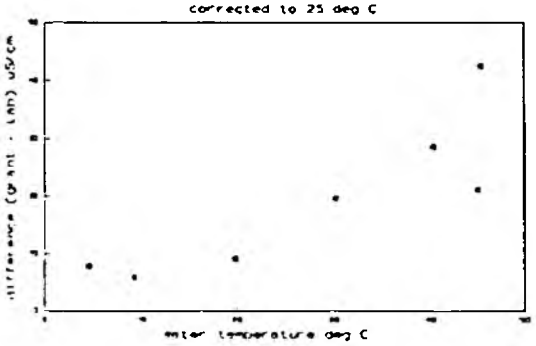
Table 4 : Instrument reading difference at different water temperatures

Water Temperature °C	Reading difference (Grant - Reference) Ammonium mg/l	Ammonia mg/l	Total ammoniacal N mg/l	Cond µS/cm
4.6	-1.3	0.23	-0.8	7.8
9.2	-2.8	0.28	-1.9	5.8
19.8	-3.0	0.37	-2.0	9.1
30.2	-1.5	0.26	-0.9	16.7
40.4	-0.5	0.19	-0.2	28.6
45.4	-0.3	0.26	-0.0	42.5
45.1	-1.8	0.12	-1.3	21.1
19.8	-3.0	0.74	-1.7	9.1

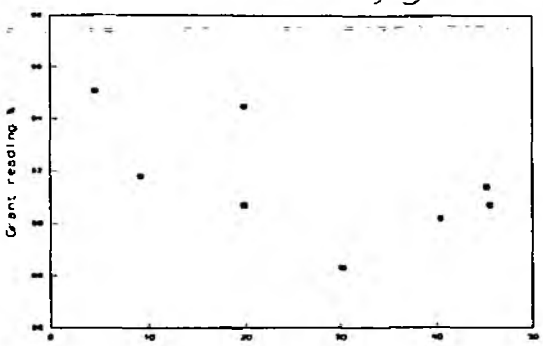
Temperature



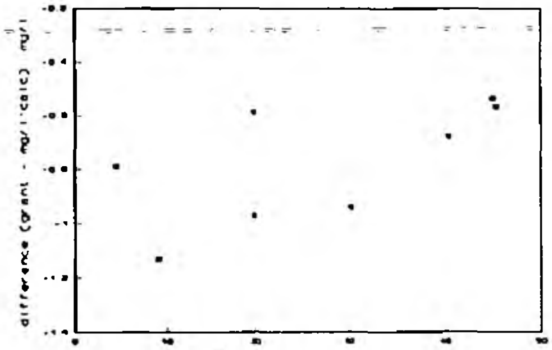
Conductivity
corrected to 25 deg C



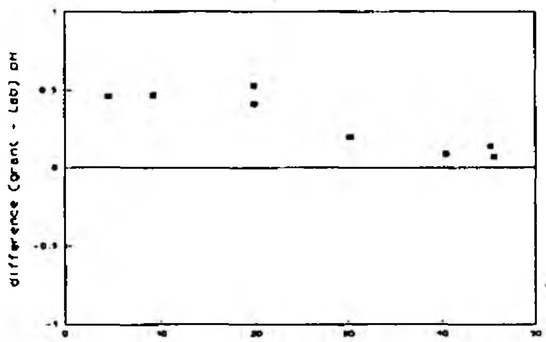
Dissolved Oxygen %



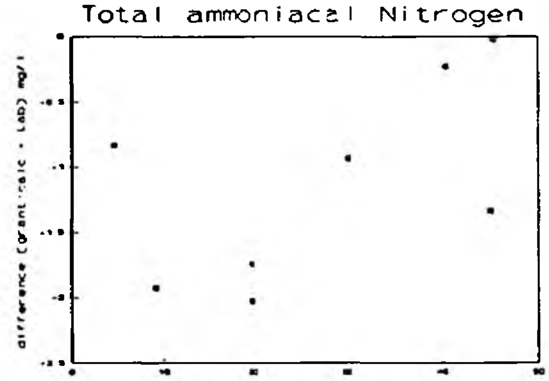
Dissolved Oxygen mg/l



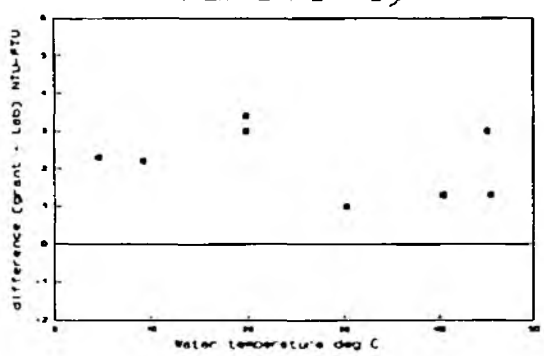
pH



Total ammoniacal Nitrogen



Turbidity

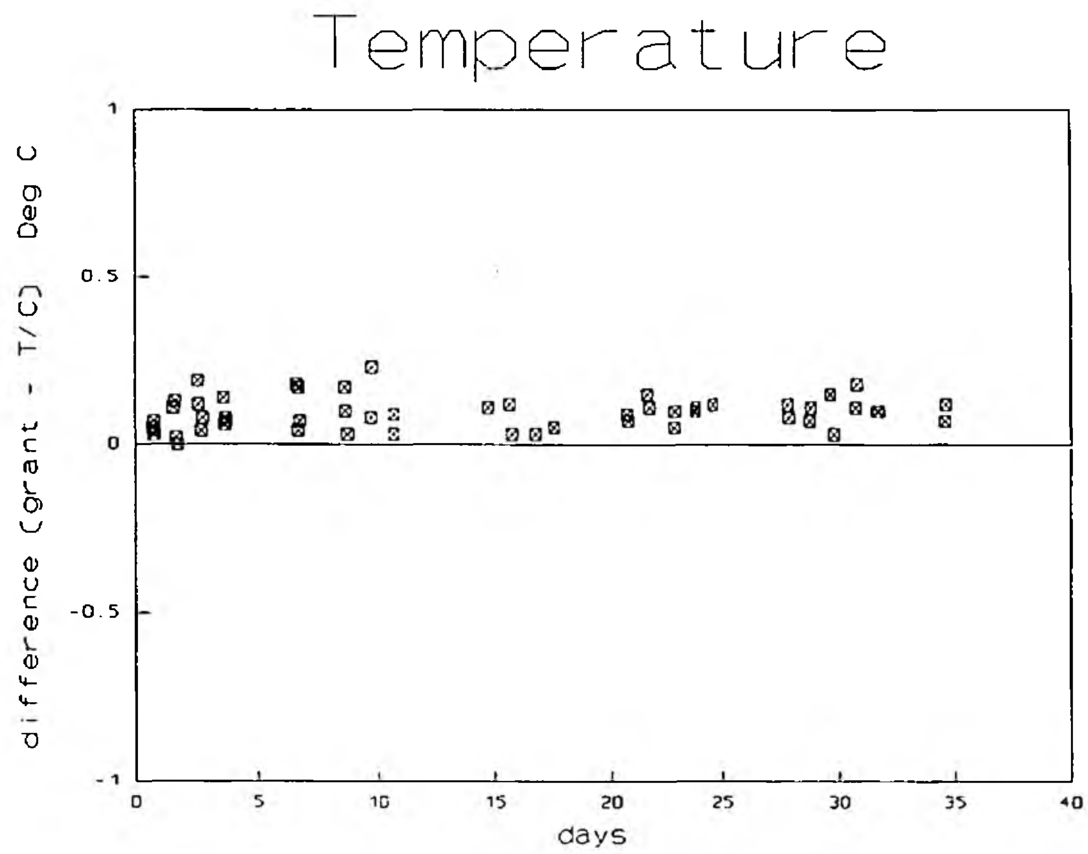


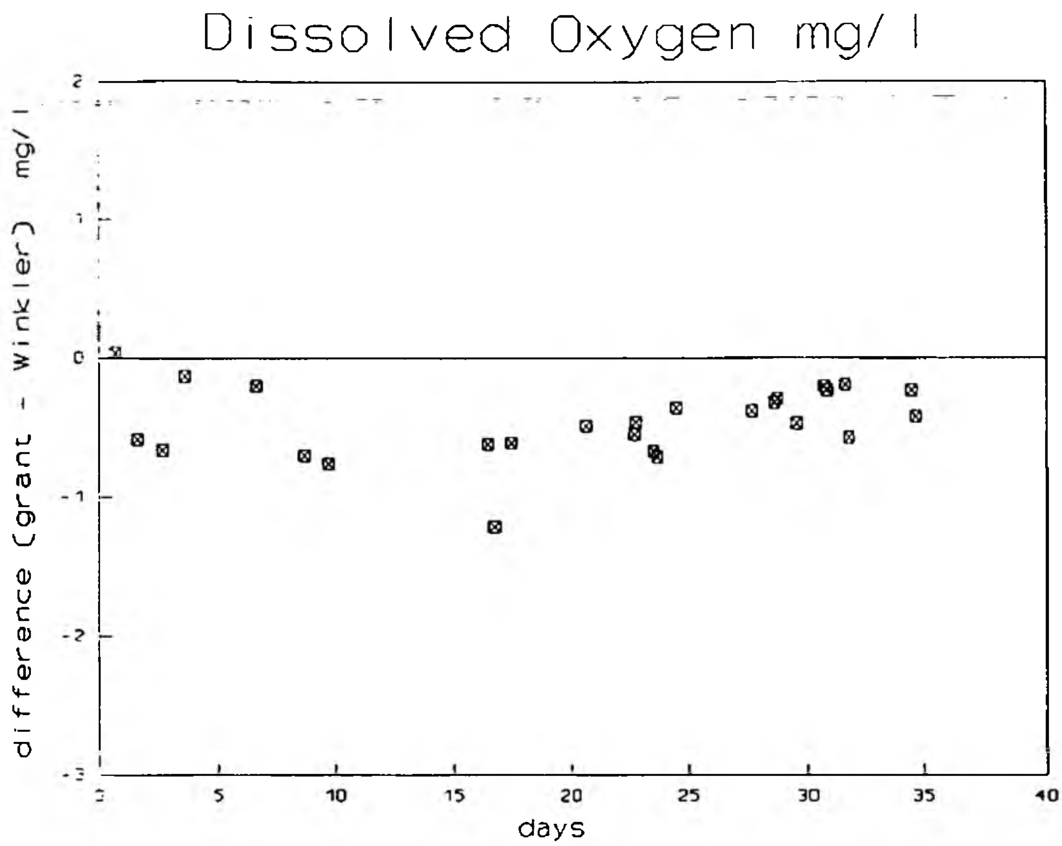
Fouling and drift - intermittent immersion

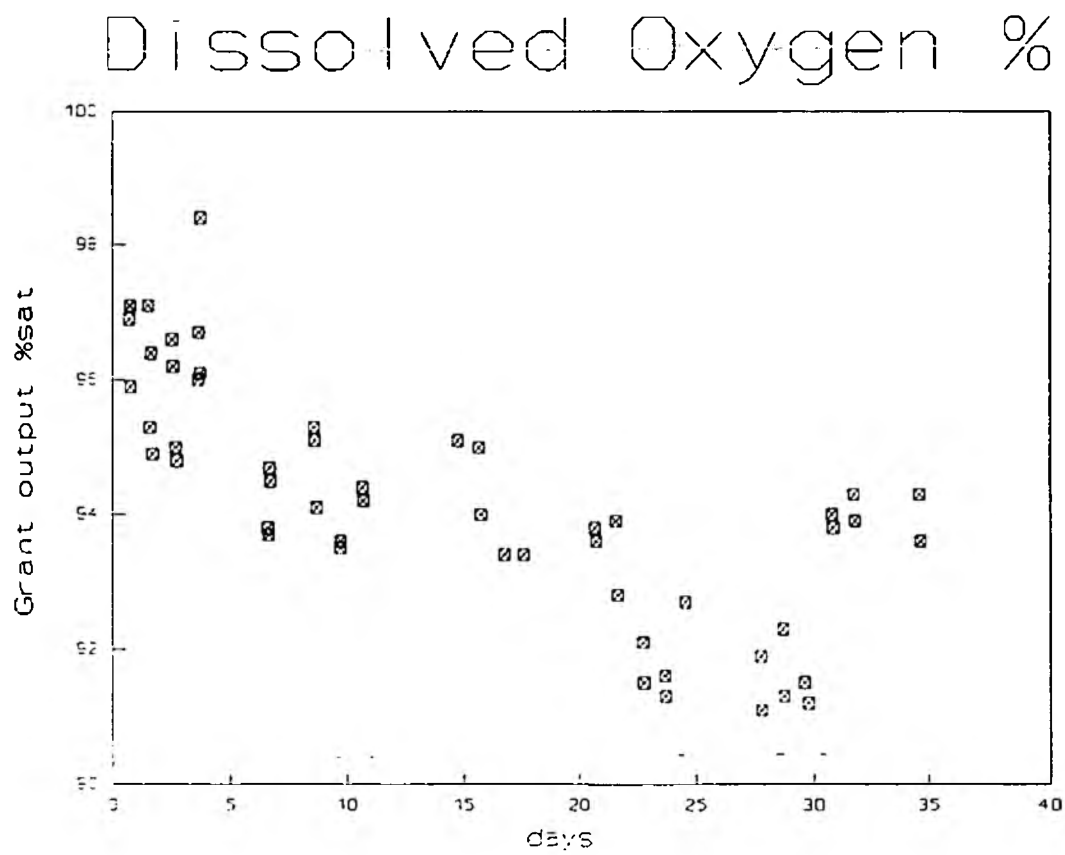
The results of this test are presented in the following graphs, rather than in a table, because of the quantity of data. The results given are the differences in reading between the instrument and laboratory analysis of a sample taken within 3 minutes of the reading. This was done 2 or 3 times each day. Up to 20 readings were made with the instrument each day. See appendix A for details of the calculations involved and an estimate of uncertainties. The author should be contacted if numerical data is required.

All the probes were stable throughout the test but, as previously stated, the response of the ammonium probe slowed considerably during the test.

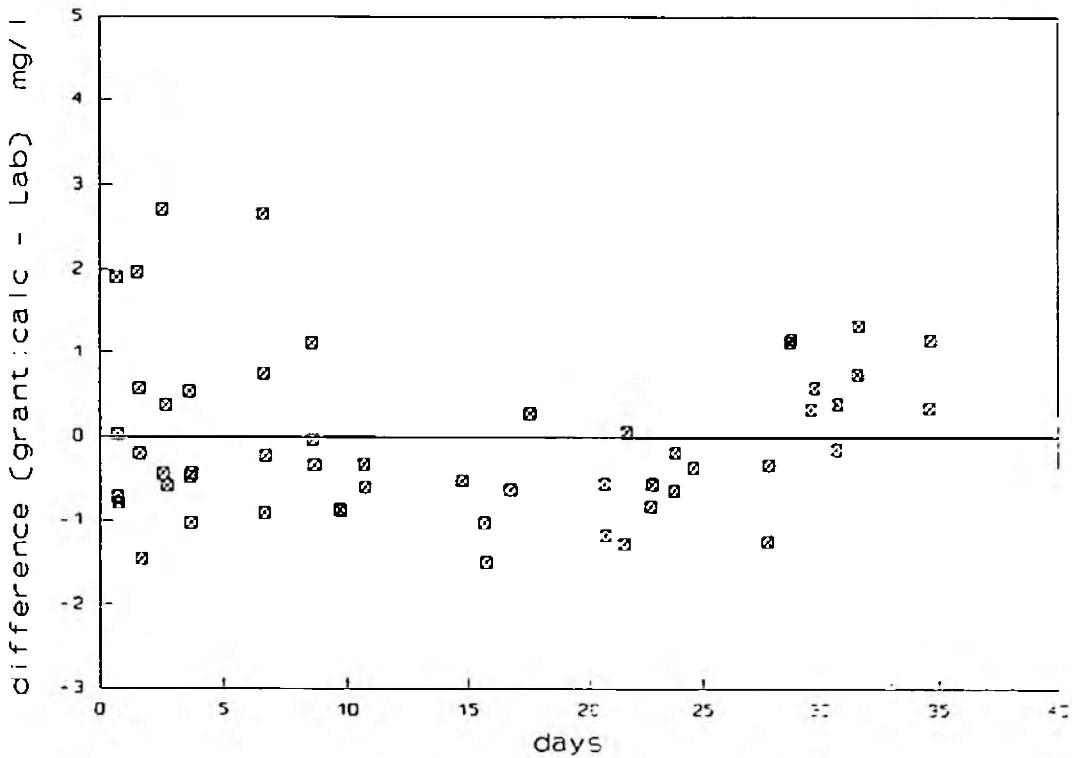
The drift in the dissolved oxygen % sat data follows changes in atmospheric pressure during the test. This highlights the necessity of daily calibration of the sensor during use to reduce this effect. This drift is not apparent when the mg/l values are compared to winkler analysis.



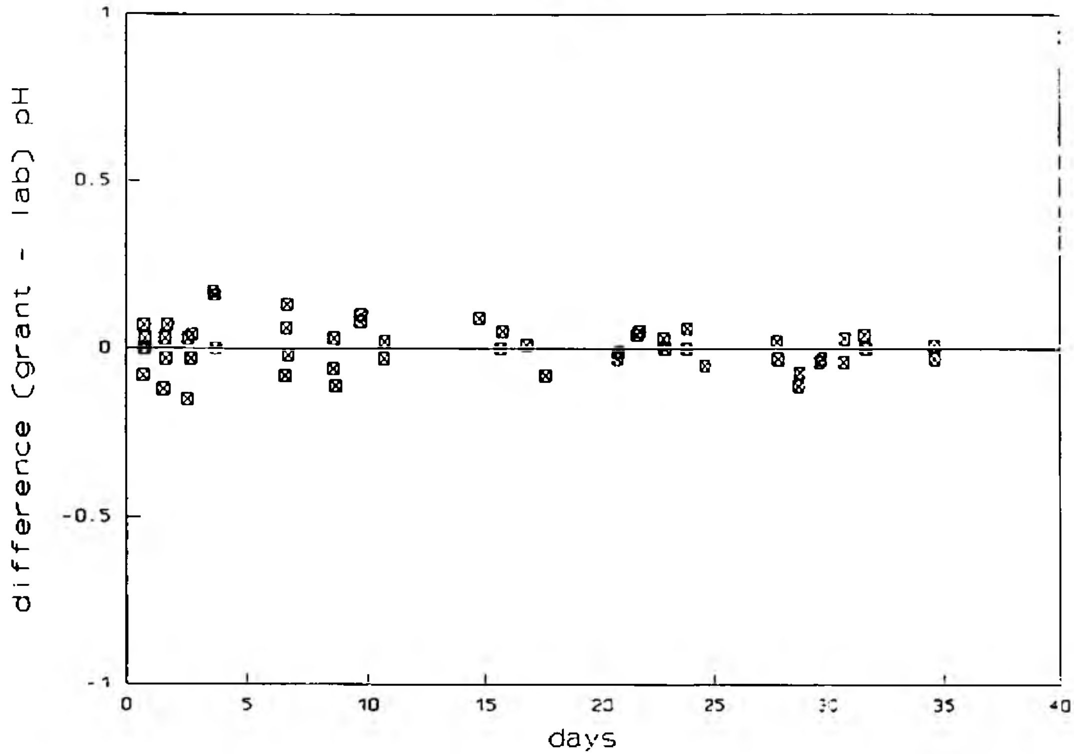

Dissolved Oxygen mg/l
difference (grant - Winkler) mg/l
days


Dissolved Oxygen %
Grant output %sat
days

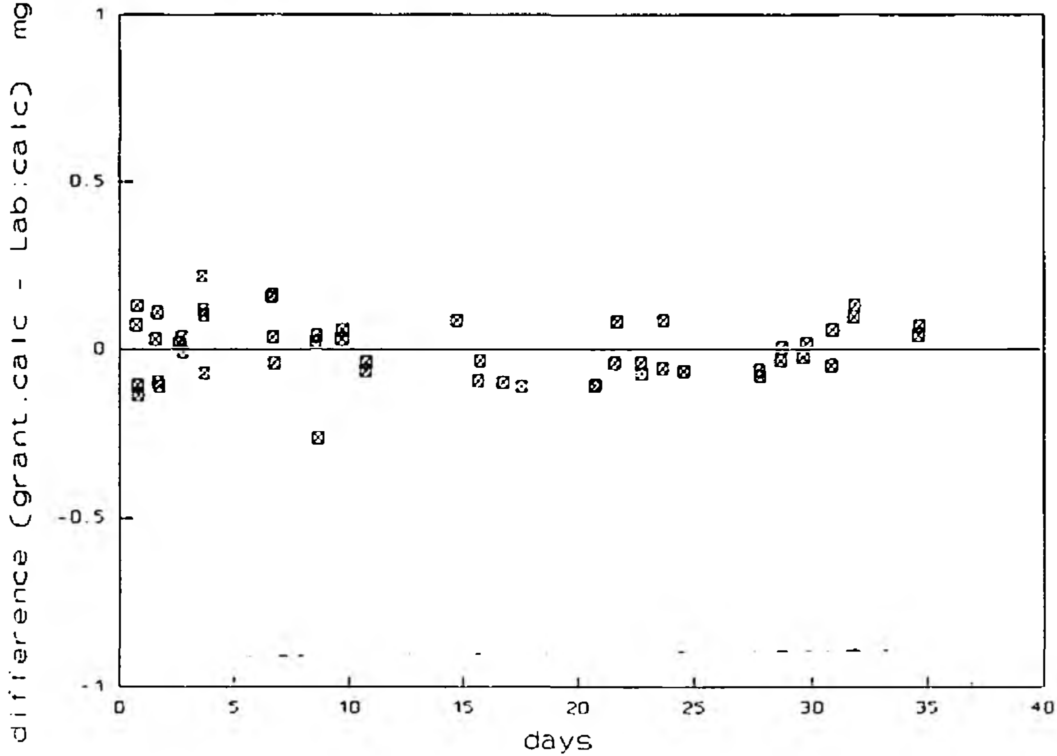
Total Ammoniacal N



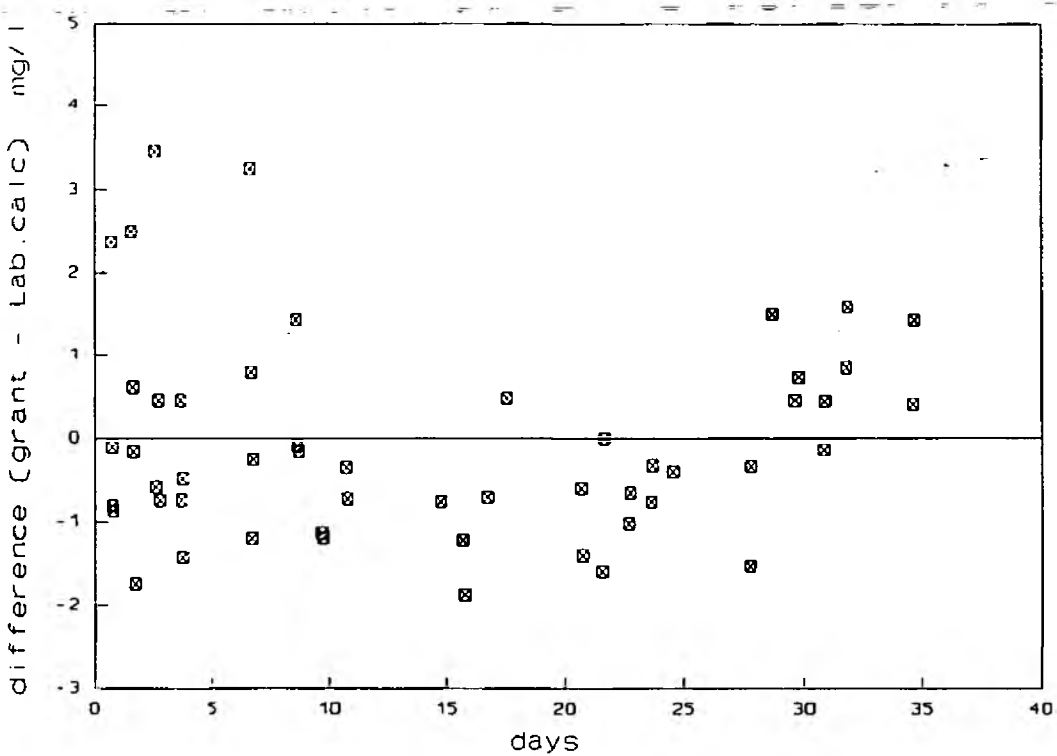
pH



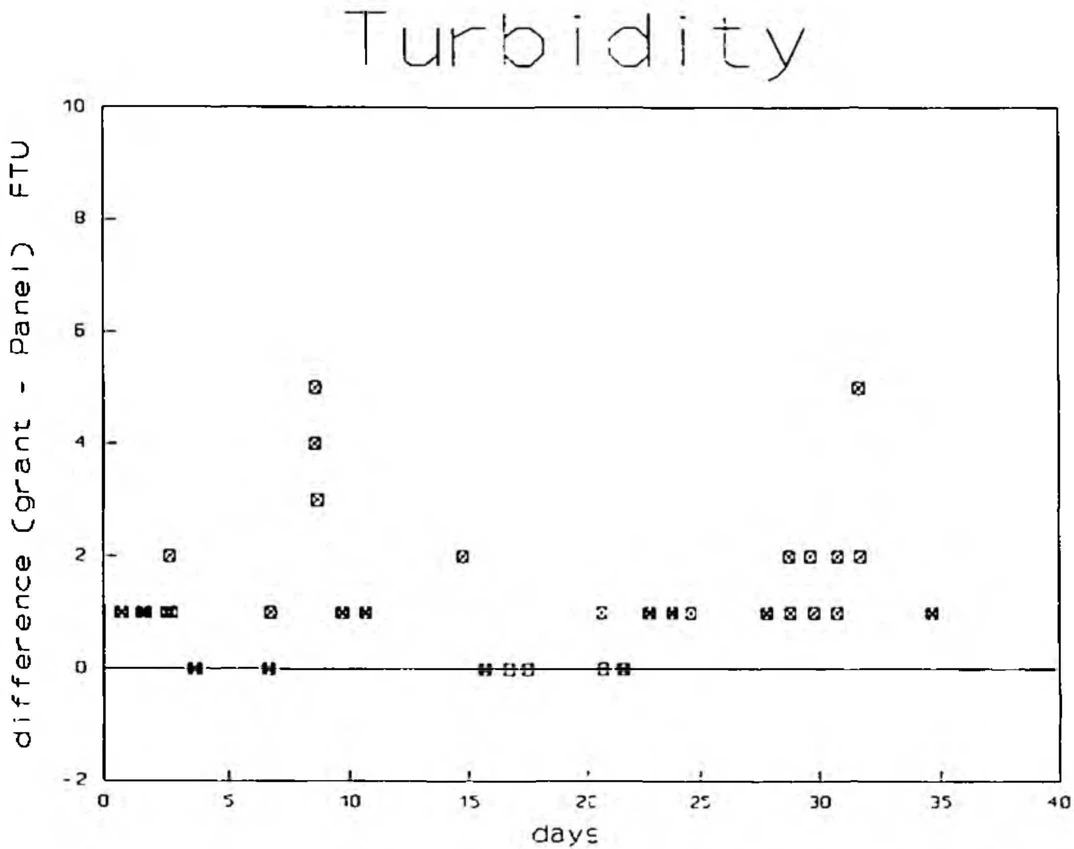
Ammonia

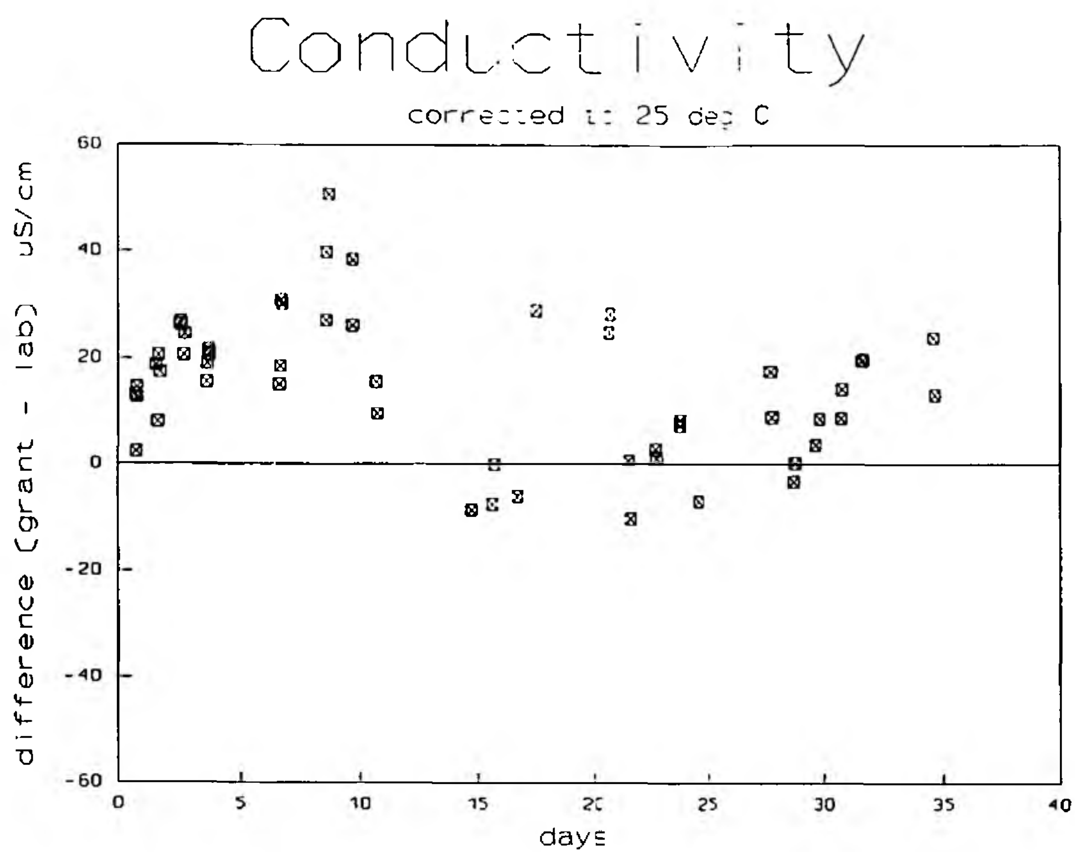

difference (grant.calc - Lab:calc) mg/l
1
0.5
0
-0.5
-1
0
5
10
15
20
25
30
35
40
days

Ammonium



difference (grant - Lab.calc) mg/l
5
4
3
2
1
0
-1
-2
-3
0
5
10
15
20
25
30
35
40
days


Turbidity
difference (grant - Panel) FTU
10
8
6
4
2
0
-2
0
5
10
15
20
25
30
35
40
days



Conductivity
corrected to 25 deg C
difference (grant - lab) uS/cm
60
40
20
0
-20
-40
-60
0
5
10
15
20
25
30
35
40
days

Salinity

Table 5 below shows the difference in readings obtained between the grant\YSI 3800 and laboratory results. The uncertainties quoted below are estimates.

The salinity values are calculated from laboratory analysis of chloride levels.

The dissolved oxygen reference values are from winkler titration carried out on the boat.

The pH reference measurements were made with a Russel electrode within a CSP system, there were no corrections made for salinity in either the reference measurements or the 3800 measurements. Because of this it is not possible to attribute the trend show in these results to changes in the instrument.

The conductivity reference values have an uncertainty of ±3 mS/cm.

Ammonium measurements are not included because the electrode response time was too long, and because of the large interference caused by sodium and potassium in the sea water. The turbidity results are omitted because of uncertainty in the reference measurements. The temperature probe was not tested.

Table 5 : Instrument reading difference at different salinities

Water Salinity %o	Reading difference (Grant - Reference)				
	Salinity %o	Cond mS/cm	D/O %	D/O mg/l	pH
37.6	-3.2	0.8	-0.9	0.2	-0.6
37.6	-3.2	0.4	0.8	0.4	-0.6
36.7	-3.2	-1.7	1.6	0.4	-0.5
34.3	-3.3	-0.8	0.8	0.4	-0.4
29.3	-0.5	1.3	3.2	0.4	-0.4
26.7	-2.2	0.3	2.1	0.4	-0.3
20.8	-0.7	-2.9	2.2	0.3	-0.2
15.5	-0.2		2.3	0.3	-0.2
12.0	-0.3		2.6	0.3	-0.1
9.0	-0.1		3.2	0.4	
9.0				0.3	0.0
6.1	1.4	4.0	2.6	0.3	0.1
5.6	0.0	-0.2	2.1	0.3	0.1
3.4	0.2	1.4	1.0	0.2	0.0
2.4	0.1		1.3	0.2	0.1
1.4	0.3	0.7	0.9	0.2	0.2

5. Test procedures

Water Flow Rate

The probe was calibrated according to manufacturer's instructions ie dissolved oxygen was calibrated at 100%, turbidity at 0, 200 and 800 FTU, pH at 4,7,and 10, and ammonium at 1 and 100 mg/l. The additional temperature and conductivity calibration points for ammonium were not set. Temperature and conductivity were not calibrated since they are factory set.

The sonde was then be placed in the large flow tank containing an isolated sample of river water. The flow rate was varied from 0.04 to 0.37 m/s, measured by an electromagnetic flow meter.

Ammonium Chloride was added to the tank to give approximately 10 mg/l ammonium, and it was aerated throughout the test to maintain the DO level at 100%. The temperature was monitored by a Type E thermocouple and samples were taken during the test for analysis by a NAMAS accredited laboratory of pH, conductivity, total ammoniacal N, and turbidity.

Water temperature

The dissolved oxygen probe was calibrated in air, according to the manufacturer's instructions, and the ammonium probe was calibrated at 1 and 100 mg/l. The optional ammonium calibration points to correct for temperature and conductivity were not set.

The sonde was placed in a tank of recirculated river water to which was added Ammonium Chloride to give approximately 10 mg/l ammonium, and which was aerated throughout the test to maintain the DO level at 100%. The water temperature was stabilised at the following temperatures and the instrument outputs noted : 4.6°C, 9.2°C, 19.8°C, 30.2°C, 40.4°C, and 45.4°C. The test was repeated at two decreasing temperatures.

The temperature was monitored by a Type E thermocouple and samples were taken at each temperature for analysis by a NAMAS accredited laboratory of pH, conductivity, total ammoniacal N, and turbidity.

Fouling and Drift - intermittent immersion

The probe was calibrated according to manufacturer's instructions ie dissolved oxygen was calibrated at 100%, turbidity at 0, 200 and 800 FTU, pH at 4,7,and 10, and ammonium at 1 and 100 mg/l. The additional temperature and conductivity calibration points for ammonium were not set. Temperature and conductivity were not calibrated since they are factory set.

The sonde was then regularly immersed (up to 20 times) in class 1 river water then returned to its storage condition on each working day for one month. In order to generate a measurable level of ammonium it was necessary to trap a sample of water and add a known amount of ammonium chloride. The temperature was monitored by a Type E thermocouple and samples were taken during the test for analysis by a NAMAS accredited laboratory of pH, conductivity, total ammoniacal N, turbidity, and dissolved oxygen.

The trend in levels of D/O, temperature, pH, conductivity, ammonium concentration, and turbidity of the water were monitored using standard water quality instruments.

The sonde was also occasionally immersed in the fish breeding ponds at Fobney

Mead, and was used once in estuarine conditions at Crossness. During the last week of the test the sonde was placed in the intermittent immersion tank at Fobney to be immersed automatically up to 10 times because of the pressure of time.

Salinity

The instrument was taken on a normal monitoring run into the Thames estuary. It was mounted in a bucket with a continuous supply of river\sea water taken from the normal monitoring supply pumped into the boat. Measurements were made in water with salinity levels varying from 36‰ to 1‰ and were compared to laboratory analysis of samples taken at the same time. Winkler titration were carried out on the boat as part of the regular monitoring, along with chloride titration.

Laboratory analysis provided values for pH, conductivity, chloride, and ammonium concentration. The reference salinity values were calculated from laboratory chloride analysis.

6. References

A Chappell and M Loewenthal : Test protocol for Grant/YSI 3800 water quality meter.

M Loewenthal : Evaluation report on Grant 3800 water quality meter.

I Baldwin : Protocol for investigation of ion selective ammonium electrodes and their applications in field measurement.

BSI : BS6068:section 2.15 (1986) Determination of dissolved oxygen - electrochemical probe method.

D Neville et al : NRA evaluation reports on DO meters.

Acknowledgements

Thanks must be given to Mr M.Loewenthal and the AWQMS staff, and to the Laboratory staff at Fobney Mead.

Appendix : Calculations and Reference measurements

Dissolved Oxygen
For mg/l values the reference measurements are made by Winkler titration. The uncertainty is assumed to be ±0.5mg/l from observation.
For %sat values the water is aerated to 100%, or to other values, by bubbling air or Oxygen\Nitrogen certified mixtures through river water. The uncertainty is assumed to be ±3% from observation.

Saline Dissolved Oxygen
For mg/l values the reference measurements are made by Winkler titration. The uncertainty is assumed to be ±0.5mg/l from observation.
The %sat values are obtained by calculating the oxygen solubility from the temperature and the chloride values using the tables given in BS6068, then calculating the % saturation from the winkler values. The chloride levels were obtained by laboratory analysis of the samples submitted.

Temperature
The reference measurements were made using a type E thermocouple with the cold junction compensation within a Schlumberger IMP data acquisition unit. The uncertainty is taken as ±0.1°C.

pH
The pH is compared against laboratory measurements made using an automated CSP pH meter. During the drift test the readings were confirmed by comparison with the monitor panel. The traceable uncertainty is ±20% of reading.

Conductivity
The conductivity is compared against laboratory measurements made using an automated CSP conductivity meter. The laboratory readings were given as conductivity at 20°C, this adjusted to 25°C for comparison with the instrument values using a temperature coefficient for the water of 1.91% per °C. The traceable uncertainty of the laboratory values is ±20% of reading.

Salinity
The salinity values of sea and estuarine water were calculated from laboratory measurements of chloride in samples submitted for analysis by the following relationship:

$$SALINITY = CHLORIDE \times 1.80655$$

Turbidity
Turbidity was measured in the laboratory using a Hach 2000 turbidimeter, and these results were used to check the values obtained in the temperature and flow tests. For the drift test the turbidity readings were compared against a pHox 750L on-line turbidimeter.

Ammonium and Ammonia

An equilibrium is set up between ammonium and ammonia gas in an aqueous solution by a reversible reaction involving hydrogen ions.

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

The relationship between ratios of ammonium and ammonia, and pH are known so the instrument measures ammonium directly using an ISE then calculates the ammonia concentration from the ammonium level, pH, and temperature.

The reference values were calculated from the laboratory measurements of Total ammoniacal Nitrogen (TotN) and pH (pH), and the site measurements of absolute temperature in Kelvin (T). The calculations are based on the following relationship between ammonium and ammonia in water :

$$\frac{|NH_3|}{|NH_4^+|} = \frac{10^{pH}}{10^{c}}$$

where

$$c = \frac{2729.69}{T} + 0.1105 - 0.000071T$$

The flow injection system adds alkali to the sample before measurement and the level of ammonia in the sample after that is given by A :

$$A = TotN \times \frac{17}{14}$$

Hence the levels of ammonium and ammonia in the original sample are calculated from :

$$|NH_3| = A / \left(1 + \frac{17 \times 10^{c}}{18 \times 10^{pH}}\right)$$

and

$$|NH_4^+| = A / \left(\frac{17}{18} + \frac{10^{pH}}{10^{c}}\right)$$

Total Ammoniacal Nitrogen

The laboratory measurements were made using an automated flow injection system with a traceable uncertainty of ±20% of reading. The instrument values were calculated from the ammonium and ammonia readings using the following equation:

$$TotN = \left(|NH_4^+| \times \frac{14}{18}\right) + \left(|NH_3| \times \frac{14}{17}\right)$$